CONSEQUENCES OF THE MASS SPECTROMETRIC AND INFRARED ANALYSIS OF OILS AND ASPHALTENES FOR THE CHEMISTRY OF COAL LIQUEFACTION

By

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CHAPTER I

INTRODUCTION

Chemical analysis provides information essential to the elucidation of the reaction sequences occurring during coal liquefaction and for the determination of their kinetic paramters. Such information is a necessary component in the development of economical coal conversion processes inasmuch as it directly influences catalyst development, selection of appropriate reaction conditions, and reactor design. Chemical analysis of the various feed and process streams associated with commercial liquefaction processes will be mandatory in order to provide for process monitoring and to insure compliance with environmental and biological standards.

The chemistry of coal liquefaction has been historically considered in terms of preasphaltenes, asphaltenes, and oils. For example, the yields of these fractions have been used to assess both the kinetics and mechanism of coal liquefaction (1-5). Preasphaltenes, asphaltenes, and oils constitute a partial characterization of coal liquids according to solvent extraction. In view of the importance assigned to these solubility fractions in considering the process of coal liquefaction, it is surprising that a paucity of detailed compositional data exists for coal-liquid derived oils, asphaltenes, and preasphaltenes. In this regard, it should be noted that some characterization data have been reported for oils, total asphaltenes

(6-9), and for fractions derived from further separations of total asphaltenes (10-14). Both the importance assigned to these materials and the limited amount of characterization data for them induced us to conduct a detailed molecular analysis of the oils and asphaltenes obtained from a COED coal liquid.

The coal liquid was separated by simple solvent extraction into oils, asphaltenes, and a residue. Mass spectrometry, chromatographic separation methods, and infrared spectroscopy were used to obtain detailed compositional data for the oil and asphaltene fractions. The data obtained for the asphaltenes were compared to those similarly obtained for the oils.

CHAPTER II

METHODS, RESULTS AND DISCUSSION

Methods and Results

Separations

A coal-derived liquid, which was provided by the FMC Corporation, was obtained from Colorado Bear Mine Coal by the COED process (15). The properties of the COED liquid are presented in Table I. It is important to note that the coal liquid has a low sulfur content of 0.35 weight percent and a relatively high oxygen content of 7.15 weight percent. A 19-gram sample of the liquid was separated into oils (pentane solubles), asphaltenes (pentane insolubles/benzene solubles), and residue as shown in Figure 1. The oils, the asphaltenes, and the residue accounted for 25%, 57%, and 18% of the total liquid, respectively.

The oil fraction was separated into acids, bases, and neutrals using ion-exchange chromatography (16, 17). The oil neutral fraction was then separated into saturate and aromatic concentrates by silica-gel chromatography. This separation scheme is illustrated in Figure 2. The asphaltenes were separated into acids, bases, and neutrals as shown in Figure 3. The procedure is similar to the procedure used in the separation of the oils, except that benzene replaced pentane as the eluent. It should be noted that three column volumes of

TABLE I

FMC OIL PROPERTIES

Coal Source	Colorado Bear Mines
Process	COED
Carbon	83.05 wt%
Hydrogen	8.35
Sulfur	0.35
Nitrogen	1.13
Oxygen	7.15
Ash	Nil
^{o}API Gravity @ 60^{o}F	-4.5
Pour Point, F	118
Flash Point, F	350

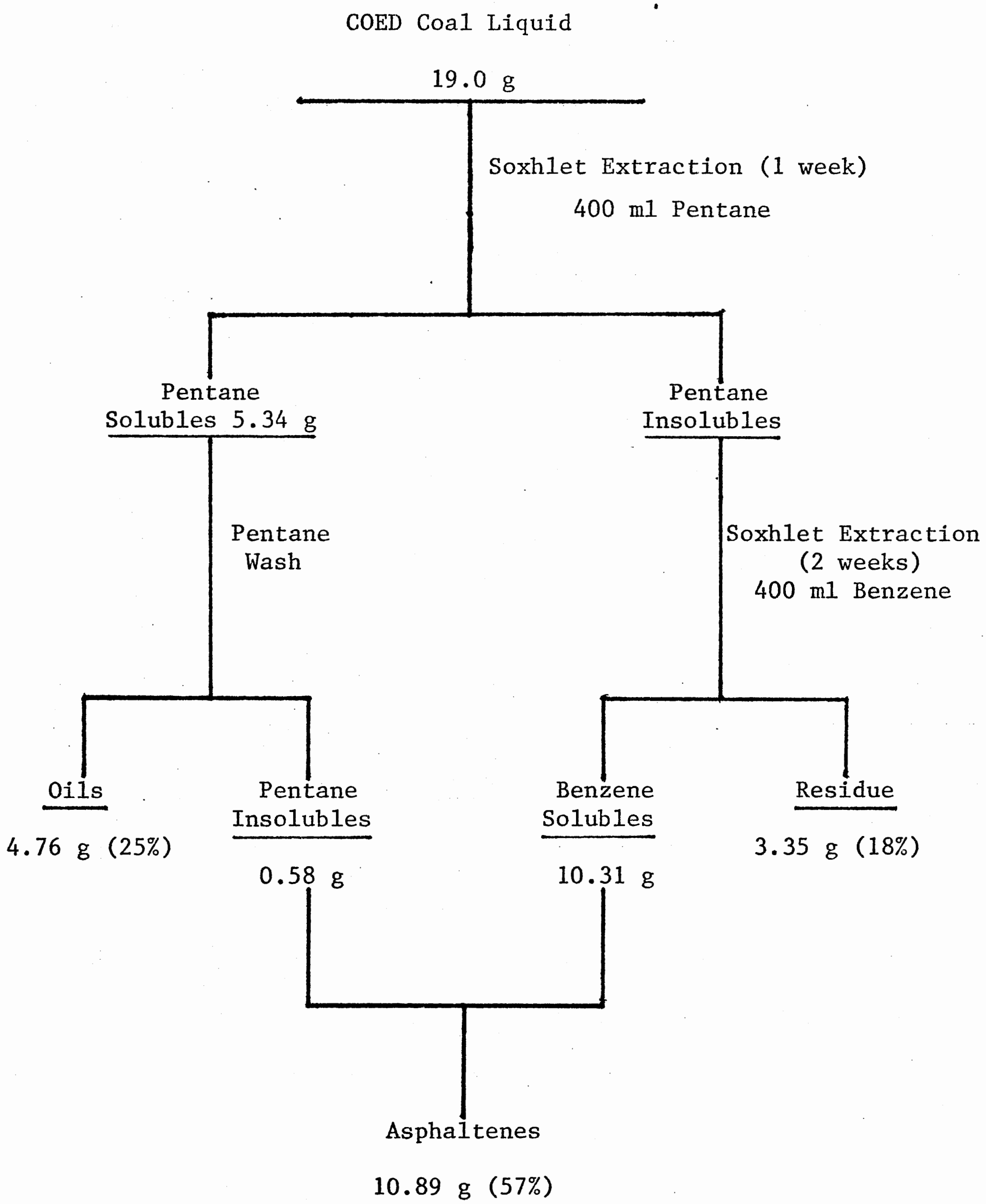

Figure 1. Solvent Separation of a COED Liquid into Oils, Asphaltenes, and Residue

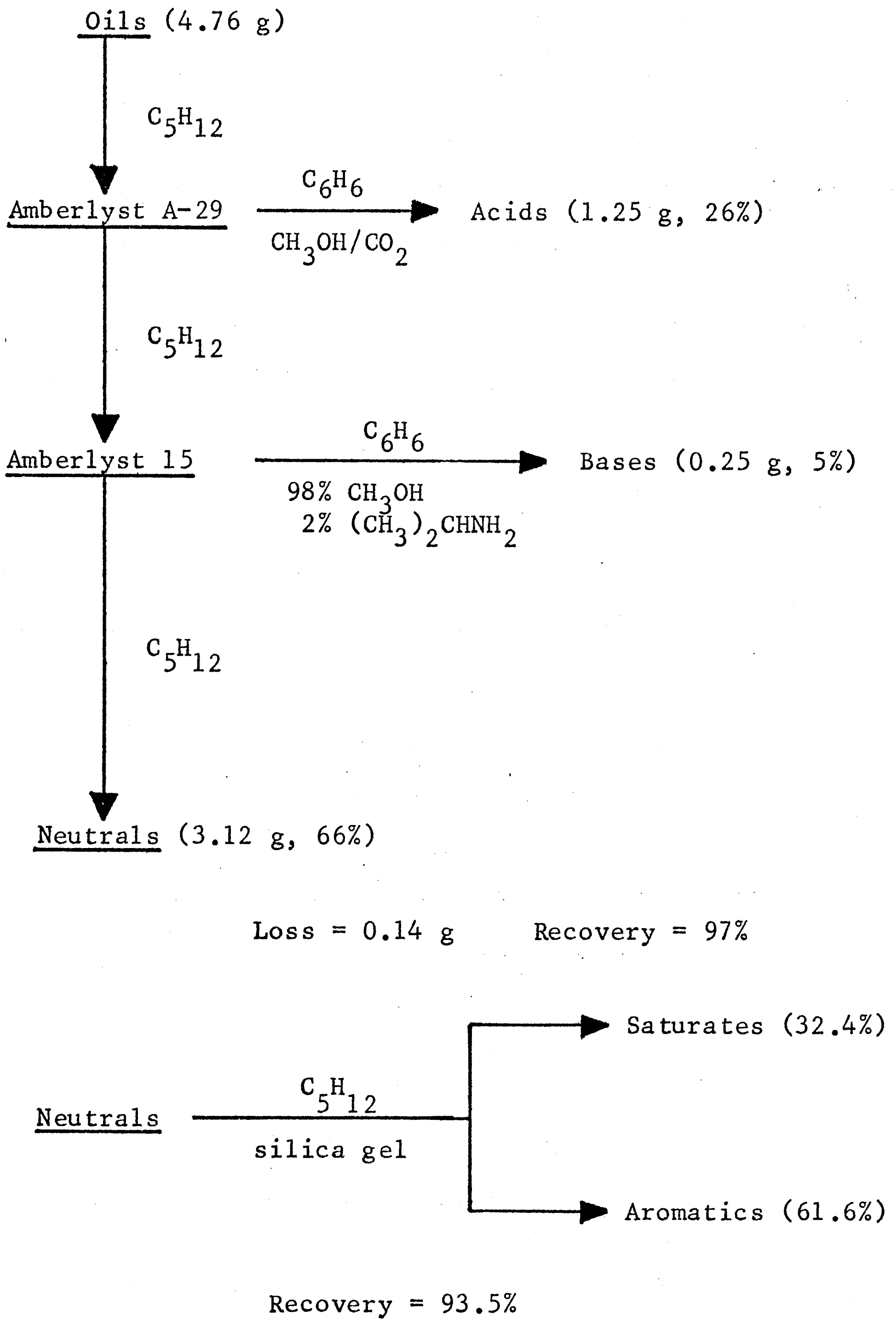

Figure 2. Chromatographic Separation of Oils

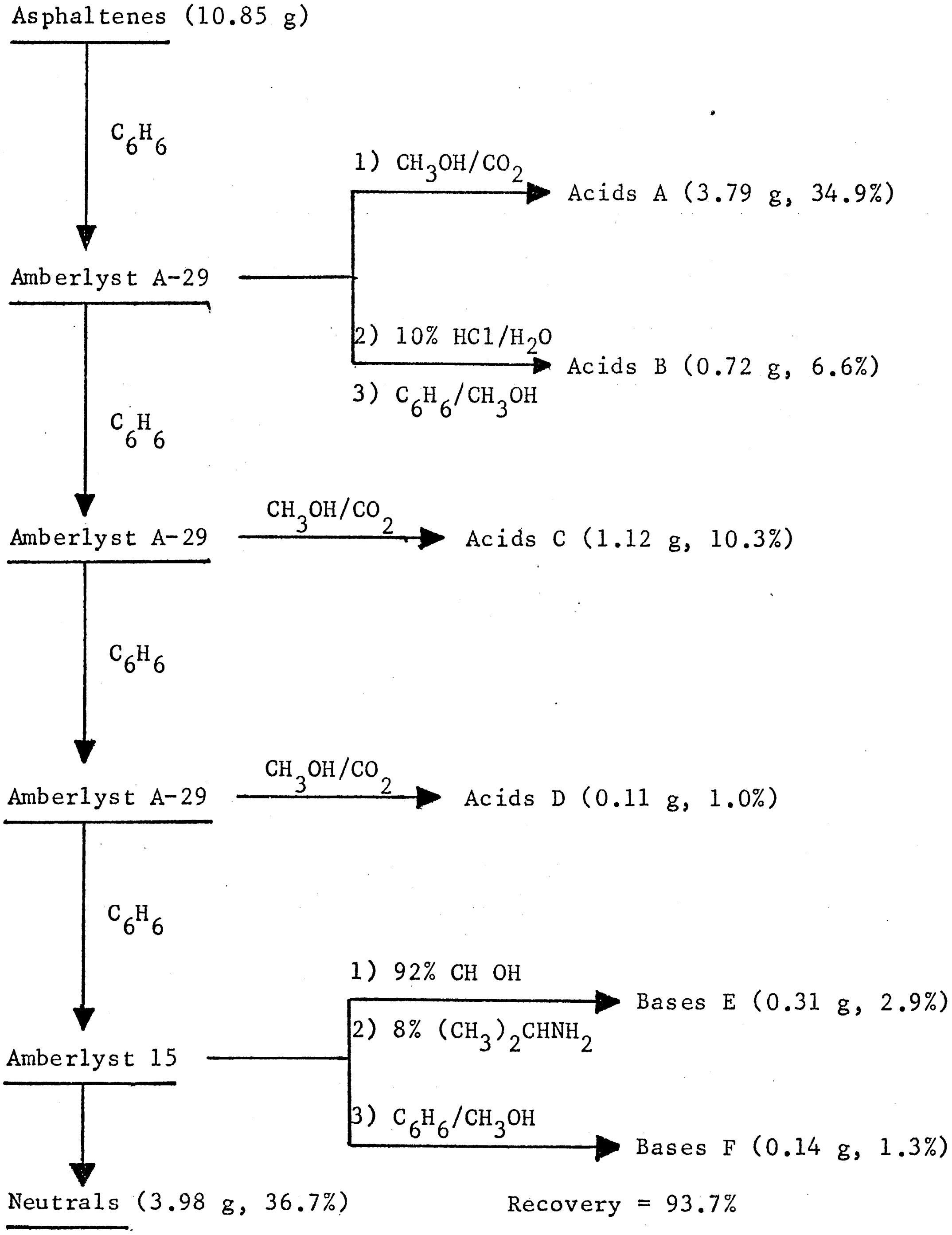

Figure 3. Chromatographic Separation of Asphaltenes

anion-exchange resin were required for complete removal of the acidic components in the asphaltene fraction. The asphaltene neutrals were then extracted with pentane and found to be 88.2% soluble. The pentane soluble asphaltene neutrals were subsequently separated into saturate and aromatic concentrates using silica-gel chromatography as shown in Figure 4.

The weight percent of the total liquid accounted for by each fraction is given in Table II. The oil neutrals constitute the largest compound class in the oil fraction, while the asphaltene acids make up the largest compound class in the asphaltenes. It is also evident that the oil neutrals contain a higher percentage of saturates than do the asphaltene neutrals.

Infrared Spectroscopy

Infrared spectroscopy was used to investigate the nature of the functional groups possessed by the compounds present in the various fractions. The approach was based upon the published methodologies for both petroleum heavy ends (18-20) and coal liquefaction products (6,21), i.e., with the exception of asphaltene acid fraction B, solution IR spectra were obtained for the oil and asphaltene fractions. In addition, matrix-isolation IR spectra were also obtained for the oil fractions and some asphaltene fractions. Both techniques yielded similar qualitative results. However, in some cases, the matrix-isolation spectra exhibited significantly better resolution than did the solution spectra. The solution spectra of the oil and asphaltene neutrals were acquired using CCl_4 as the solvent. Since the remaining fractions were all insoluble in CCl_4, the IR spectra for

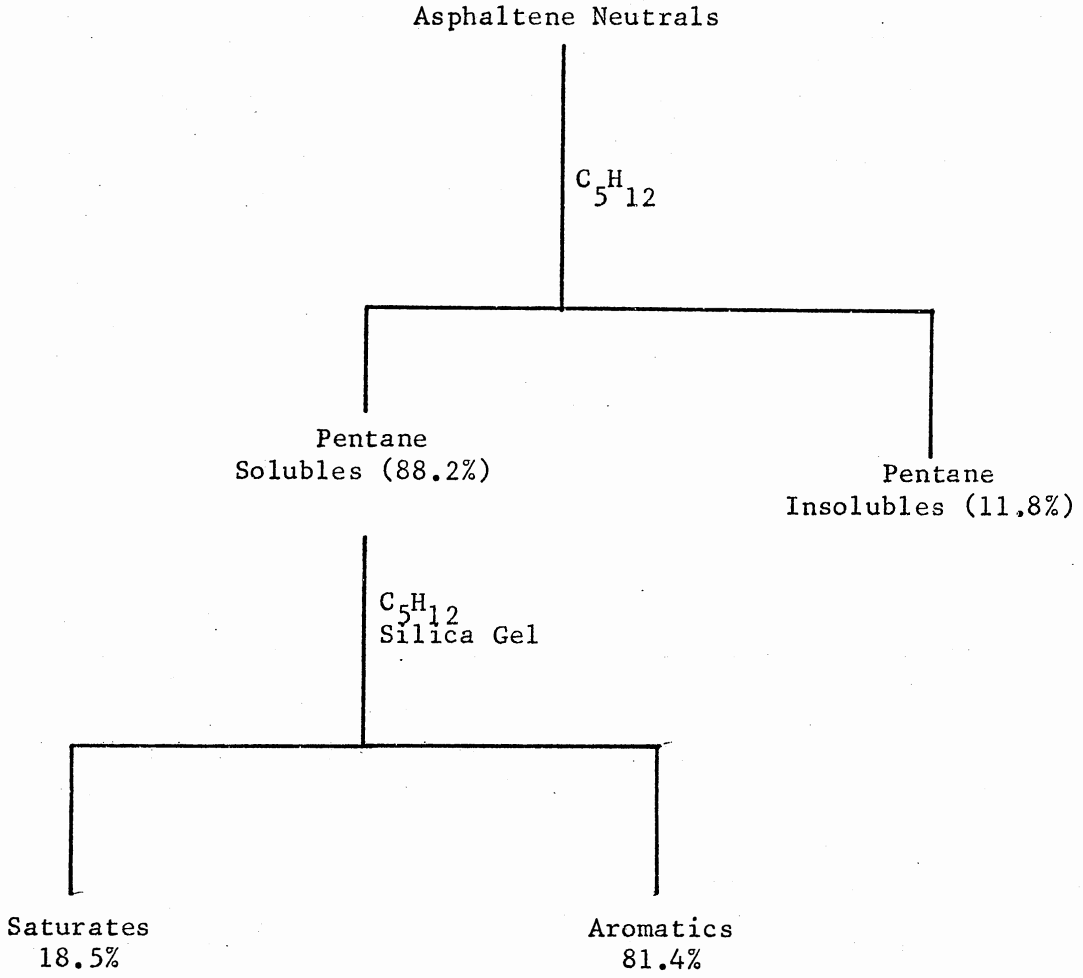

Figure 4. Separation of Asphaltene Neutrals

TABLE II

SEPARATION DATA FOR COED COAL-DERIVED LIQUID

Group Type	Weight Percent of Total Liquid		
	Oils		Asphaltenes
Acids	6.5	A	19.9
		B	3.8
		C	5.9
		D	0.6
		Total	30.2
Bases	1.3	E	1.6
		F	0.7
		Total	2.3
Neutrals			
Saturates	5.3		3.9 (5.2)[a]
Aromatics	10.1		17.0
Total	23.2		53.4
Sample Loss	1.8		3.6

[a] Results obtained from LV/EI/MS analysis.

them were obtained using $CDCl_3$ as the solvent. The IR spectra of asphaltene acid fraction B was obtained using a KBr pellet due to its insolubility in conventional solvents.

The significant regions in the IR spectra of the oil and asphaltene neutrals are presented in Figures 5 and 6, respectively. Figure 5 is a matrix-isolation spectrum of the oil neutrals, whereas Figure 6 is a solution spectrum of the asphaltene neutrals. Figures 7-11 are the important regions of the various acid fractions. Figures 7, 8 and 10 are matrix-isolation spectra of the oil acids, asphaltene acid fraction A, and asphaltene acid fraction C, respectively. Figure 9 is the KBr spectrum of asphaltene acid fraction B and Figure 11 is a solution spectrum of asphaltene acid fraction D. Figures 12-14 are the significant regions in the IR spectra of the various base fractions. Solution spectra of asphaltene base fraction E and asphaltene base fraction F are shown in Figures 13 and 14, respectively. Figure 12 is the matrix-isolation spectrum of the oil base fraction.

Mass Spectrometry

The compound types and the weight percents of the individual homologs present in the aromatic fractions from the oils and asphaltenes were determined from high-resolution 70-eV electron impact mass spectrometry (EI/MS) and high- and low-resolution field ionization mass spectrometry (FI/MS) at Oklahoma State University using a CEC 21-110B. Corresponding analytical data were also obtained for various asphaltene fractions from high-resolution low-voltage EI/MS at Exxon using an AEI MS-50.

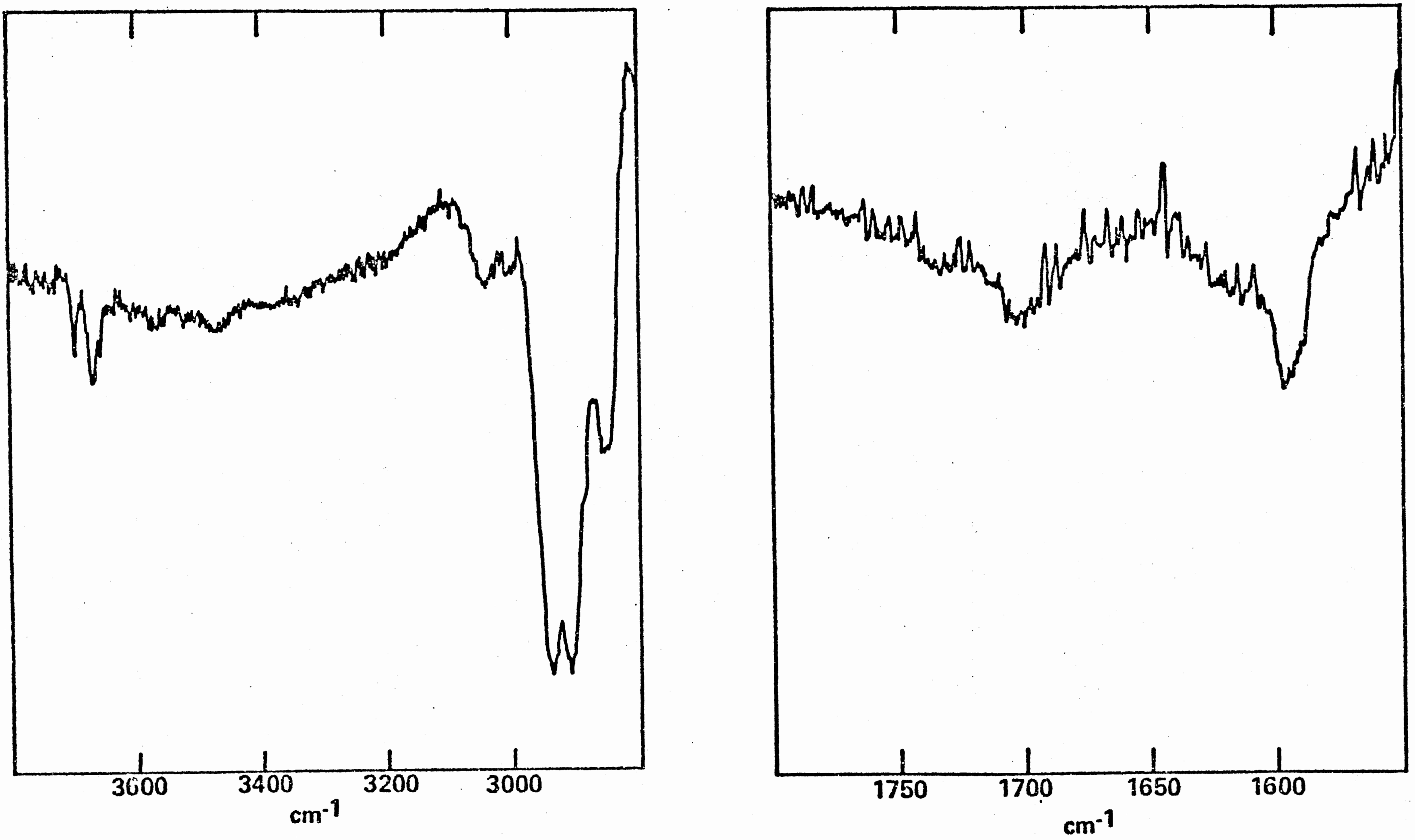

Figure 5. Partial Matrix-Isolation IR Spectrum of Oil Neutrals

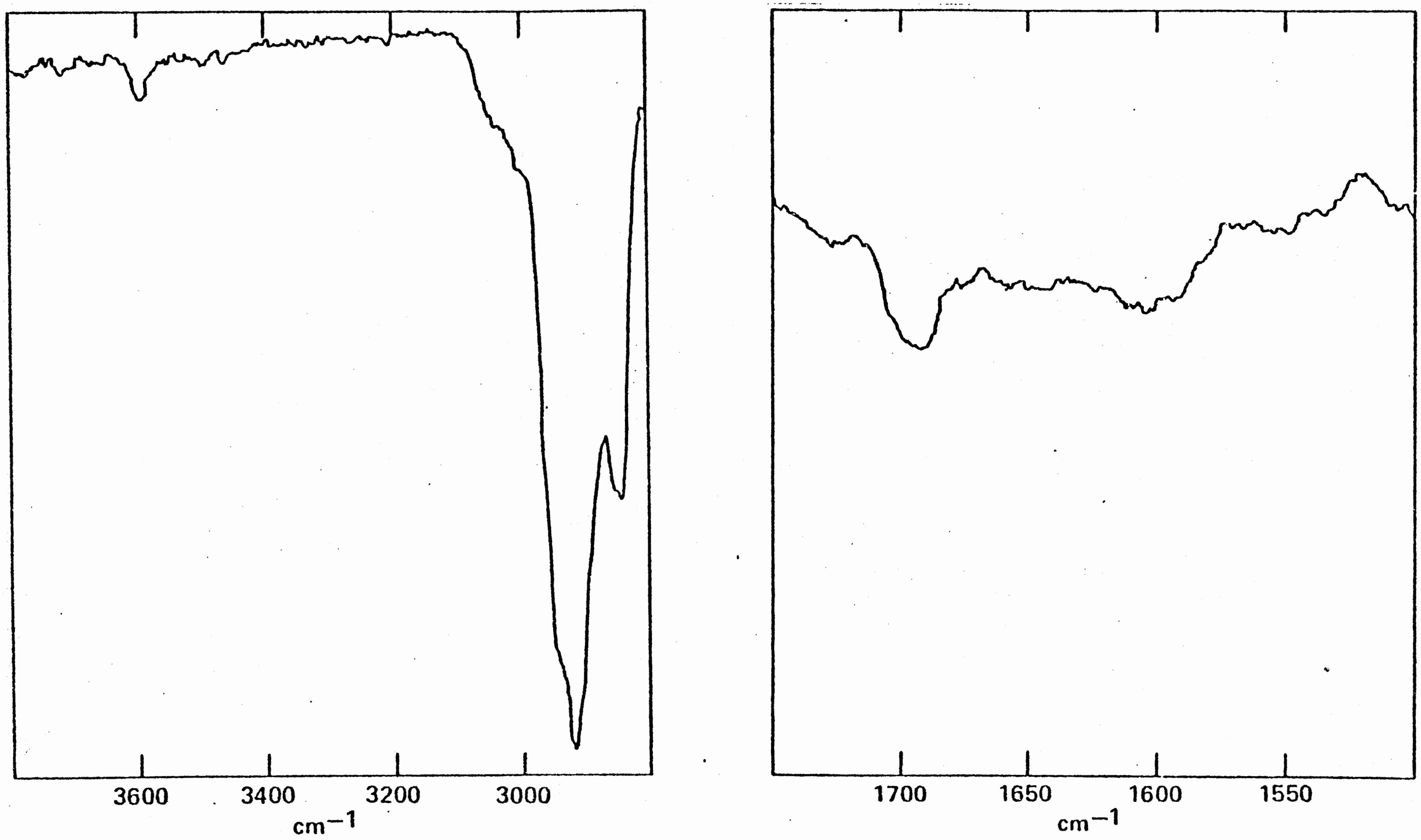

Figure 6. Partial Solution (CCl_4) IR Spectrum of Asphaltene Neutrals

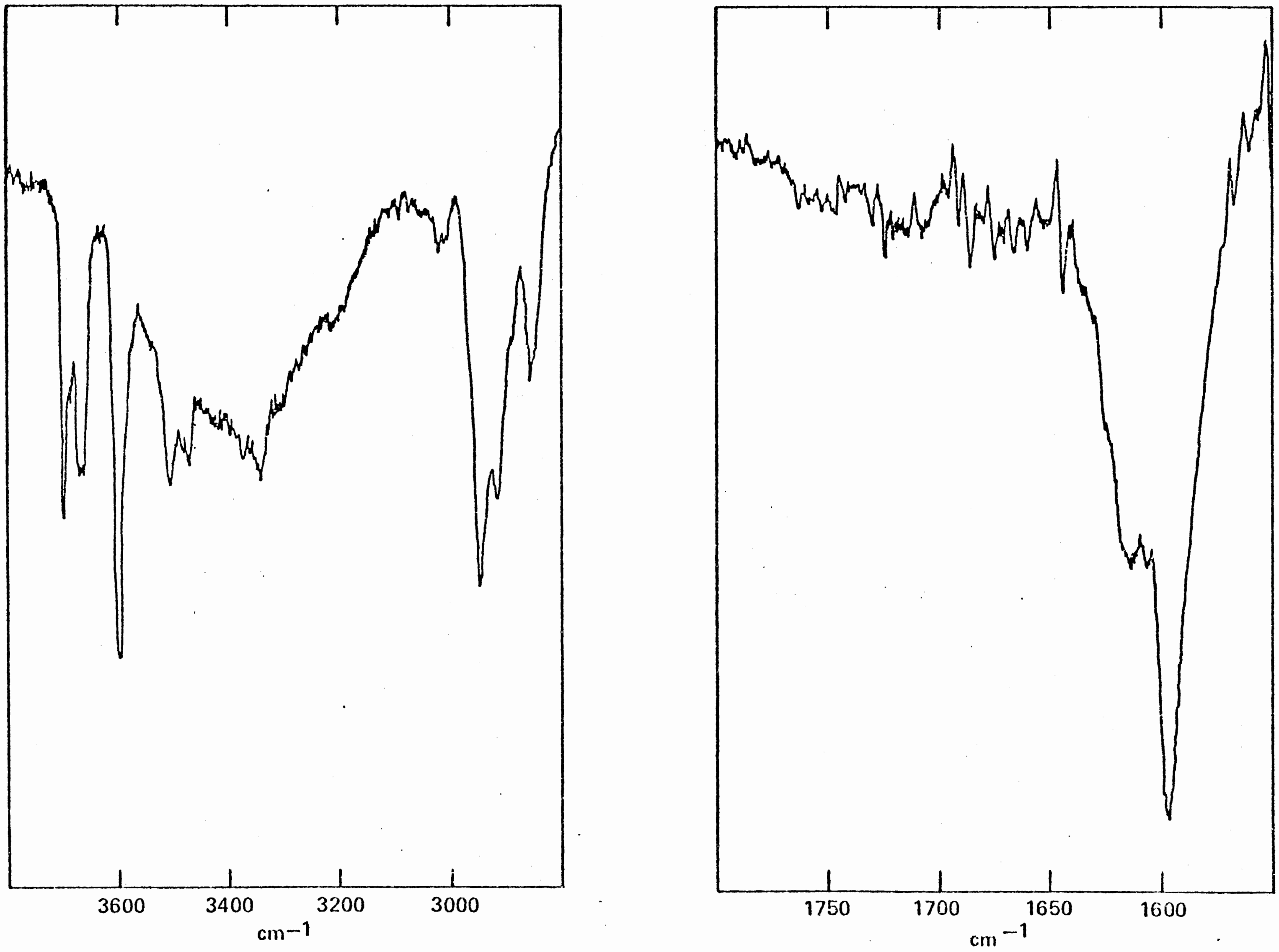

Figure 7. Partial Matrix-Isolation IR Spectrum of Oil Acids

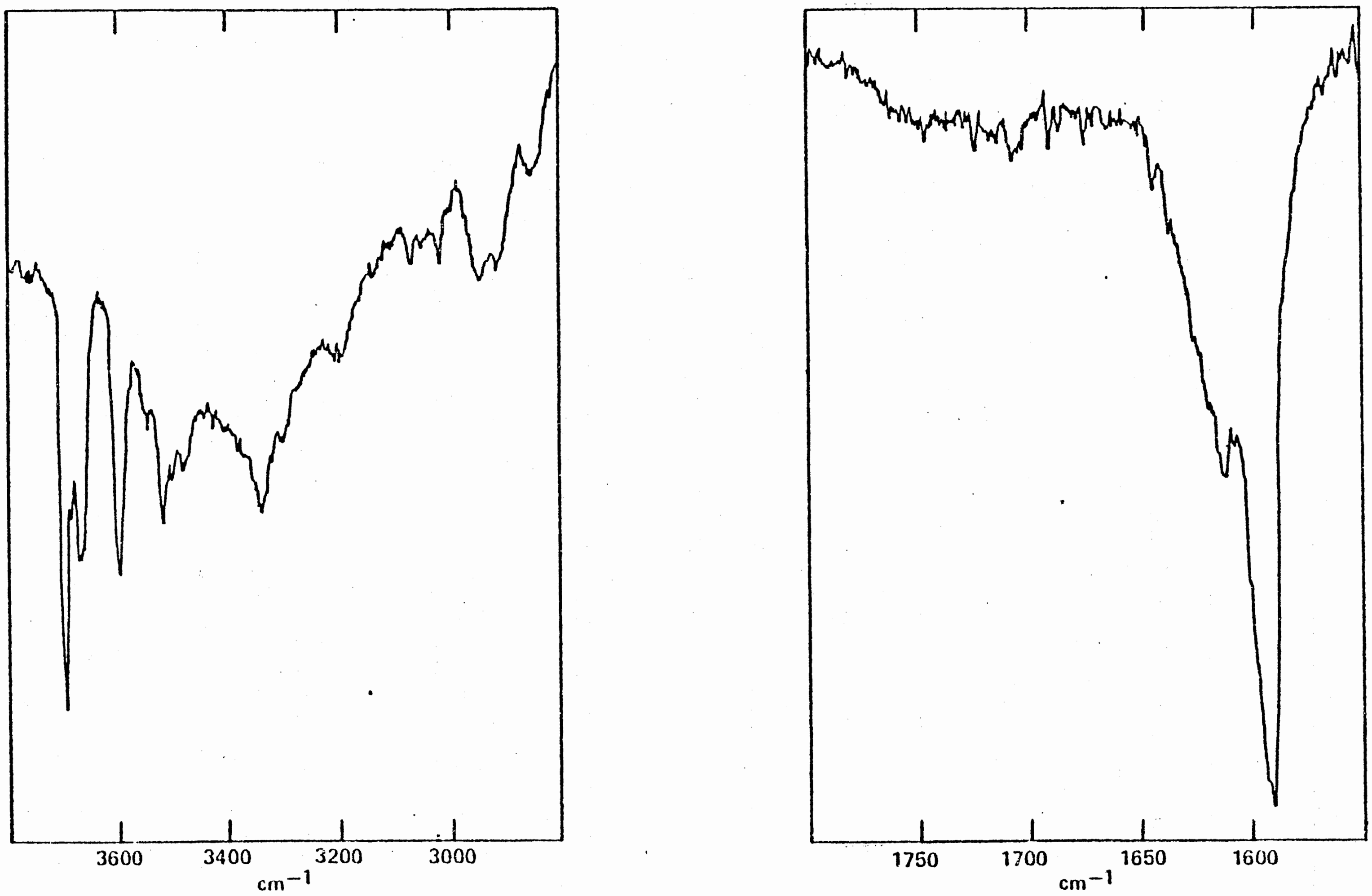

Figure 8. Partial Matrix-Isolation IR Spectrum of Asphaltene Acid Fraction A

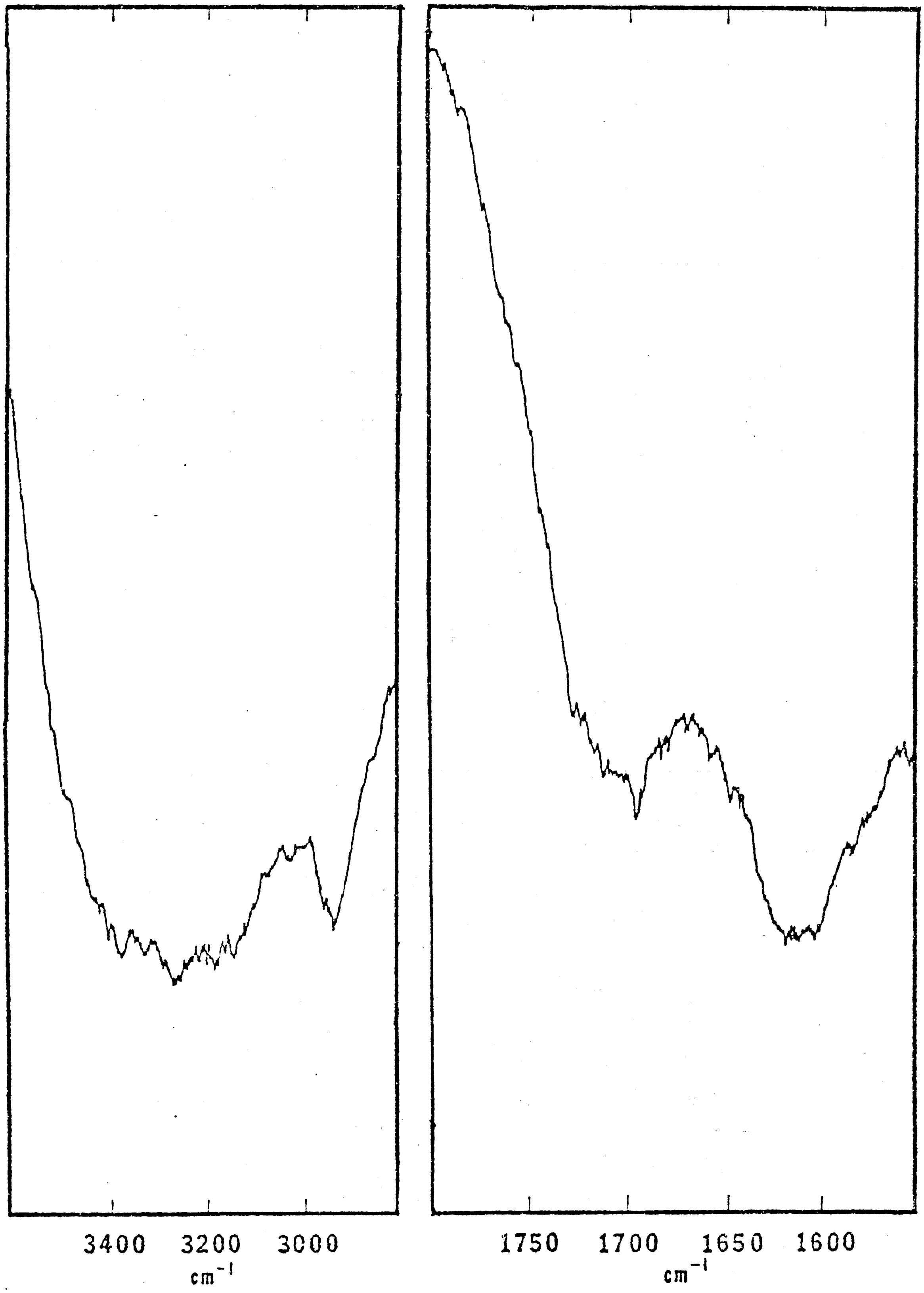

Figure 9. Partial KBr IR Spectrum of Asphaltene Acid Fraction B

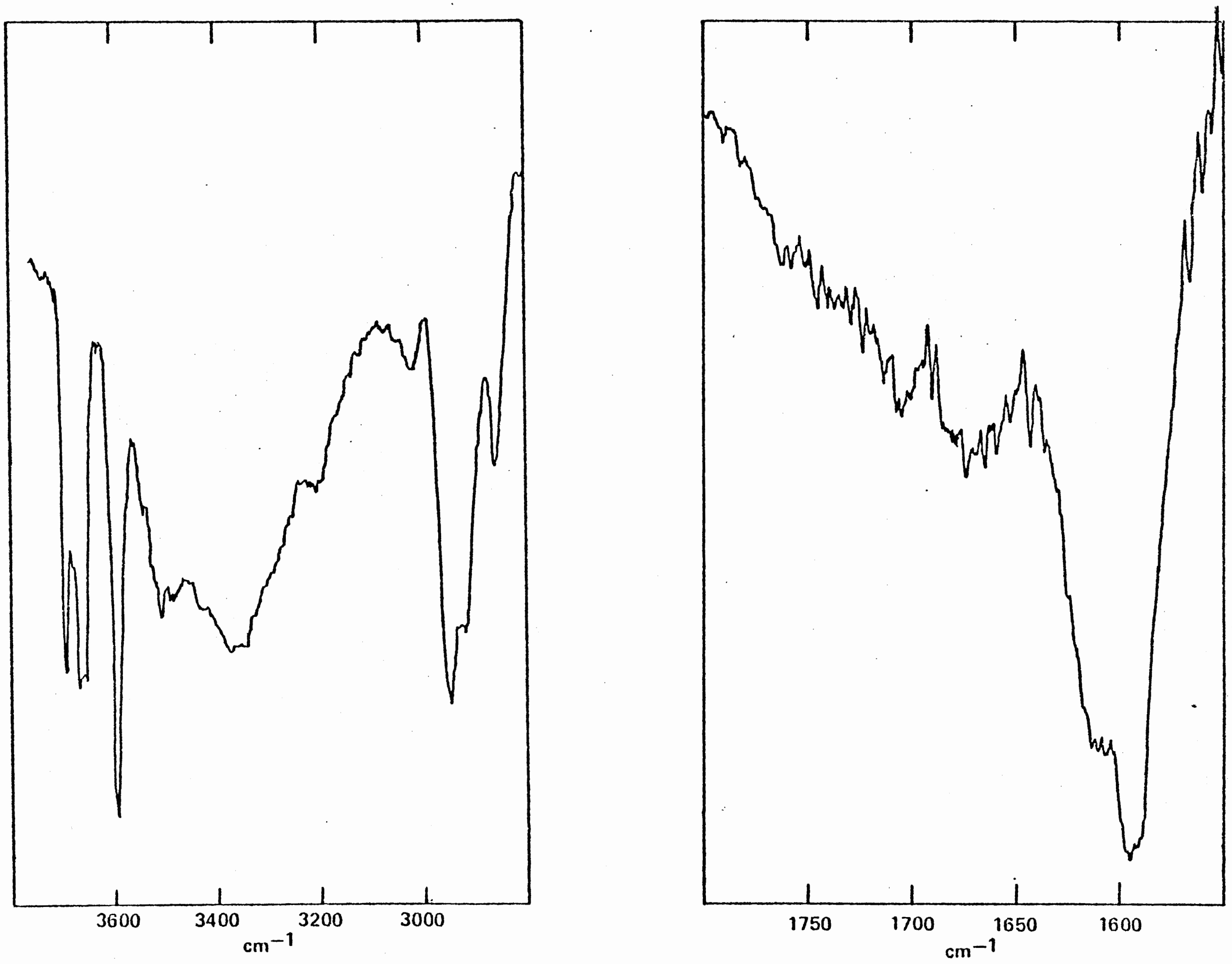

Figure 10. Partial Matrix-Isolation IR Spectrum of Asphaltene Acid Fraction C

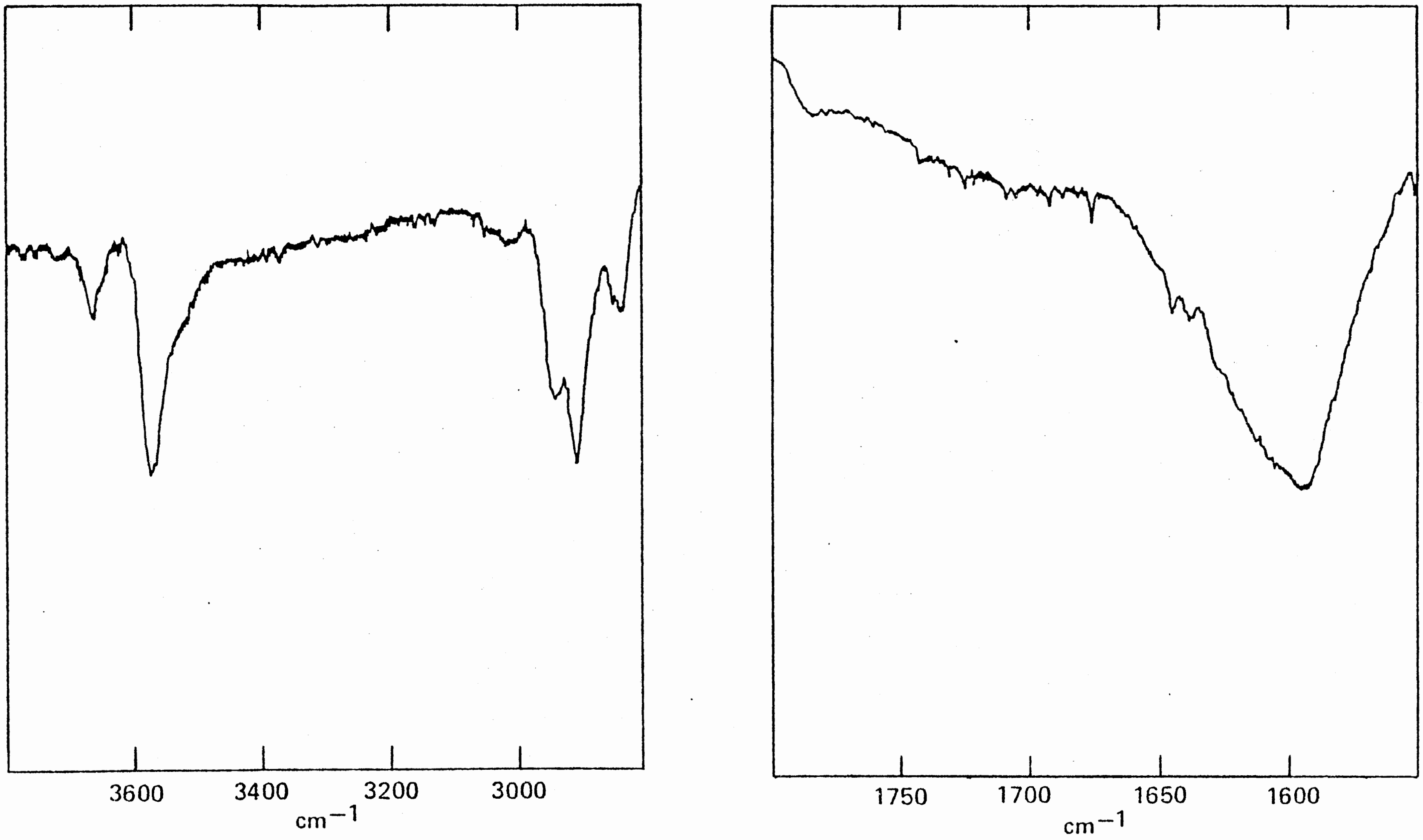

Figure 11. Partial Solution ($CDCl_3$) IR Spectrum of Asphaltene Acid Fraction D

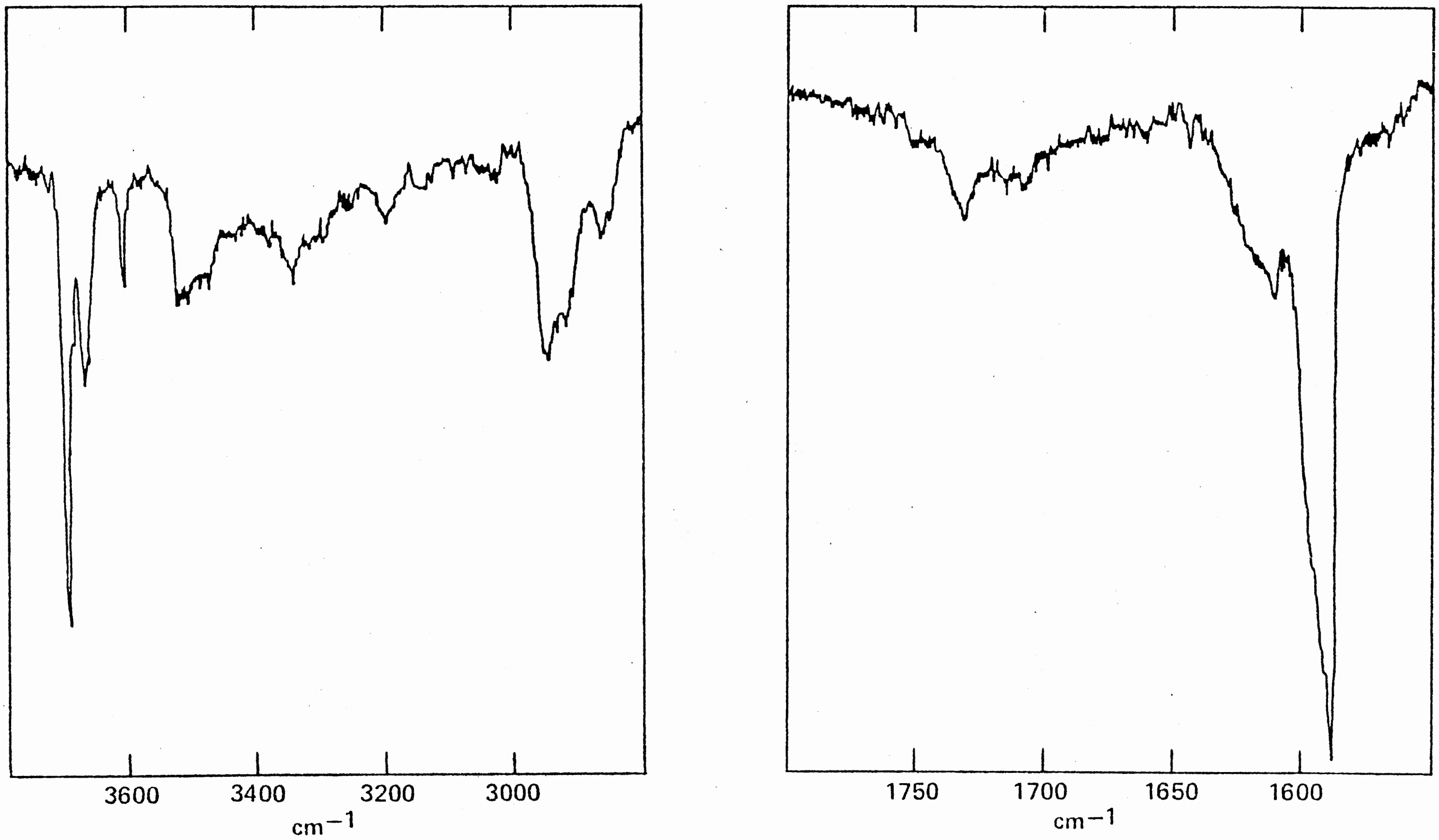

Figure 12. Partial Matrix-Isolation IR Spectrum of Oil Bases

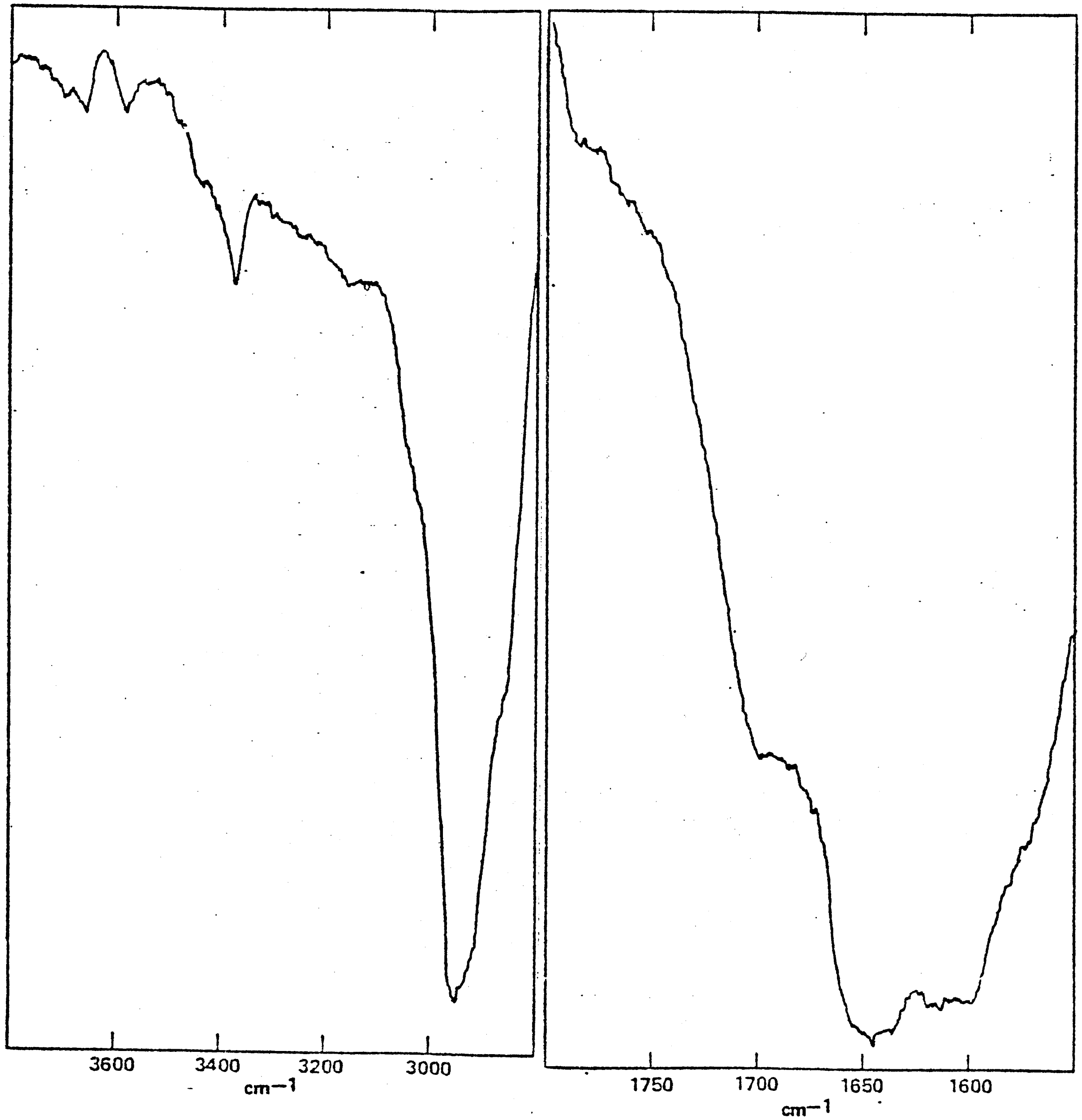

Figure 13. Partial Solution ($CDCl_3$) IR Spectrum of Asphaltene Base Fraction E

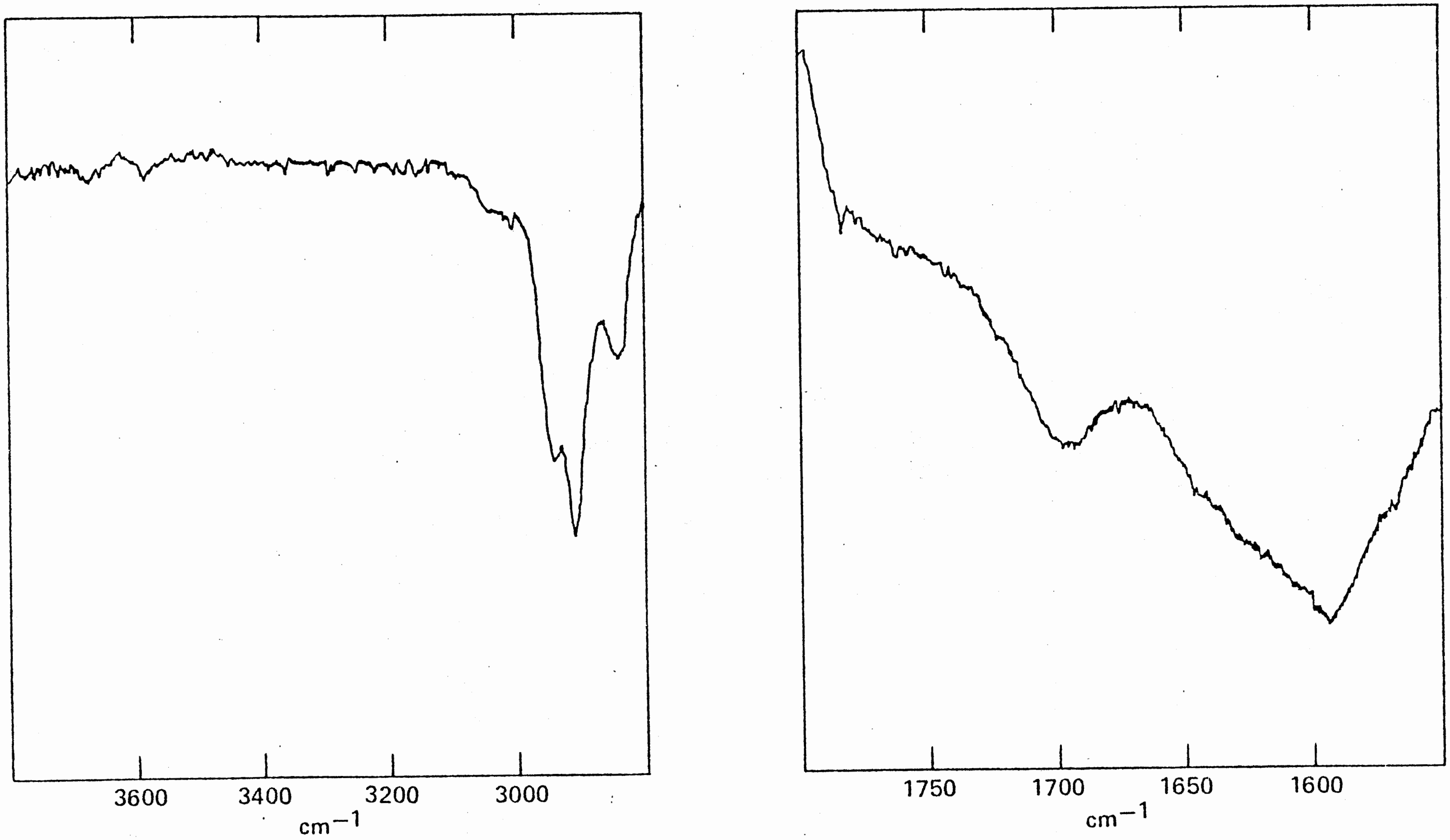

Figure 14. Partial Solution ($CDCl_3$) IR Spectrum of Asphaltene Base Fraction F

The samples were introduced into all-glass batch inlet systems on both mass spectrometers. Table III summarizes the amount of each fraction volatile at ca. 320° C in both mass spectrometers. There is good agreement between percent volatilities obtained at OSU and Exxon.

The high-resolution 70-eV EI mass spectra obtained at OSU were recorded on photographic plates at a resolution of ca. 20,000. The data were recovered by reading the line positions corresponding to the m/e values in the spectrum of the sample with respect to the line positions corresponding to the m/e values of the ions in the mass spectrum of perfluorokerosene. The data were then computer processed to obtain precise ion masses based upon both the C=12 and $CH_2=14$ (22) mass scales.

Since the decimal fractions of the molecular weights within a given Z series are identical in the $CH_2=14$ mass scale, use of these molecular weights facilitates organization of the data in Z series. Most probable molecular formulas were then assigned to each experimental exact mass. The difference between the experimental exact masses and 95% of those calculated for the assigned molecular formulas was $\leq$5mmu.

Quantitative data obtained for the asphaltenes and oils at OSU were acquired from high- and low-resolution FI/MS. Field-ionization mass spectrometry has been shown to be ideally suited to a molecular-ion group-type analysis of aromatic hydrocarbons and aromatic compounds containing heteroatoms (23,24). For compounds of the general formula $C_NH_{2N+Z(H,N_a,O_b,S_c)}N_aO_bS_c$, equation II-1 expresses the weight percent of the ith homolog in the jth specific Z series in terms of both the molecular ion intensities, $I(Z_j)_i$, and gram sensitivities, $S(g_j)_i$, for all

TABLE III

PERCENT OF FRACTION VOLATILE AT 300-320° C IN BATCH INLET SYSTEMS

Class	Fraction		Percent Volatile in	
			MS-50	21-110B
Oils	Acids			100%
	Bases			100
	Neutral Aromatics			100
Asphaltenes	Acids	A	47%	50
		B	32	31
		C	78	75
		D	50	44
	Bases	E	80	77
		F	59	63
	Neutrals (Saturates & Aromatics)		97	97

specific Z series, i.e., $Z(H,N_a,O_b,S_c)$. In equation II-1 the specific Z values are designated as Z_j and equal $n-2(j)$ for $j=1,2,3,\ldots \underline{1}$ for each value of a, b, and c in the general molecular formula where n=4 or 3 for even or odd values of a, respectively.

$$WP(Z_j)_i = \frac{I(Z_j)_i/S(g_j)_i}{\sum_{j=1}^{l} \sum_{i=1}^{m} I(Z_j)_i/S(g_j)_i} \times 100 \qquad \text{II-1}$$

The available data indicate that the relative mole sensitivities, $S(M_j)_i$, for field ionization of aromatic compounds of present interest are essentially constant within a specific Z series (23). Thus, substitution of the expression $S(g_j)_i = MW(Z_j)_i/S(M_j)$ into equation II-1 leads to equation II-2. For the general case FI/MS molecular-ion abundances were converted to weight percents via equation II-2 making the reasonable approximation that all $S(M_j) = 1$ (23). Weight percents

$$WP(Z_j)_i = \frac{I(Z_j)_i \cdot MW(Z_j)_i/S(M_j)}{\sum_{j=1}^{l} \sum_{i=1}^{m} I(Z_j)_i \cdot MW(Z_j)_i/S(M_j)} \times 100 \qquad \text{II-2}$$

for both the oil and asphaltene aromatic neutrals were also calculated including FI relative mole sensitivities. The relative mole sensitivities used were either the reported values or estimated from a plot of -Z number vs. FI-S(M) (23). As expected, both approaches yield similar results.

The molecular-ion abundances used to calculate weight percents were obtained as follows. The total molecular-ion abundance at a nominal mass was obtained from the low-resolution FI spectra. Multiplet ratios obtained from high-resolution FI spectra were then used to factor the nominal mass ion abundances into individual ion abundances. In order to retain reasonable sensitivity, the high-resolution FI mass spectra were recorded at a resolution of *ca*. 10,000. However, at this resolution it was possible to resolve two ion m/e values differing in mass by *ca*. 1 part in 20,000 with approximately a 70% valley. The fall-off in the molecular-ion intensities in the high mass region of the high-resolution FI/MS of a number of the fractions effectively precluded determination of the individual molecular ion intensities at a given nominal m/e value. In these instances, the molecular-ion intensities in the low-resolution FI/MS of these fractions were factored into intensities for the component molecular ions by extrapolating the ratios of the specific Z series molecular-ion intensities observed in the lower mass region of the high-resolution FI/MS.

The corresponding quantitative data obtained from Exxon were calculated from LV/EI molecular-ion abundances via equation II-1. Low voltage electron impact sensitivities and the relationship $S(g)_i = K(Z_j)/MW(Z_j)_i$ were used to obtain the weight percents of the individual homologs (25). The resolution of the AEI MS-50 was *ca*. 40,000 when the mass spectra of the various asphaltene fractions were obtained.

Carbon-number distributions obtained for the oil and asphaltene aromatic neutrals by FI/MS are presented in Tables IV-VI. These data were calculated using FI relative mole sensitivities. Corresponding carbon-number distributions obtained for the asphaltene

TABLE IV

CARBON-NUMBER DISTRIBUTION FOR OIL AROMATIC NEUTRALS

		Weight Percents (x 10^3) for Carbon Number																						
Z Series	Parent Formula	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	Total
-6	C_6H_6	2.2	3.1	7.9	13.3	27.1	37.4	60.7	54.0	73.2	109.9	117.4	115.5	79.1	61.9	40.1	31.3	35.7	34.1	27.2	18.4	12.2			972.7
-8	C_9H_{10}		1.0	12.2	53.5	90.6	181.1	146.2	69.6	74.0	85.2	95.5	86.9	65.4	45.2	31.9	28.6	71.2	33.2	24.1	12.7	9.0			1217.1
-10	C_9H_8	4.0	6.4	11.3	21.2	57.4	83.4	93.9	76.4	69.7	85.5	96.3	76.8	59.2	56.6	44.2	46.3	59.1	24.5	25.2	14.4	11.4	13.0		1036.2
-12	$C_{10}H_8$		4.8	36.9	204.7	497.1	337.2	243.7	87.4	60.2	58.8	72.0	54.5	61.2	56.1	51.3	59.2	47.4	36.2	36.3	31.9	43.4	32.5		2112.8
-14	$C_{12}H_{10}$				11.6	48.2	122.9	163.4	140.2	102.5	100.6	72.1	51.5	44.6	50.0	46.2	40.9	37.3	40.2	51.0	60.5	56.4	39.2		1290.3
-16	$C_{12}H_8$				5.0	16.8	39.6	58.5	74.9	80.9	83.6	76.4	51.8	40.2	43.3	42.3	41.6	40.1	39.5	46.8	85.9	52.3	32.2		951.7
-18	$C_{14}H_{10}$						22.5	47.3	77.8	106.3	96.0	70.7	58.9	52.4	47.8	41.8	37.8	33.6	39.8	76.1	86.1	53.8	23.0		971.7
-20	$C_{15}H_{10}$							17.0	10.7	17.0	30.2	9.5	23.7	15.0	16.0	14.1	19.4	18.9	21.7	27.3	32.9	22.3	14.8		310.5
-22	$C_{16}H_{10}$								6.2	15.7	9.6	8.7	19.3	18.0	16.9	20.0	21.1	28.4	82.6	44.0	35.9	21.0	15.0		362.4
-24	$C_{18}H_{12}$										11.5	4.1	4.2	5.9	3.9	7.8	7.6	10.7	20.4	16.9	17.4	10.0	15.7	18.0	154.1
-26	$C_{18}H_{10}$										5.7	7.2	5.0	12.6	6.1	5.6	6.3	8.7	7.0	6.6	6.7	7.8	10.6	8.0	103.9
-8(0)	C_8H_8O		6.4	16.1	9.4	14.6	18.4	25.5	21.3	33.3															145.0
-10(0)	C_8H_6O	1.4	8.5	31.5	55.9	44.5	32.4	34.2	39.0	32.2															279.6
-12(0)	$C_{10}H_8O$			9.3	10.1	22.3	22.3	29.9	17.5	18.2	26.5	24.4	17.4												204.9
-14(0)	$C_{12}H_{10}O$							14.2	12.9	8.7															35.8
-16(0)	$C_{12}H_8O$				12.8	39.8	55.3	55.8	49.8	16.3	14.6	16.7	12.8												273.9
-18(0)	$C_{14}H_{10}O$						3.8	6.0	12.2	11.4	13.5	29.3	24.9	22.9	15.0	7.3									146.3

TABLE V

CARBON-NUMBER DISTRIBUTION FOR AROMATIC HYDROCARBON TYPES PRESENT IN THE ASPHALTENE NEUTRALS

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																	
		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
-6	C_6H_6	5.4	8.6	11.2	15.3	26.0	64.5	82.2	84.1	53.1	40.3	29.0	17.6	21.6	9.5	7.6	14.5	11.9	14.4
-8	C_9H_{10}			3.6	7.4	19.6	59.3	79.9	88.2	116.0	83.4	21.7	17.0	28.3	12.6	17.7	18.0	11.2	11.7
-10	C_9H_8			7.8	13.1	14.4	20.0	37.0	53.9	65.1	50.0	71.1	40.1	46.2	27.3	20.7	23.4	19.6	20.3
-12	$C_{10}H_8$				6.0	8.4	37.8	208.4	187.1	162.8	78.9	67.8	75.3	43.9	36.2	27.9	22.6	56.1	23.2
-14	$C_{12}H_{10}$						11.5	23.5	73.4	96.8	115.1	118.8	87.4	46.1	24.0	30.9	23.0	24.6	19.7
-16	$C_{12}H_8$						16.4	17.0	36.9	52.9	84.3	71.2	59.1	58.1	77.6	48.9	44.3	27.5	40.0
-18	$C_{14}H_{10}$								38.7	63.5	75.3	67.7	75.8	76.8	57.0	56.6	33.5	34.3	29.7
-20	$C_{15}H_{10}$									1.7	12.9	10.1	35.2	63.8	44.6	55.2	46.3	29.3	36.3
-22	$C_{16}H_{10}$										5.2	22.8	57.4	78.7	56.1	61.1	42.2	39.9	34.7
-24	$C_{18}H_{12}$												14.5	37.0	56.5	56.7	60.3	39.2	38.6
-26	$C_{18}H_{10}$												8.3	15.1	32.3	35.4	67.3	42.8	56.7
-28	$C_{20}H_{12}$														32.2	43.0	37.8	47.0	49.2
-30	$C_{22}H_{14}$																11.1	45.4	185.2
-32	$C_{22}H_{12}$																2.0	18.7	21.9
-34	$C_{23}H_{12}$																1.6	1.9	4.8
-36	$C_{24}H_{12}$																		9.5

TABLE V (Continued)

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																	
		25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	Total
-6	C_6H_6	4.7	9.8	4.8	4.1	3.3	3.6	2.0											549.1
-8	C_9H_{10}	11.4	10.3	11.0	16.8	5.7	5.8	4.4	4.9	3.9	3.4	3.0	2.7	4.9					683.8
-10	C_9H_8	12.6	16.9	20.1	13.9	27.0	26.7	10.8	7.8	7.1	12.2	15.0	15.5	13.6	12.8	9.6	12.3		763.9
-12	$C_{10}H_8$	17.7	25.8	16.5	24.5	45.7	28.8	9.5	10.6	10.6	10.3	11.3	13.3	10.2	10.6	9.9	8.3		1306.0
-14	$C_{12}H_{10}$	22.4	16.1	26.8	45.8	49.1	38.8	32.3	21.5	17.7	18.3	16.5	13.5	20.0	15.4	14.6	12.0		1075.6
-16	$C_{12}H_8$	17.6	27.5	29.1	66.1	42.8	25.8	26.9	69.5	15.9	18.6	15.8	16.3	15.6	14.7	12.6	18.5		1067.5
-18	$C_{14}H_{10}$	39.4	41.9	97.1	131.0	93.7	38.3	24.8	22.6	20.3	19.5	18.3	21.9	17.9	17.1	28.7	22.1		1263.5
-20	$C_{15}H_{10}$	28.9	62.4	53.1	60.3	48.2	27.0	21.1	24.6	23.0	21.9	15.5	10.4	20.6	22.6	17.8	18.1		810.9
-22	$C_{16}H_{10}$	46.5	360.7	81.4	52.3	32.0	21.3	23.1	17.4	19.6	15.3	13.5	11.8	10.7	19.4	17.2	15.3	8.0	1163.6
-24	$C_{18}H_{12}$	47.0	139.5	64.1	36.6	32.0	21.0	20.3	25.0	17.9	16.4	11.3	10.4	10.7	9.4	8.9	7.6	8.5	784.4
-26	$C_{18}H_{10}$	231.7	78.8	44.3	34.3	29.1	24.3	19.6	22.8	12.2	11.0	10.4	11.6	13.7	10.5	10.9	10.2	8.6	841.9
-28	$C_{20}H_{12}$	54.2	39.3	32.9	27.6	13.8	11.4	14.5	5.2	3.5	2.9	2.9	2.7		3.2	2.5			425.8
-30	$C_{22}H_{14}$	96.5	50.2	35.7	29.4	29.7	26.3	11.0	4.7	13.3	2.8	3.3	2.8	2.8	2.7	2.6	2.2		557.7
-32	$C_{22}H_{12}$	45.8	28.6	40.4	19.8	15.5	19.1	11.2	13.0	3.7	2.8	3.1	3.0	3.5	2.8	2.8			257.7
-34	$C_{23}H_{12}$	6.0	7.2	18.7	24.4	30.8	28.0	26.3	15.9	15.0	12.0	10.5	21.9	14.7	8.7	11.6	4.7	5.0	269.7
-36	$C_{24}H_{12}$	5.9	6.1	3.1	12.6	12.7	8.9	7.0	7.0	5.3	5.9	4.6	4.1	3.5	3.2	5.9	5.2	5.2	115.7

TABLE VI

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN THE ASPHALTENE NEUTRALS

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																	
		8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
-8(0)	C_8H_8O	1.1	1.4	3.2	10.9	13.8	17.9	43.4	49.0	61.6	16.0	23.6	14.3						
-10(0)	C_8H_6O	0.4	0.7	3.3	8.3	6.8	20.6	30.3	33.7	51.0	25.3	27.7	24.7	17.4	21.2	11.0	11.4	5.8	10.1
-12(0)	$C_{10}H_8O$			1.0	3.8	6.0	11.9	31.3	40.7	29.5	33.0	38.2	32.1	18.2	20.6	17.2	14.7	11.1	11.2
-14(0)	$C_{12}H_{10}O$					3.1	8.6	15.5	20.1	15.1	18.3	18.0	21.5	10.6	20.2	12.5	23.6	23.3	17.9
-16(0)	$C_{12}H_8O$					4.9	20.7	50.6	61.6	31.5	50.3	38.4	35.1	26.3	22.4	18.5	12.7	24.2	15.7
-18(0)	$C_{14}H_{10}O$							7.8	16.0	23.6	47.2	39.3	34.3	34.5	23.0	24.3	22.9	20.7	10.4
-20(0)	$C_{14}H_8O$								34.4	50.2	34.0	16.2	23.4	23.3	33.1	25.9	23.2	20.8	25.4
-22(0)	$C_{16}H_{10}O$									6.0	5.8	42.6	49.9	38.0	37.0	44.0	32.7	34.8	19.9
-24(0)	$C_{17}H_{10}O$											11.1	27.7	22.0	32.4	19.8	29.8	28.4	19.0
-26(0)	$C_{18}H_{10}O$											3.5	14.0	14.8	16.7	23.7	19.9	32.7	24.5
-28(0)	$C_{20}H_{12}O$													7.0	21.5	17.5	9.4	13.4	23.5
-30(0)	$C_{21}H_{12}O$														5.7	9.7	10.0	12.0	14.6
-32(0)	$C_{22}H_{12}O$																6.1	20.9	4.3

TABLE VI (Continued)

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number															
		26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	Total
-8(0)	C_8H_8O																256.2
-10(0)	C_8H_6O	12.8	10.6	7.4	7.7	5.8	4.7	4.7	3.8	4.3	3.6						375.1
-12(0)	$C_{10}H_8O$	15.5	10.2	9.7	9.2	7.9	5.7	5.2									383.9
-14(0)	$C_{12}H_{10}O$	12.3	11.8		11.8		4.1										268.3
-16(0)	$C_{12}H_8O$	16.6	19.3	20.2	12.6	17.9	12.0	9.8	10.2	9.1	7.5	11.1	8.5	8.1	6.7		582.5
-18(0)	$C_{14}H_{10}O$	15.0	17.4	18.0	22.8	16.5	42.7	9.8	11.4	9.7	9.9	9.5	9.0	7.7			503.4
-20(0)	$C_{14}H_8O$	30.5	14.6	15.0	22.7	12.2	13.7	12.4	11.9	12.2	11.2	10.3	9.8	9.3			486.4
-22(0)	$C_{16}H_{10}O$	23.6	14.4														348.7
-24(0)	$C_{17}H_{10}O$	29.4	24.7	16.8	18.9	16.9	17.4	10.3	10.2	8.3	9.5	8.0					360.6
-26(0)	$C_{18}H_{10}O$	19.3	21.2	14.9	14.2	14.0	11.7	8.3	7.7	7.9	9.7	10.0	8.8	8.3	5.3		319.1
-28(0)	$C_{20}H_{12}O$	15.5	16.7	11.5	16.0	9.0	11.3	8.1	7.9	7.6	8.4	9.8	7.6	7.8	7.4	6.2	243.1
-30(0)	$C_{21}H_{12}O$	15.1	8.9	13.4	12.4	9.5	8.5	5.6	2.9	4.8	4.3	3.5	5.2	4.0	3.9	3.2	157.2
-32(0)	$C_{22}H_{12}O$	8.7	7.2	14.5	7.6	10.7	4.6	12.9	2.7	3.2	2.7	2.8	2.6	2.5	2.2		116.2

TABLE VII

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR AROMATIC HYDROCARBON TYPES PRESENT IN THE ASPHALTENE NEUTRALS

Z Series	Molecular Formula for Parent Compound	Weight Percents (x 10^3) for Carbon Number 7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
-6	C_6H_6	17.7	18.9	18.4	22.3	12.9	20.4	21.3	19.9	31.3	16.8	12.8	17.0	20.6	11.9	11.6	4.1	7.3	12.1	6.6
-8	C_9H_{10}			17.5	32.5	37.6	54.7	55.8	97.4	80.6	28.2	40.5	15.1	21.8	15.0	10.9	11.7	11.2	16.2	10.2
-10	C_9H_8			2.6	12.8	36.7	36.6	56.6	48.5	56.8	38.3	30.3	22.8	26.0	26.7	13.6	13.1	16.0	14.1	9.7
-12	$C_{10}H_8$				23.3	23.6	100.1	263.3	213.2	128.7	64.8	34.0	35.2	23.3	27.4	22.3	15.0	15.0	25.0	9.7
-14	$C_{12}H_{10}$						7.8	24.3	77.2	109.8	98.3	75.5	48.8	40.0	37.1	27.0	22.6	27.9	17.3	15.3
-16	$C_{12}H_8$						3.2	6.0	19.9	42.7	56.3	65.5	65.5	66.0	48.6	54.4	43.2	41.0	38.4	29.4
-18	$C_{14}H_{10}$								15.0	31.3	71.7	100.5	81.6	65.8	38.3	41.0	24.3	28.7	31.5	24.5
-20	$C_{15}H_{10}$									0.9	9.5	23.3	46.1	64.9	53.6	53.4	45.2	33.7	29.1	30.4
-22	$C_{16}H_{10}$										2.0	7.1	24.1	49.0	64.8	55.3	41.3	37.2	33.7	58.1
-24	$C_{18}H_{12}$												6.1	25.3	51.0	72.8	55.8	44.2	37.1	71.6
-26	$C_{18}H_{10}$													0.2	7.1	30.8	48.8	49.5	64.1	360.4
-28	$C_{20}H_{12}$														4.6	14.3	35.4	49.8	53.6	64.4
-30	$C_{22}H_{14}$																8.3	54.1	484.3	229.7
-32	$C_{22}H_{12}$																	17.9	21.3	59.2
-34	$C_{24}H_{14}$																		0.5	5.3
-36	$C_{24}H_{12}$																		0.3	
-38	$C_{26}H_{14}$																			
-40	$C_{28}H_{16}$																			
-42	$C_{28}H_{14}$																			

TABLE VII (Continued)

Z Series	Molecular Formula for Parent Compound	Weight Percents (x 10^3) for Carbon Number 26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	Total
-6	C_6H_6	8.3	7.5	8.5	7.1	12.2	11.1	4.8	13.3	10.7	8.2			10.2			7.5				430.6
-8	C_9H_{10}	13.6	16.5	9.9	30.4	16.0	22.3	15.0	16.7	17.5	9.0				10.0	14.1	9.0				756.7
-10	C_9H_8	16.7	21.4	20.6	19.2	43.2	15.6	9.4	11.7	7.0	12.1	9.4		5.4	9.2	11.7					673.4
-12	$C_{10}H_8$	16.8	20.7	27.2	44.5	35.4	12.9	6.3	7.0	6.6	4.1	8.5					4.6		5.6		1224.0
-14	$C_{12}H_{10}$	21.3	39.4	51.0	72.8	48.3	24.1	17.7	10.4	11.4	8.0	16.7		6.3		9.0	9.9				975.0
-16	$C_{12}H_8$	37.7	66.0	147.1	88.2	64.6	22.4	33.5	10.9	17.5	11.9	6.5				5.3	12.8				1104.2
-18	$C_{14}H_{10}$	46.8	126.3	184.8	154.9	59.7	37.2	13.3	11.7	11.2	7.8	7.1	11.7				24.1				1250.7
-20	$C_{15}H_{10}$	54.4	76.0	96.6	83.1	45.2	21.6	13.4	17.0	15.0	16.2	10.0	10.9	7.5	3.6	6.0		3.2	3.1	9.7	882.3
-22	$C_{16}H_{10}$	525.5	123.8	80.4	56.8	23.8	14.8	7.8	5.1	10.5	9.9	5.8	4.3			4.3					1245.3
-24	$C_{18}H_{12}$	156.4	63.4	57.8	33.7	21.9	10.9	12.9	7.5	7.1	6.3	6.0	3.1		5.3			3.6			759.6
-26	$C_{18}H_{10}$	135.8	76.2	37.9	22.1	13.6	10.0	7.1	8.8	6.6	8.0	3.9	6.1		4.4		3.2	1.9			906.6
-28	$C_{20}H_{12}$	52.7	40.3	23.3	18.9	0.5	4.4	5.6	4.3	5.1	4.9	5.1	4.1			2.7	2.0	3.7			399.7
-30	$C_{22}H_{14}$	58.8	19.9	15.0	13.4	9.4	8.7	5.6	3.6	4.3	3.2	4.1	3.1	4.8		1.9		3.6			935.5
-32	$C_{22}H_{12}$	30.1	6.6	7.0	3.7	3.6	3.2	5.3	1.9	3.4	2.6		3.6	1.2	2.6	2.2	2.4	3.2	2.6		183.3
-34	$C_{24}H_{14}$		5.1	7.1	6.1	6.3	5.1	1.2	1.9	2.0	1.9	1.9	1.9	0.9	2.7	1.9					51.7
-36	$C_{24}H_{12}$	0.2	1.5		6.1		4.8	3.6		3.2	3.2	3.4		1.7		1.9		1.5	1.2		32.6
-38	$C_{26}H_{14}$	3.7	2.9		5.8		4.1	2.9		1.2	2.7	3.1				1.4	1.2				28.9
-40	$C_{28}H_{16}$			5.3	1.0		2.0	5.6	1.0		1.4			1.2		1.0					18.5
-42	$C_{28}H_{14}$				1.2				0.7			0.7			1.7						4.3

TABLE VIII

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN THE ASPHALTENE NEUTRALS

Z Series	Molecular Formula for Parent Compound	Weight Percents (x 10^3) for Carbon Number																	
		8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
-8(0)	C_8H_8O	2.0	4.8	9.2	31.8	58.3	36.4	27.4	15.5	13.1	16.0	2.6	13.9		4.8	10.5		4.8	5.3
-10(0)	C_8H_6O		2.0	12.8	29.1	30.4	31.8	32.3	36.4	20.9	14.3	18.0	7.1	9.9	5.1	6.8	5.4	6.1	11.9
-12(0)	$C_{10}H_8O$			2.6	4.8	13.9	20.4	25.7	27.4	21.9	20.6	19.6	12.9	10.4	6.0	7.0	7.7	9.2	6.3
-14(0)	$C_{12}H_{10}O$					1.7	6.1	11.1	16.8	22.3	22.6	16.2	11.2	14.6	11.6	12.1	11.2	12.8	9.5
-16(0)	$C_{12}H_8O$					3.4	14.3	35.0	48.3	43.7	34.5	25.3	23.5	19.4	13.6	15.5	13.6	13.4	10.2
-18(0)	$C_{14}H_{10}O$							2.2	8.2	16.2	22.3	27.9	26.2	25.3	28.1	20.6	22.8	16.3	11.6
-20(0)	$C_{14}H_8O$								1.9	2.4	12.4	8.2	17.5	16.7	26.5	20.2	25.5	20.9	16.2
-22(0)	$C_{16}H_{10}O$									4.8	15.0	24.0	38.3	31.5	25.2	26.7	21.8	23.0	20.1
-24(0)	$C_{17}H_{10}O$										2.4	3.7	6.6	13.1	19.2	21.3	30.4	25.5	22.4
-26(0)	$C_{18}H_{10}O$											1.7	3.6	7.1	11.4	14.1	17.2	24.0	27.4
-28(0)	$C_{20}H_{12}O$													4.8	7.8	17.9	20.7	25.5	21.9
-30(0)	$C_{21}H_{12}O$														1.9	4.8	7.7	12.9	22.1
-32(0)	$C_{22}H_{12}O$																7.1	8.3	10.9
-34(0)	$C_{24}H_{14}O$																	3.6	6.0
-36(0)	$C_{24}H_{12}O$																	1.5	2.2

TABLE VIII (Continued)

Z Series	Molecular Formula for Parent Compound	Weight Percents (x 10^3) for Carbon Number 26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	Total
-8(0)	C_8H_8O	8.3	6.8	6.3	10.2	6.8	6.0	9.2	10.4	10.0	10.5		16.2	12.6					369.4
-10(0)	C_8H_6O	6.0	5.4	4.4	12.2	10.5			6.5	6.8	5.8	8.2	10.4	8.0		5.4	7.5		377.4
-12(0)	$C_{10}H_8O$	7.5	13.1	8.3	10.7	7.5	7.1	6.0			6.3		4.1			3.7		7.7	298.0
-14(0)	$C_{12}H_{10}O$		6.1	8.0	13.3			5.3	7.8	5.3		14.6			17.7	6.1	4.8		268.3
-16(0)	$C_{12}H_8O$	13.6	11.6	15.8	15.3	13.1	6.8	11.4	9.9	5.3	7.7			6.3			4.6		434.9
-18(0)	$C_{14}H_{10}O$	15.1	16.8	25.2	17.0	15.8	15.1	8.5	9.2	5.1	8.3		3.7						367.4
-20(0)	$C_{14}H_8O$	13.1	18.9	29.8	14.3	17.5	8.2	10.4	9.0	11.6	9.4	5.1		4.8	6.0				326.1
-22(0)	$C_{16}H_{10}O$	19.4	20.9	17.3	10.2	13.1	7.8		10.0	6.1	5.1			2.9		3.2			346.1
-24(0)	$C_{17}H_{10}O$	28.4	27.4	17.5	14.5	12.1	6.3	11.7	4.8	5.8	4.6	4.6	6.3		4.8	2.2			295.5
-26(0)	$C_{18}H_{10}O$	30.4	28.2	15.5	13.9	11.9	12.2	4.9	5.3	6.6	6.3	3.2	7.3		2.9		2.6		257.7
-28(0)	$C_{20}H_{12}O$	18.4	18.7	13.3	9.9	11.9	8.0	8.8	4.3	5.8	3.2	2.4		2.6	4.1	3.2			213.0
-30(0)	$C_{21}H_{12}O$	14.1	14.8	15.0	10.5	8.2	8.3	3.9	4.3	4.3	4.1	1.7	2.7	2.9	5.1			1.5	150.6
-32(0)	$C_{22}H_{12}O$	11.7	10.2	9.0	6.3	7.0	5.6	5.3	6.1	4.1	1.9	3.1	2.2		2.0				100.8
-34(0)	$C_{24}H_{14}O$	9.2	7.0	5.3	6.1	4.4	4.8	3.2	2.4	1.9	4.8	1.9	1.2		2.0				63.6
-36(0)	$C_{24}H_{12}O$	2.9	3.2	4.6	5.8	3.1	4.8	3.2	3.2	1.9	1.7						1.0		39.1

TABLE IX

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}S$ AROMATIC COMPOUNDS PRESENT IN THE ASPHALTENE NEUTRALS

Z Series	Molecular Formula for Parent Compound	Weight Percents ($X10^3$) for Carbon Number 8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	Total
-10(S)	C_8H_6S		1.4	6.1	8.5	6.8	4.1	2.0	1.0	1.2	0.7	0.9	0.7	0.5	0.5	0.9	0.3	0.5	0.7	0.9	1.5	1.2	0.5							40.8
-12(S)	$C_{11}H_{10}S$				1.2	3.9	12.6	17.9	16.0	12.2	7.8	6.5	6.0	4.4	3.6	4.4	2.7	2.4	3.4	6.3	8.2	11.7	7.7	3.9	2.9	1.7	1.9	1.2		150.2
-14(S)	$C_{12}H_{10}S$					1.5	1.5	2.4	3.1	3.6	3.1	3.1	2.2	2.6	2.0	1.9	1.7	1.4	1.7	3.1	6.6	3.9	2.9	1.0	1.5	0.5	0.9	0.5		52.7
-16(S)	$C_{12}H_8S$					1.5	3.7	9.0	11.1	9.0	7.1	4.3	4.4	2.7	3.1	3.4	2.7	5.1	13.8	20.1	16.8	6.5	4.1	1.4	1.4	1.2	0.9	0.9		134.2
-18(S)	$C_{14}H_{10}S$								2.2	3.9	7.7	10.9	8.8	8.8	7.5	5.6	4.8	4.9	8.8	12.4	15.6	13.4	7.3	3.6	2.2	2.7	2.4	2.6		136.1
-20(S)	$C_{14}H_8S$								1.0	1.0	4.9	2.2	1.9	1.4	1.4	1.2	2.0	18.0	4.3	2.7	1.9	0.9	0.5	0.3						45.6
-22(S)	$C_{16}H_{10}S$									0.9		8.2	10.7	8.2	6.5	5.4	10.5	23.0	9.4	8.5	4.9	3.2	1.5	1.9	1.0	1.0				104.8
-24(S)	$C_{17}H_{10}S$											0.9	3.2	6.8	6.8	8.8	21.9	8.2	4.6	2.2	1.4	0.9	0.7	0.5	0.5	0.3	0.5	0.2	0.3	68.7
-26(S)	$C_{18}H_{10}S$													4.1	6.0	5.1	6.1	5.1												26.4
-28(S)	$C_{20}H_{12}S$													1.4	2.0	4.9	2.4	0 5												11.2
-30(S)	$C_{21}H_{12}S$														6.5		2.7													9.2

TABLE X

CARBON-NUMBER DISTRIBUTION FOR OIL AROMATIC ACIDS

Z Series	Molecular Formula for Parent Compound	Weight Percents ($X10^3$) for Carbon Number																				Total
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
-6(O)	C_6H_6O	6.4	98.1	344.5	352.5	203.7	96.8	53.9	38.1	18.3	9.2	6.1	24.0	26.5	20.1	16.5	14.8	11.4	9.3			1350.2
-8(O)	$C_9H_{10}O$				81.8	199.5	225.2	163.7	112.8	47.2	21.7	18.7	18.8	25.5	23.6	19.9	25.7	11.7	7.3	6.7		1009.8
-10(O)	C_9H_8O				5.2	17.4	32.2	44.6	67.1	71.3	59.9	45.9	20.4	14.1	13.5	12.4	11.4	15.0	7.8	7.7		445.9
-12(O)	$C_{10}H_8O$					23.5	63.4	88.3	56.5	34.5	37.0	38.1	29.1	26.7	19.6	12.9	8.4	5.3	4.6	3.9		451.8
-14(O)	$C_{12}H_{10}O$							11.6	37.7	77.8	78.0	54.6	44.7	32.1	24.2	17.0	13.8	10.9	8.2	5.3		415.9
-16(O)	$C_{12}H_8O$							2.7	15.5	43.1	35.5	35.6	33.7	30.2	25.3	21.3	16.1	12.1	8.7	6.3		286.1
-18(O)	$C_{14}H_{10}O$									4.8	11.9	41.0	49.9	55.6	60.9	52.5	44.6	36.2	29.0	23.7		410.1
-20(O)	$C_{15}H_{10}O$										2.8	7.6	13.9	16.0	21.2	23.0	16.5	14.8	11.4	9.3		136.5
-22(O)	$C_{16}H_{10}O$											4.5	7.5	17.6	12.7	14.1	14.2	25.7	14.6	12.2	11.1	134.2
-6(O_2)	$C_6H_6O_2$	19.7	35.7	50.0	37.4	21.2	7.4															171.4
-8(O_2)	$C_9H_{10}O_2$				5.6	8.7	8.8	3.1	9.8	11.5	14.7	10.0	13.2	14.4	16.5	14.8	11.4	9.3				151.8
-10(O_2)	$C_9H_8O_2$				16.0	40.9	47.1	28.2	35.0	23.5	15.0	11.7	12.7	11.8	8.5	15.4	8.8	7.3	4.5			286.4
-12(O_2)	$C_{10}H_8O_2$					2.7	11.7	11.9	11.9	13.0	8.6	20.4	18.8	16.9	18.6	17.1	10.0	11.7	11.5			184.8
-14(O_2)	$C_{12}H_{10}O_2$							13.0	19.2	24.6	22.8	29.1	26.7	26.1	21.6	16.7	15.9	13.8	11.7			241.2
-16(O_2)	$C_{12}H_8O_2$							9.4	20.5	39.0	54.6	44.7	38.6	30.2	25.4	20.7	16.3	13.7	8.8			321.9
-18(O_2)	$C_{14}H_{10}O_2$									21.3	50.9	50.6	47.5	45.5	38.3	35.5	29.0	20.9	15.1			354.6
-15(N)	$C_{12}H_9N$							7.5	16.3	26.1	33.9	24.0										107.8

TABLE XI

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION A

		Weight Percents (x 10^3) for Carbon Number																						
% Series	Parent Formula	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	
-6(0)	C_6H_6O	52.5	289.7	187.2	22.7	18.2	9.6																	579.9
-8(0)	$C_9H_{10}O$				32.0	14.9	15.4	5.0	3.8															71.1
-10(0)	C_9H_8O				3.3	22.9	26.7	31.1	15.7	27.8	23.2	19.5												170.2
-12(0)	$C_{10}H_8O$					43.4	158.8	146.3	44.3	36.5	48.6	48.9	37.4	19.7										583.2
-14(0)	$C_{12}H_{10}O$							8.6	40.4	62.8	46.0													157.8
-16(0)	$C_{12}H_8O$							4.2	42.3	103.1	73.4	25.2	23.0	6.3										277.5
-18(0)	$C_{14}H_{10}O$									26.3	75.0	102.8	52.5	25.4	31.7	17.9	11.9							343.5
-20(0)	$C_{15}H_{10}O$										27.9	28.5	58.2	54.6	66.3	7.7	5.7	13.0						261.9
-22(0)	$C_{16}H_{10}O$											18.2	69.1	61.7	12.4	21.9	14.0	9.5						206.8
-24(0)	$C_{17}H_{10}O$												9.7	40.0	37.4	28.2	36.5	24.4	7.0	9.6				192.8
-26(0)	$C_{18}H_{10}O$													118.0	57.7	32.5	15.6	20.9	5.9	3.2				253.8
-28(0)	$C_{20}H_{12}O$															59.1	58.6	47.8	32.8	12.2	5.5	2.0		218.0
-30(0)	$C_{21}H_{12}O$																51.4	39.2	27.8	19.0	10.0	5.2		152.6
-32(0)	$C_{22}H_{12}O$																	5.9	23.2	25.0	11.2	13.9	6.0	85.2

TABLE XII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION A

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number												
		6	7	8	9	10	11	12	13	14	15	16	17	18
$-6(O_2)$	$C_6H_6O_2$	79.2	232.9	235.1	116.6	52.5	13.1	11.3	18.7					
$-8(O_2)$	$C_9H_{10}O_2$		5.1	3.8	9.1	24.0	33.6	22.3	13.9					
$-10(O_2)$	$C_9H_8O_2$				20.8	65.6	79.8	68.4	26.2	15.1	8.6	3.6		
$-12(O_2)$	$C_{10}H_8O_2$					10.7	25.9	7.8	18.5	13.3				
$-14(O_2)$	$C_{12}H_{10}O_2$						59.9	46.5	49.7	95.0	80.0	55.7	34.4	14.4
$-16(O_2)$	$C_{12}H_8O_2$							37.7	120.4	204.6	248.9	179.4	86.3	64.5
$-18(O_2)$	$C_{14}H_{10}O_2$									34.2	75.7	87.4	88.6	95.2
$-20(O_2)$	$C_{15}H_{10}O_2$										17.1	42.9	19.1	41.3
$-22(O_2)$	$C_{16}H_{10}O_2$											23.3	72.8	44.2
$-24(O_2)$	$C_{17}H_{10}O_2$												65.3	78.2
$-26(O_2)$	$C_{18}H_{10}O_2$													48.1
$-28(O_2)$	$C_{20}H_{12}O_2$													
$-30(O_2)$	$C_{21}H_{12}O_2$													
$-32(O_2)$	$C_{22}H_{12}O_2$													
$-34(O_2)$	$C_{24}H_{14}O_2$													
$-36(O_2)$	$C_{24}H_{12}O_2$													

TABLE XII (Continued)

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number 19	20	21	22	23	24	25	26	27	28	29	Total
$-6(O_2)$	$C_6H_6O_2$												759.4
$-8(O_2)$	$C_9H_{10}O_2$												111.8
$-10(O_2)$	$C_9H_8O_2$												288.1
$-12(O_2)$	$C_{10}H_8O_2$												76.2
$-14(O_2)$	$C_{12}H_{10}O_2$	13.0											448.6
$-16(O_2)$	$C_{12}H_8O_2$	29.3	13.7										984.8
$-18(O_2)$	$C_{14}H_{10}O_2$	51.4	39.2	13.9	12.6	3.3							501.5
$-20(O_2)$	$C_{15}H_{10}O_2$	35.9	11.9	17.4	8.3	11.2	3.5						208.6
$-22(O_2)$	$C_{16}H_{10}O_2$	57.9	45.5	17.3	16.6	10.2	2.7	1.7					292.2
$-24(O_2)$	$C_{17}H_{10}O_2$	25.5	17.5	25.3	20.8	12.7	3.1	1.7	1.0				251.1
$-26(O_2)$	$C_{18}H_{10}O_2$	84.5	41.1	14.7	14.0	6.4	7.5	4.6	3.8				224.7
$-28(O_2)$	$C_{20}H_{12}O_2$		39.0	36.5	16.7	5.9	9.5	9.9	8.9	13.1			139.5
$-30(O_2)$	$C_{21}H_{12}O_2$			20.5	24.6	24.4	5.5	6.1	4.1	2.8			88.0
$-32(O_2)$	$C_{22}H_{12}O_2$				27.8	12.6	13.3	10.4	10.7	4.9	5.3		85.0
$-34(O_2)$	$C_{24}H_{14}O_2$						7.5	7.0	6.0	10.2	5.3	3.3	39.3
$-36(O_2)$	$C_{24}H_{12}O_2$							1.4	5.2	6.9	4.9		18.4

TABLE XIII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_3$ AND $C_NH_{2N+Z}O_4$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION A

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																
		12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
$-16(O_3)$	$C_{12}H_8O_3$	33.0	41.8	57.8	38.5													171.1
$-18(O_3)$	$C_{13}H_8O_3$		20.5	50.8	51.2	94.9	26.9											244.3
$-20(O_3)$	$C_{15}H_{10}O_3$				9.2	38.0	33.3	20.6										101.1
$-22(O_3)$	$C_{16}H_{10}O_3$					38.1	22.2	23.9	35.7	11.6	8.3							139.8
$-24(O_3)$	$C_{17}H_{10}O_3$						38.7	46.3	28.4	21.6	10.0	6.8	8.1	3.5				163.4
$-26(O_3)$	$C_{18}H_{10}O_3$							18.2	21.0	19.0	10.4	12.7	9.3	5.0	3.8	2.7	2.9	105.0
$-28(O_3)$	$C_{20}H_{12}O_3$									4.9	7.0	6.4	7.5	4.6	3.8			34.2
$-30(O_3)$	$C_{21}H_{12}O_3$											15.8	15.9	7.4	4.4			43.5
$-32(O_3)$	$C_{22}H_{12}O_3$												9.1	4.0	4.1	2.8		20.0
$-16(O_4)$	$C_{12}H_8O_4$	9.9	14.6	24.0	10.7													59.2
$-18(O_4)$	$C_{13}H_8O_4$		46.7	82.2	24.6	36.0	13.0	5.2	8.4									216.1
$-26(O_4)$	$C_{18}H_{10}O_4$									6.6	6.8	2.7	1.7					17.8
$-28(O_4)$	$C_{20}H_{12}O_4$										4.2	6.2	5.0	3.8	2.7			21.9

TABLE XIV

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION B

Z	Parent	Weight Percents (x 10^3) for Carbon Number																							
Series	Formula	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	Total
-6(0)	C_6H_6O	1.8	2.7	2.7	2.9	0.9																				11.0
-8(0)	$C_9H_{10}O$				1.7	29.4	13.3	10.1	6.1	2.3																62.9
-10(0)	C_9H_8O				2.9	5.0	4.0	5.1	1.4	0.9																19.3
-12(0)	$C_{10}H_8O$					3.3	9.0	8.6	3.8	1.9	1.3															27.9
-14(0)	$C_{12}H_{10}O$							2.7	2.9	5.9	5.0	10.4	6.1	5.1												38.1
-16(0)	$C_{12}H_8O$							1.8	2.6	4.3	7.6	9.1	4.6	2.8	2.3											35.1
-18(0)	$C_{14}H_{10}O$									2.4	4.3	1.6	2.1	2.0	1.3	1.9	1.1	1.1								17.8
-20(0)	$C_{15}H_{10}O$										4.1	3.2	5.0	4.6	2.2	1.1	1.8									22.0
-22(0)	$C_{16}H_{10}O$											3.6	5.7	7.5	3.4	15.3	27.6	10.1	1.5	1.2						75.9
-24(0)	$C_{17}H_{10}O$												1.8	3.0	14.8	6.0	1.1	2.0	0.6	0.5						29.8
-26(0)	$C_{18}H_{10}O$														5.4	4.2	3.8	2.4	3.2	1.4	0.7					21.1
-28(0)	$C_{20}H_{12}O$															5.3	4.2	2.3	4.7	2.5	2.1	0.9	0.2			22.2
-30(0)	$C_{21}H_{12}O$																	3.5	1.9	2.0	2.9	1.6	0.6	1.2	1.2	14.9
-32(0)	$C_{22}H_{12}O$																			1.5	1.4	2.2	0.9			6.0

TABLE XV

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION B

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																						
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
$-6(O_2)$	$C_6H_6O_2$	15.8	39.3	35.5	13.5	8.0	3.7	4.1	3.0															122.9
$-8(O_2)$	$C_7H_6O_2$		1.9	3.5	4.7	4.5	3.3																	17.9
$-10(O_2)$	$C_9H_8O_2$				4.8	7.5	9.8	8.2	5.4	12.1	1.6	2.3												51.7
$-12(O_2)$	$C_{10}H_8O_2$					8.5	9.1	7.7	4.6	4.6	2.0	5.9												42.4
$-14(O_2)$	$C_{11}H_8O_2$						2.2	6.1	8.7	6.4	4.5	1.0												28.9
$-16(O_2)$	$C_{12}H_8O_2$							2.9	4.9	8.1	8.2	5.1	5.1	0.8	2.1	1.9								39.1
$-18(O_2)$	$C_{14}H_{10}O_2$									4.3	2.8	5.5	3.5	3.4	4.5	0.8	0.6							25.4
$-20(O_2)$	$C_{15}H_{10}O_2$										4.1	2.4	4.7	4.9	2.2	3.2	2.8	3.5	1.4					29.2
$-22(O_2)$	$C_{16}H_{10}O_2$											2.5	0.8	7.0	4.1	3.6	3.5	4.0	2.2	3.2				30.9
$-24(O_2)$	$C_{17}H_{10}O_2$												1.7	2.2	4.1	3.1	17.3	3.3	1.5					33.2
$-26(O_2)$	$C_{18}H_{10}O_2$													4.5	5.0	3.9	2.8	2.7	2.3	1.8	0.7			23.7
$-28(O_2)$	$C_{20}H_{12}O_2$															2.1	3.6	3.2	2.3	1.8	1.7	0.6	1.2	16.5
$-30(O_2)$	$C_{21}H_{12}O_2$																1.4	1.2	2.5	2.1	1.3	0.9	1.2	10.6
$-32(O_2)$	$C_{22}H_{12}O_2$																	1.3	1.1	2.3	1.6	0.6		6.9
$-34(O_2)$	$C_{24}H_{14}O_2$																			1.4	2.2	0.3		3.9
$-36(O_2)$	$C_{24}H_{12}O_2$																			0.7	3.2	6.8	3.5	14.2

TABLE XVI

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_3$ AND $C_NH_{2N+Z}O_4$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION B

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number															
		12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	Total
-14(O_3)	$C_{12}H_{10}O_3$	4.6	7.6	3.3	2.5												18.0
-16(O_3)	$C_{12}H_8O_3$	1.9	4.7	8.5	7.1	4.5											26.7
-18(O_3)	$C_{13}H_8O_3$			1.2	2.3	2.5	1.0										7.0
-20(O_3)	$C_{15}H_{10}O_3$				1.1	2.4	3.4	4.5	1.9								13.3
-22(O_3)	$C_{16}H_{10}O_3$					2.7	2.9	1.1	1.6	0.8							9.1
-24(O_3)	$C_{17}H_{10}O_3$						3.1	5.2	2.7	2.0							13.0
-26(O_3)	$C_{18}H_{10}O_3$										1.2	1.2	3.0	1.3	0.6	0.3	7.6
-28(O_3)	$C_{20}H_{12}O_3$									2.0	1.2	1.4	1.4	2.7	1.2		9.9
-30(O_3)	$C_{21}H_{12}O_3$										0.4	0.5	1.8	1.7	0.6		5.0
-18(O_4)	$C_{13}H_8O_4$		2.7	5.6	3.7	4.2	1.3	0.6									18.1
-20(O_4)	$C_{15}H_{10}O_4$					2.1	2.5	0.9									5.5
-22(O_4)	$C_{16}H_{10}O_4$					1.7	1.6	3.0	3.0	2.0							11.3
-24(O_4)	$C_{17}H_{10}O_4$						0.8	0.5									1.3
-26(O_4)	$C_{18}H_{10}O_4$											2.2					2.2
-28(O_4)	$C_{20}H_{12}O_4$										1.2	1.3	1.0	0.6	0.9		5.0

TABLE XVII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION C

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																						
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
-6(0)	C_6H_6O	1.3	3.0	144.8	177.7	74.6	20.6	5.9	6.6	1.5														436.0
-8(0)	$C_9H_{10}O$				29.4	113.5	107.1	51.5	20.8	10.3	3.0													335.6
-10(0)	C_9H_8O				1.8	6.6	16.0	34.3	37.4	24.5	18.7	2.5												141.8
-12(0)	$C_{10}H_8O$					1.0	5.8	7.6	35.1	31.4	27.8	9.6	4.7											123.0
-14(0)	$C_{12}H_{10}O$							2.0	7.7	30.4	51.5	29.8	27.2	6.3										154.9
-16(0)	$C_{12}H_8O$								1.1	16.7	71.8	115.5	57.9	29.5	20.0	14.8								327.3
-18(0)	$C_{14}H_{10}O$									1.4	6.2	11.5	37.4	55.1	43.7	23.6	14.9							193.8
-20(0)	$C_{15}H_{10}O$										2.9	4.5	8.3	23.5	35.1	28.9	22.2	13.4						138.8
-22(0)	$C_{16}H_{10}O$											4.4	4.7	18.1	44.1	57.6	26.7	26.8	14.5	9.3	5.3			211.5
-24(0)	$C_{17}H_{10}O$												5.0	8.5	12.9	15.2	27.8	31.9	25.8	18.1	6.2			151.4
-26(0)	$C_{18}H_{10}O$													4.7	7.7	5.8	13.5	20.3	22.1	20.8	19.1	12.0		126.0
-28(0)	$C_{20}H_{12}O$															4.7	9.7	20.1	17.5	17.8	14.5	7.3		91.6
-30(0)	$C_{21}H_{12}O$																			16.2	23.5	15.5		55.2
-32(0)	$C_{22}H_{12}O$																			2.9	5.3	10.1		18.3
-34(0)	$C_{24}H_{14}O$																				3.0	9.7	9.0	21.7

TABLE XVIII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION C

Z	Parent	Weight Percents (x 10^3) for Carbon Number																					
Series	Formula	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
$-6(O_2)$	$C_6H_6O_2$	2.4	6.2	5.2	3.6	1.7																		19.1
$-8(O_2)$	$C_9H_{10}O_2$				3.6	3.9	2.9	2.6	2.2															15.2
$-10(O_2)$	$C_9H_8O_2$				1.7	10.2	21.1	19.0	11.4	7.4														70.8
$-12(O_2)$	$C_{10}H_8O_2$					5.3	4.3	6.5	6.7	3.7	10.0	5.6												42.1
$-14(O_2)$	$C_{12}H_{10}O_2$							2.4	4.9	5.6	8.2	9.4	5.1	5.8	3.9									45.3
$-16(O_2)$	$C_{12}H_8O_2$							1.1	4.8	11.9	28.2	16.8	23.3	23.6	14.5									124.2
$-18(O_2)$	$C_{14}H_{10}O_2$									6.1	20.8	22.4	27.7	13.3	20.7	5.9	3.8							120.7
$-20(O_2)$	$C_{15}H_{10}O_2$											1.7	13.2	16.4	16.6	14.9	21.3	13.4	7.5					105.0
$-22(O_2)$	$C_{16}H_{10}O_2$											4.1	6.7	14.0	21.7	25.9	18.3	24.3	15.1					130.1
$-24(O_2)$	$C_{17}H_{10}O_2$												2.0	9.8	18.4	15.4	27.7	24.6	18.6	17.9	14.8	9.2		158.4
$-26(O_2)$	$C_{18}H_{10}O_2$														1.1	3.6	11.3	17.0	18.8	18.6	15.2	7.4		93.0
$-28(O_2)$	$C_{20}H_{12}O_2$															1.9	2.9	6.5	10.4	10.7	11.3	9.6		53.3
$-30(O_2)$	$C_{21}H_{12}O_2$																	3.5	8.0	11.1	13.8	16.8		53.2
$-32(O_2)$	$C_{22}H_{14}O_2$																				11.1	17.4	15.1	43.6
$-34(O_2)$	$C_{24}H_{14}O_2$																				4.3			4.3

TABLE XIX

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_3$ AND $C_NH_{2N+Z}O_4$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION C

		Weight Percents (x 10^3), for Carbon Number															
Z Series	Parent Formula	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
$-18(O_3)$	$C_{13}H_8O_3$	1.3	3.3	6.3	6.3												17.2
$-20(O_3)$	$C_{15}H_{10}O_3$			3.7	3.7	13.3	5.9	23.5	18.9	4.4							73.4
$-22(O_3)$	$C_{16}H_{10}O_3$						4.7	7.5	5.0	4.8	4.5	4.3					30.8
$-24(O_3)$	$C_{17}H_{10}O_3$								3.5	5.5	5.0						14.0
$-26(O_3)$	$C_{18}H_{10}O_3$							18.2	3.4	5.1	7.0	8.4	7.4	5.3	6.2	8.8	69.8
$-28(O_3)$	$C_{20}H_{12}O_3$								1.1	1.8	3.6	3.9	7.6	7.4			25.4
$-18(O_4)$	$C_{13}H_8O_4$			5.1	8.8												13.9
$-26(O_4)$	$C_{18}H_{10}O_4$										4.8						4.8
$-28(O_4)$	$C_{20}H_{12}O_4$											2.6	6.2				8.8

TABLE XX

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION D

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number																							
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	Total
-6(0)	C_6H_6O	0.6	0.8	1.6	0.7	0.9	0.3	0.4	0.4																5.7
-8(0)	$C_9H_{10}O$				0.3	0.4	0.4	1.2	0.7	0.2	0.1	0.3													3.6
-10(0)	C_9H_8O				0.8	0.9	0.6	2.1	1.1	1.3	1.2	0.2													8.2
-12(0)	$C_{10}H_8O$					0.3	2.2	1.1	1.2	1.1	0.7	0.8	0.6	0.3											8.3
-14(0)	$C_{12}H_{10}O$							0.2	0.3	0.2	0.6	1.0	2.0	0.5											4.8
-16(0)	$C_{12}H_8O$								0.9	0.9	0.9	1.5	0.5	0.7	1.0	0.3									6.7
-18(0)	$C_{14}H_{10}O$									0.4	0.7	0.5	1.2	1.3	0.6	0.8	0.3		0.2						6.0
-20(0)	$C_{15}H_{10}O$										0.6	0.5	0.6	0.5	0.7	1.1	0.5	1.0	0.2						5.7
-22(0)	$C_{16}H_{10}O$											0.2	0.3	0.2	1.1	1.6	1.4	0.7	1.2	0.8	0.9				8.4
-24(0)	$C_{17}H_{10}O$													0.5	0.8	1.3	0.9	1.3	0.5	0.5	0.5	0.8			7.1
-26(0)	$C_{18}H_{10}O$														0.5	0.8	1.1	0.7	0.4	0.6	0.4	0.5			5.0
-28(0)	$C_{20}H_{12}O$															0.7	0.4	1.0	0.6	0.8	0.5	0.4			4.4
-30(0)	$C_{21}H_{12}O$																	0.4	0.8	0.3	0.8	0.7	0.8	0.8	4.6
-32(0)	$C_{22}H_{12}O$																	0.3	0.2		0.7	1.2			2.4
-34(0)	$C_{24}H_{14}O$																				0.4	0.4	0.4		1.2

TABLE XXI

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION D

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number 6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
$-6(O_2)$	$C_6H_6O_2$	0.9	0.9	0.8	0.5	0.2	0.4																	3.8
$-8(O_2)$	$C_9H_{10}O_2$			0.8	0.9	0.6	1.1	0.6																4.0
$-10(O_2)$	$C_9H_8O_2$				0.4	0.3	0.5	0.8	0.7	0.6	0.5	0.2												4.0
$-12(O_2)$	$C_{10}H_8O_2$					0.2	0.9	0.9	0.5	0.5	0.7	0.5	0.3	0.7										5.2
$-14(O_2)$	$C_{12}H_{10}O_2$							0.6	0.6	0.8	0.8	0.6	0.3	0.2										3.9
$-16(O_2)$	$C_{12}H_8O_2$								0.9	0.6	0.4	1.0	1.1	0.5	0.8									5.3
$-18(O_2)$	$C_{14}H_{10}O_2$									0.7	1.0	2.1	1.3	0.7	1.2	1.3	0.4							8.7
$-20(O_2)$	$C_{15}H_{10}O_2$												0.6	1.2	0.8	0.8	0.9	0.8						5.1
$-22(O_2)$	$C_{16}H_{10}O_2$											0.5	0.5	0.7	0.6	0.5	0.3	0.6	0.4	0.4				4.5
$-24(O_2)$	$C_{17}H_{10}O_2$												0.8	0.5	1.2	1.4	0.7	0.6	0.4	0.9	1.3	0.9		8.7
$-26(O_2)$	$C_{18}H_{10}O_2$															0.9	0.6	1.0	1.0	1.1	0.8	1.0		6.4
$-28(O_2)$	$C_{20}H_{12}O_2$															0.4	1.4	0.8	1.2	0.7	0.5			5.0
$-30(O_2)$	$C_{21}H_{12}O_2$																	0.6	0.8	1.0	0.4			2.8
$-32(O_2)$	$C_{22}H_{12}O_2$																		0.7	0.8	0.7	0.8	0.8	3.8
$-34(O_2)$	$C_{24}H_{14}O_2$																			0.7				0.7
$-36(O_2)$	$C_{24}H_{12}O_2$																				0.4	0.4		0.8

TABLE XXII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}O_3$ AND $C_NH_{2N+Z}O_4$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION D

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number 13	14	15	16	17	18	19	20	21	22	23	24	25	Total
-16(O_3)	$C_{12}H_8O_3$	0.2	0.5	0.6	0.5	0.4	0.4								2.6
-18(O_3)	$C_{14}H_{10}O_3$		0.8		0.4	0.5	0.4	0.5	0.6						3.2
-20(O_3)	$C_{15}H_{10}O_3$					0.3	0.6	0.4	0.4	1.0					2.7
-22(O_3)	$C_{16}H_{10}O_3$					0.8	0.5	0.8	0.5						2.6
-24(O_3)	$C_{17}H_{10}O_3$							0.3	0.3	0.2	0.9	0.4			2.1
-26(O_3)	$C_{18}H_{10}O_3$								1.1	0.6	0.4				2.1
-28(O_3)	$C_{20}H_{12}O_3$								0.6	0.5	1.0	0.5	0.8		3.4
-30(O_3)	$C_{21}H_{12}O_3$									0.4	0.6	0.7	1.0	0.6	3.3
-32(O_3)	$C_{22}H_{12}O_3$											0.5	0.7		1.2
-18(O_4)	$C_{14}H_{10}O_4$					0.4									0.4
-20(O_4)	$C_{15}H_{10}O_4$							0.3							0.3
-22(O_4)	$C_{16}H_{10}O_4$				0.3	0.3									0.6
-26(O_4)	$C_{18}H_{10}O_4$							0.3	0.6		0.7	0.4			2.0
-28(O_4)	$C_{20}H_{12}O_4$										0.6	0.9			1.5

TABLE XXIII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}NO$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION D

Z	Weight Percents (x 10^3) for Carbon Number										
Series	7	8	9	10	11	12	13	14	15	16	17	Total
-5(NO)	3.3	1.8	1.1	1.1	1.3							8.6
-9(NO)		0.5	0.5	2.1								3.1
-11(NO)				1.7	5.0	1.3	1.3					9.3
-15(NO)						0.5	1.1	1.6	1.2			4.4
-17(NO)								1.5	2.4	2.3	1.1	7.3
-19(NO)							0.6	1.4	0.5			2.5

TABLE XXIV

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION C

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number														
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
-6(0)	C_6H_6O	8.7	18.5	244.1	227.6	69.9	18.0	3.3	1.4	1.4						
-8(0)	$C_9H_{10}O$				27.6	88.1	67.1	24.6	8.1	4.1	1.5	0.8				
-10(0)	C_9H_8O				3.0	9.1	16.5	19.8	15.2	8.8	4.9	1.7	0.9		0.7	
-12(0)	$C_{10}H_8O$					2.4	7.8	12.4	31.2	24.2	15.0	7.3	2.2	1.8	0.9	1.4
-14(0)	$C_{12}H_{10}O$							1.9	6.5	18.2	27.0	22.4	10.7	4.0	3.5	0.9
-16(0)	$C_{12}H_8O$								2.3	12.7	47.6	51.9	38.1	18.5	9.4	3.7
-18(0)	$C_{14}H_{10}O$									2.4	4.6	8.7	24.2	33.4	26.2	12.6
-20(0)	$C_{15}H_{10}O$									2.7	2.3	1.8	6.4	18.5	25.6	21.8
-22(0)	$C_{16}H_{10}O$											1.1	2.0	10.0	36.5	50.6
-24(0)	$C_{17}H_{10}O$												0.6	1.8	3.4	8.2
-26(0)	$C_{18}H_{10}O$													0.6	1.1	2.3
-28(0)	$C_{20}H_{12}O$															1.8
-30(0)	$C_{21}H_{12}O$															
-32(0)	$C_{22}H_{14}O$															
-34(0)	$C_{24}H_{14}O$															
-36(0)	$C_{24}H_{12}O$															

TABLE XXIV (Continued)

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number 21	22	23	24	25	26	27	28	29	30	31	32	33	Total
-6(0)	C_6H_6O														592.9
-8(0)	$C_9H_{10}O$														221.9
-10(0)	C_9H_8O														80.6
-12(0)	$C_{10}H_8O$	0.9													107.5
-14(0)	$C_{12}H_{10}O$	1.0													96.1
-16(0)	$C_{12}H_8O$	1.8	1.1	0.9	1.1	1.0									194.8
-18(0)	$C_{14}H_{10}O$	7.3	4.2	2.2	1.6	1.8	1.2	1.2	1.6	0.7					133.9
-20(0)	$C_{15}H_{10}O$	17.5	11.0	5.0	3.2	2.0	1.6	1.4	1.4	0.7					122.9
-22(0)	$C_{16}H_{10}O$	40.5	19.0	12.0	7.1	6.6	6.1	2.6	1.7	0.8					196.6
-24(0)	$C_{17}H_{10}O$	23.0	34.5	26.0	14.8	10.0	6.0	4.0	1.9	2.3	3.0	0.9			140.4
-26(0)	$C_{18}H_{10}O$	8.4	16.5	19.9	17.5	19.1	10.4	6.1	2.2	2.2	3.3	0.8	0.6		111.0
-28(0)	$C_{20}H_{12}O$	1.6	5.0	8.7	11.9	12.6	10.1	5.5	3.5	2.4	1.2	0.8			65.1
-30(0)	$C_{21}H_{12}O$	1.9	2.1	3.4	6.5	9.2	9.0	4.5	4.3	2.4	1.1	1.1			45.5
-32(0)	$C_{22}H_{14}O$		0.8	1.4	1.4	3.8	4.2	3.4	3.6	2.4	1.7	0.9	0.6	0.5	24.7
-34(0)	$C_{24}H_{14}O$				1.8	1.6	1.1	0.9	1.9	2.1		1.2	0.7	0.5	11.8
-36(0)	$C_{24}H_{12}O$				0.8	1.4	1.2	1.1	1.2	0.8	0.9				7.4

TABLE XXV

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}O_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE ACID FRACTION C

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number														
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$-6(O_2)$	$C_6H_6O_2$	2.1	8.3	4.4	1.9	1.5							0.9			
$-8(O_2)$	$C_9H_{10}O_2$				1.1	3.4	2.7		1.3							
$-10(O_2)$	$C_9H_8O_2$				5.5	15.7	20.5	14.3	7.4	3.6	1.8	1.0		1.2		
$-12(O_2)$	$C_{10}H_8O_2$					1.2	3.0	4.2	5.1	3.2	3.1	1.9	1.1	1.2		
$-14(O_2)$	$C_{12}H_{10}O_2$							1.4	2.3	2.4	2.4	5.7	2.2	1.9	2.2	1.7
$-16(O_2)$	$C_{12}H_8O_2$							1.5	5.1	16.6	24.5	21.4	15.3	7.8	4.8	3.2
$-18(O_2)$	$C_{14}H_{10}O_2$									2.2	6.8	10.1	13.5	17.0	11.7	8.3
$-20(O_2)$	$C_{15}H_{10}O_2$										0.6	2.7	6.1	13.7	14.6	11.3
$-22(O_2)$	$C_{16}H_{10}O_2$											1.2	2.8	10.3	16.2	20.9
$-24(O_2)$	$C_{17}H_{10}O_2$													2.7	14.6	20.5
$-26(O_2)$	$C_{18}H_{10}O_2$														0.7	3.1
$-28(O_2)$	$C_{20}H_{12}O_2$															0.9
$-30(O_2)$	$C_{21}H_{12}O_2$															
$-32(O_2)$	$C_{22}H_{14}O_2$															
$-34(O_2)$	$C_{24}H_{14}O_2$															
$-36(O_2)$	$C_{24}H_{12}O_2$															

TABLE XXV (Continued)

Z Series	Parent Formula	Weight Percents (x 10^3) for Carbon Number 21	22	23	24	25	26	27	28	29	30	31	32	33	Total
$-6(O_2)$	$C_6H_6O_2$	1.2													20.2
$-8(O_2)$	$C_9H_{10}O_2$														8.6
$-10(O_2)$	$C_9H_8O_2$														70.9
$-12(O_2)$	$C_{10}H_8O_2$					1.3									25.4
$-14(O_2)$	$C_{12}H_{10}O_2$		0.9					0.9							24.2
$-16(O_2)$	$C_{12}H_8O_2$	4.0	1.3		0.9		1.3								107.7
$-18(O_2)$	$C_{14}H_{10}O_2$	4.6	2.7	1.5	1.8	2.7		1.4	1.1						85.4
$-20(O_2)$	$C_{15}H_{10}O_2$	10.2	8.1	5.7	3.3	2.8	2.5	2.0	1.5						85.1
$-22(O_2)$	$C_{16}H_{10}O_2$	15.4	13.5	8.9	5.0	5.1	2.8	3.7	1.7						107.2
$-24(O_2)$	$C_{17}H_{10}O_2$	19.3	20.0	14.3	9.9	6.0	4.2	3.1	2.5	1.7	1.2	0.8	1.3		122.2
$-26(O_2)$	$C_{18}H_{10}O_2$	12.3	17.3	15.3	13.9	12.3	6.8	4.9	3.8	1.7	2.0	1.7			96.0
$-28(O_2)$	$C_{20}H_{12}O_2$	2.3	6.0	8.9	10.4	9.9	6.0	4.5	5.2	2.1	2.7	1.5	0.9		61.2
$-30(O_2)$	$C_{21}H_{12}O_2$		1.5	5.4	9.1	9.0	10.0	6.7	5.7	3.5	3.2	1.9	1.3		57.3
$-32(O_2)$	$C_{22}H_{14}O_2$		1.4	1.7	3.0	5.6	5.5	5.4	4.4	4.0	2.8	1.9	1.2		36.8
$-34(O_2)$	$C_{24}H_{14}O_2$				0.6	1.9	1.7	3.2	2.1	4.4	2.0	1.9	2.1	1.1	20.9
$-36(O_2)$	$C_{24}H_{12}O_2$					0.1	0.1	0.2	0.3	0.3	0.2	0.2	0.4	0.2	1.9

TABLE XXVI

CARBON-NUMBER DISTRIBUTION FOR OIL AROMATIC BASES

Z Series	Molecular Formula for Parent Compound	Weight Percents (X10^3) for Carbon Number																				
		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	Total
-5(N)	C_5H_5N		0.2	1.0	3.8	3.7	2.5	1.4	0.9	1.8	5.2	4.9	5.2	1.2								31.8
-7(N)	C_8H_9N		0.8	1.9	7.3	10.4	7.1	4.6	7.1	5.2	6.4	2.6	1.3									54.7
-9(N)	C_8H_7N		0.7	0.6	2.8	2.6	4.7	10.4	9.7	6.4	7.7	4.5	5.7	4.6	2.1							62.8
-11(N)	C_9H_7N			3.2	18.8	47.4	54.8	29.3	20.4	14.5	11.0	6.0	5.2	3.8	3.7	3.9	3.5	2.3	2.0	1.1		230.9
-13(N)	$C_{11}H_9N$					1.0	6.0	14.6	17.1	16.0	13.0	10.6	6.9	4.5	7.1	5.2	4.8	3.5	2.6			112.9
-15(N)	$C_{11}H_7N$						1.0	5.6	12.2	14.4	9.0	6.6	6.8	4.7	5.2	3.9	3.6	3.8	2.9	1.9		81.6
-17(N)	$C_{13}H_9N$							9.7	17.6	18.4	8.1	8.6	8.7	6.0	3.3	2.1						82.5
-19(N)	$C_{14}H_9N$								1.2	3.1	3.6	7.0	6.6	5.2	7.3	6.8	6.7	4.9	4.2	2.9	3.0	62.5
-21(N)	$C_{15}H_9N$										1.8	2.7	7.9	9.8	10.7	9.8	9.1	7.3	6.0	3.8	2.8	71.7
-23(N)	$C_{16}H_9N$										1.7	1.4	4.5	5.2	5.6	6.9	6.9	7.1	6.4	4.5		50.2
-25(N)	$C_{17}H_9N$												3.3	2.2	2.2	2.6	3.0	3.5	3.2	3.2	1.8	25.0
-7(NO)	C_7H_7NO	0.2	0.5	1.8	3.4	4.0	1.8	1.5	1.5	3.5	4.9	5.2	6.1	5.1	3.3	2.5	2.1					47.4
-9(NO)	C_7H_5NO			2.5	4.8	6.8	6.7	12.9	6.6	6.4	4.7	5.2	5.4	3.9	3.1	1.9	1.6	0.8				73.3
-11(NO)	$C_{10}H_9NO$				0.8	2.0	4.3	5.2	4.1	2.7	3.8	4.7	4.6	4.2	3.4	2.8	1.9	1.3				45.8
-13(NO)	$C_{10}H_7NO$						2.2	1.4	1.8	2.5	3.3	2.2	2.2	2.2	2.6	2.6	2.3	2.0	1.1			28.4
-15(NO)	$C_{11}H_7NO$					0.3	2.7	8.1	7.8	6.2	4.9	6.9	7.1	7.1	5.2	4.8	3.5	2.6				67.2
-17(NO)	$C_{13}H_9NO$								4.2	11.5	12.5	8.9	6.4	5.2	4.8	4.0	4.2	2.9	2.2			66.8
-19(NO)	$C_{13}H_7NO$								8.0	14.9	11.1	8.7	10.5	8.2	7.3	8.4	5.8	5.3	4.5	3.6		96.3

TABLE XXVII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}N$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number																									
		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Total
-5N	C_5H_5N		0.5	1.6	3.8	6.2	5.8	0.7	1.4	0.4	0.8	0.7	0.8	0.9														23.6
-7N	C_8H_9N		0.4	0.5	2.7	5.7	5.2	2.2	2.2	0.5	0.5	1.1	0.8	1.5	5.5													28.8
-9N	C_8H_7N		0.2	0.5	0.9	2.6	1.6	4.3	3.5	3.7	3.4	3.2	1.5	0.7														26.1
-11N	C_9H_7N			0.4	5.2	17.5	23.5	16.2	23.8	22.3	11.9	6.4	1.8	1.7	1.0	0.8	1.3	0.7										134.5
-13N	$C_{11}H_9N$					0.3	3.4	8.9	10.7	9.6	6.1	5.3	3.8	3.7	1.7	1.5	2.0	2.8	1.5	1.9	1.7	0.8	0.6					66.3
-15N	$C_{11}H_7N$						0.9	4.3	7.3	7.7	9.4	6.5	3.4	3.3	1.5	1.3	0.7	0.5										46.8
-17N	$C_{13}H_9N$							1.8	9.2	16.5	15.7	11.2	5.0	7.7	1.9	2.9	2.5	1.5	1.8	1.5	1.2	0.5	0.3					81.2
-19N	$C_{14}H_9N$								1.1	0.7	2.8	5.2	7.2	6.7	6.7	3.0	3.0	2.5	1.2	0.4	0.3	0.2	0.2					41.2
-21N	$C_{15}H_9N$									1.8	8.0	14.9	16.7	13.9	8.2	7.2	5.5	4.1	1.8	0.5	0.4	0.3	0.4					83.7
-23N	$C_{16}H_9N$											2.0	0.8	2.2	11.6	9.5	7.8	4.0	3.4	2.1	1.4	1.1	0.7	0.8				47.4
-25N	$C_{17}H_9N$												1.8	1.2	0.8	4.2	4.9	3.2	2.6	2.1	1.1	0.9	0.6	0.6				24.0
-27N	$C_{19}H_{11}N$													1.7	5.9	6.1	6.7	6.9	0.7	1.5	1.2	1.2	0.5	0.4				32.8
-29N	$C_{21}H_{13}N$															1.5	3.9	5.8	5.0	3.1	2.1	1.5	1.4	1.3				25.6
-31N	$C_{21}H_{11}N$															1.9	1.9	3.2	4.3	2.4	1.9	1.9	0.9	0.9				19.3
-33N	$C_{23}H_{13}N$																	3.8	2.5	1.2	2.5	2.1	1.4	0.8	1.4			15.7
-35N	$C_{23}H_{11}N$																	0.5	1.6	1.2	1.7	1.2	0.8	0.8	1.1			8.9
-37N	$C_{25}H_{13}N$																						1.2	0.8	0.6	0.5	0.2	3.3
-39N	$C_{27}H_{13}N$																					1.1	0.9	0.5	0.4			2.9

TABLE XXVIII

CARBON-NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}NO$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number																									
		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Total
-7NO	C_7H_7NO	0.2	1.2	1.5	1.5	1.6	3.2	0.4	0.7	0.8																		11.1
-9NO	C_7H_5NO		0.2	1.4	2.2	3.5	5.3	3.6	1.4	1.8	0.5																	19.9
-11NO	$C_{10}H_9NO$				22.4	63.8	45.2	18.6	6.5	2.7	6.5	9.4	1.4	0.8														177.3
-13NO	$C_{10}H_7NO$					0.3	5.3	1.3	3.6	3.6	4.1	3.7	2.5															24.4
-15NO	$C_{11}H_7NO$						1.7	5.5	8.7	9.6	8.0	4.2	1.5	3.3	0.8													43.3
-17NO	$C_{13}H_9NO$							2.0	7.3	11.8	13.6	12.2	6.5	5.5	2.5	1.5	1.0											63.9
-19NO	$C_{13}H_7NO$							0.9	0.5	1.3	3.6	9.4	5.8	6.8	3.9	1.6												33.8
-21NO	$C_{15}H_9NO$									1.1	2.0	5.9	7.4	5.7	5.2	1.5	0.8											29.6
-23NO	$C_{16}H_9NO$											1.6	3.9	6.8	0.8	4.6	1.6	2.4	1.1	0.8	0.5							24.1
-25NO	$C_{18}H_{11}NO$												0.7	2.0	3.2	3.2	3.3	3.4	1.6	0.8	0.2							18.4
-27NO	$C_{20}H_{13}NO$														2.1	3.2	4.5	3.9	1.5	0.8	0.3							16.3
-29NO	--															1.5	0.0	0.0	0.4	0.6								2.5
-31NO	--																	0.5	2.7	1.2	0.6							5.0
-33NO	--																		1.2	0.5								1.7
-35NO	--																		2.1	0.8								2.9

TABLE XXIX

CARBON NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}N$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION F

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number 7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Total
-5N	C_5H_5N		0.1	0.2	0.3	0.8	1.6	1.7	1.4	2.3	2.3	0.3	0.3															11.3
-7N	C_8H_9N		0.1	0.2	0.4	0.9	1.0	1.0	1.3	0.5	0.2	0.3	0.2	0.2	0.2													6.5
-9N	C_8H_7N		0.1	0.2	0.2	0.5	0.1	0.6	1.3	1.7	1.5	0.7	0.5	0.7	0.2													8.3
-11N	C_9H_7N			0.2	0.2	0.7	1.2	1.8	2.4	1.7	2.0	2.1	1.7	0.9	0.8	0.7	0.5	0.5										17.4
-13N	$C_{11}H_9N$					0.2	0.6	2.1	3.6	3.6	2.9	2.1	2.0	0.9	0.8	0.6	0.3	1.0	0.4	0.4								21.5
-15N	$C_{11}H_7N$						0.9	2.6	3.0	3.4	3.7	2.5	1.8	1.7	0.3	1.2	0.6	0.2										21.9
-17N	$C_{13}H_9N$							0.8	2.1	4.6	5.3	4.4	3.5	2.9	2.0	1.2	1.4	1.1	0.5	0.4								30.2
-19N	$C_{14}H_9N$											1.0	2.8	3.0	2.1	1.8	0.5	1.2	1.0	0.9	0.5	0.2						15.0
-21N	$C_{15}H_9N$									0.5	0.5	1.0	3.7	4.4	5.2	4.9	4.4	3.2	2.7	1.9	0.7	0.5	0.5	0.3	0.2	0.1		33.7
-23N	$C_{16}H_9N$										1.4	1.0	3.4	3.9	3.8	3.7	2.7	2.9	1.1	0.8	0.5	0.4	0.3	0.2				26.1
-25N	$C_{17}H_9N$												1.1	1.2	1.5	2.5	2.0	1.4	0.5	0.6	0.5	0.3	0.3	0.1				12.0
-27N	$C_{19}H_{11}N$													0.6	3.0	3.1	2.6	2.6	1.9	1.2	1.1	0.7	0.5	0.2				17.5
-29N	$C_{21}H_{13}N$															1.4	1.2	2.5	2.0	1.6	0.6	0.2	0.5	0.2				10.2
-31N	$C_{21}H_{11}N$															1.0	1.7	1.4	1.6	1.1	1.3	0.9	0.5	0.5				10.0
-33N	$C_{23}H_{13}N$																	1.1	0.9	0.5	0.9	0.5	0.5	0.4	0.2			5.0
-35N	$C_{23}H_{11}N$																	0.6	0.8	1.3	1.0	1.0	0.6	0.5	0.4			6.2
-37N	$C_{25}H_{13}N$																			1.3	1.2	0.9	0.7	0.7	0.3			5.1
-39N	$C_{27}H_{13}N$																					0.3	0.1	0.3	0.2			0.9

TABLE XXX

CARBON NUMBER DISTRIBUTION FOR $C_NH_{2N+Z}NO$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION F

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number 7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Total
-7NO	C_7H_7NO	0.02	0.1	0.1	0.3	0.6	0.9	0.6	1.5																			4.2
-9NO	C_7H_5NO		0.1	0.2	0.4	1.0	2.0	1.6	0.7	0.5																		6.5
-11NO	$C_{10}H_9NO$				0.6	2.0	3.9	3.8	2.1	0.8	0.5	0.3	0.2															14.2
-13NO	$C_{10}H_7NO$					0.2	0.9	1.9	2.3	2.7	1.4	1.5	0.9															11.8
-15NO	$C_{11}H_7NO$					0.2	0.4	2.2	3.3	3.9	3.0	2.8	1.2	1.2	0.6	0.3												19.1
-17NO	$C_{13}H_9NO$							0.9	2.5	2.3	5.0	4.6	3.4	2.1	1.8	0.6	0.6											23.8
-19NO	$C_{13}H_7NO$							0.1		0.2	0.7	1.7	1.9	2.3	2.1	1.1	0.5	0.5										11.1
-21NO	$C_{15}H_9NO$											3.3	3.3	3.5	2.5	1.9	1.2	0.7	0.3									16.7
-23NO	$C_{16}H_9NO$											0.8	1.6	2.1	2.0	1.5	1.1	0.7	0.5									10.3
-25NO	$C_{18}H_{11}NO$												0.3	0.4	1.1	2.0	0.7	0.7	0.4	0.2	0.1							5.9
-27NO	$C_{20}H_{13}NO$												0.7	0.8	1.4	1.7	1.7	1.1	0.8	0.4	0.5	0.2						9.3
-29NO	---														0.6	0.3	0.3	0.8	0.7	0.5	0.5	0.2						3.9
-31NO	---																		0.5	1.1	0.6	0.4	0.4					3.0
-33NO	---																			0.4	0.6	0.5	0.5					2.0
-35NO	---																1.1		0.5	0.3	0.2	0.5	0.4	0.2				3.2

TABLE XXXI

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}N$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number 7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	Total
-5(N)	C_5H_5N	2.8	6.6	10.0	6.2	2.9	1.9		0.6	2.0	1.5	0.7	1.0			1.0										37.2
-7(N)	C_8H_9N		0.3	1.2	4.6	8.2	5.9	4.0	2.4	1.9	0.8	0.9	1.0		1.3	0.9	1.5									34.9
-9(N)	C_8H_7N		0.4	1.0	2.0	2.7	4.4	4.0	4.4	4.8	2.9	1.7	1.0	1.1	1.1		1.2				1.3					34.1
-11(N)	C_9H_7N			0.6	5.6	20.6	31.1	23.7	11.2	4.6	3.2	2.9	2.6	1.5	0.8	0.8	1.1	0.8			0.7					111.8
-13(N)	$C_{11}H_9N$					0.8	3.2	9.4	14.7	11.3	9.1	4.1	2.2	1.5	1.1	1.3	0.9	0.7	0.5	1.1			1.0			62.9
-15(N)	$C_{11}H_7N$						3.6	6.9	10.4	9.6	7.5	5.1	3.3	2.6	1.6	1.3	1.3		0.6	1.3	0.8					60.0
-17(N)	$C_{13}H_9N$							1.7	8.7	19.7	19.0	14.0	8.5	7.7	3.8	2.4	2.1	1.5	0.9	0.9	0.6	0.9				92.4
-19(N)	$C_{14}H_9N$								0.7	0.7	2.4	3.7	6.3	5.6	4.9	1.8	2.1	1.6	1.4	1.0	0.7	1.0	0.5			34.3
-21(N)	$C_{15}H_9N$									1.1	3.4	9.1	11.5	10.9	8.4	4.5	4.3	2.6	1.6	1.3	1.4	1.2	0.9			62.5
-23(N)	$C_{16}H_9N$											0.7	2.5	6.6	7.4	8.3	5.6	4.0	2.2	1.5	1.2	1.2	1.0	0.8		43.0
-25(N)	$C_{17}H_9N$												1.3	0.8	1.7	2.7	4.3	4.5	4.0	2.5	2.4	2.0	0.9	0.9		28.0
-27(N)	$C_{19}H_{11}N$													0.7	2.2	4.6	5.5	5.8	4.9	3.3	2.3	1.8	1.2	1.1		33.4
-29(N)	$C_{21}H_{13}N$															0.5	2.0	3.6	4.4	3.9	3.1	2.4	1.4	1.0		22.3
-31(N)	$C_{21}H_{11}N$																0.8	1.7	2.8	3.4	2.3	2.3	2.0	1.2		16.5
-33(N)	$C_{23}H_{13}N$																	0.4	0.7	1.1	1.6	1.4	1.3	0.6		7.2
-35(N)	$C_{23}H_{11}N$																	0.4	0.3	0.4	0.4	0.7	0.9	0.7		3.8
-37(N)	$C_{25}H_{13}N$																			0.3		0.6	0.4	0.3		1.7
-39(N)	$C_{27}H_{15}N$																					0.3	0.2		0.2	0.7
-41(N)	$C_{27}H_{13}N$																					0.2		0.2		0.4

TABLE XXXII

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}NO$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z Series	Molecular Formula For Parent Compound	Weight Percents (X 10^3) for Carbon Number																								Total
		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
-7(NO)	C_7H_7NO	0.2	1.5	1.9	1.6	1.0	0.4	0.1	0.2	0.2	0.1							0.3								7.5
-9(NO)	C_7H_5NO	0.2	0.4	1.4	3.2	2.6	2.2	2.3	1.9	0.5	0.8			0.5												16.1
-11(NO)	$C_{10}H_9NO$				15.2	44.5	33.7	14.3	4.7	2.3	1.3	1.2	0.4	1.1	0.7		3.9									123.6
-13(NO)	$C_{11}H_9NO$					0.2	1.4	3.6	4.7	4.1	2.2	0.8	1.0	0.5	0.3	0.3	0.2	0.2	0.2	0.2						19.9
-15(NO)	$C_{11}H_7NO$						0.6	1.4	2.2	2.4	2.0	1.6	1.4	1.2	0.6	0.3	0.4	0.4	0.2	0.4		0.3				15.5
-17(NO)	$C_{13}H_9NO$								2.3	6.9	8.3	6.7	4.5	4.5	2.5	1.7	1.8	0.9	1.7	1.0	0.7	1.1				44.7
-19(NO)	$C_{13}H_7NO$									0.3	1.5	3.4	3.9	3.4	3.4	2.5	1.4	1.8	1.1	0.7	0.9	0.6				24.8
-21(NO)	$C_{15}H_9NO$									0.2	1.3	2.3	4.0	4.6	3.2	3.0	1.8	1.3	1.4	1.1	0.8	0.5				25.5
-23(NO)	$C_{16}H_9NO$											0.5	1.1	2.9	3.7	4.0	2.6	2.2	2.1	1.4	1.2	1.5				23.2
-25(NO)	$C_{18}H_{11}NO$												0.5	1.4	2.5	4.4	3.6	5.2	3.6	2.6	1.2	1.2	1.1			27.3
-27(NO)	$C_{20}H_{13}NO$														2.2	4.8	5.0	5.3	3.7	3.6	1.8	1.9	2.1			30.4
-29(NO)	$C_{20}H_{11}NO$														0.7	1.0	2.8	2.5	4.1	3.3	3.5	2.3	1.6			21.8
-31(NO)	------														0.3	0.6	1.1	2.5	2.0	2.5	2.7	2.4	1.2			15.3
-33(NO)	------																	0.5	1.5	1.7	2.5	1.6	1.8			9.6
-35(NO)	------																	0.3	0.4	0.6	0.8	1.0	0.7			3.8
-37(NO)	------																		0.5		0.4		0.6			1.5
-39(NO)	------																				0.3		0.6	0.2		1.1
-41(NO)	------																					0.3				0.3

TABLE XXXIII

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}NO_2$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z(N,O_2) Series	Weight Percents (x 10^3) for Carbon Number																					
	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Total
-5		0.2	0.4		0.3																	0.9
-7	0.2		0.2		0.2	0.3																0.9
-9					0.2	0.4		0.2	0.3													1.1
-11			0.2		0.5	0.4	0.4	0.4	0.3			0.3	0.2									2.7
-13							0.7	0.8	0.5		0.4											2.4
-15						0.4	2.1	2.7	2.3	0.7	0.6	0.7	0.6									10.1
-17								0.5	1.3	1.2	1.3	0.8	0.5									5.6
-19										0.4	1.1	0.9	0.8	1.1	0.6	0.2	0.5					5.6
-21										0.3	1.5	2.0	1.7		1.1	0.7		0.5				7.8
-23											0.6	0.8	1.4		1.7	1.1	1.5	0.6				7.7
-25												0.3	0.5	0.7	1.4	1.4	1.9	1.2	1.1	1.0	1.1	10.6
-27														0.8	0.9	1.0	2.0	1.6	1.0	1.1		8.4
-29															0.5	1.1	1.0	1.0	1.1	1.1	0.5	6.3
-31																0.2	0.7	0.9	0.7	1.2	0.5	4.2
-33																	0.3			0.5	0.4	1.2
-35																	0.2				0.3	0.5
-37																				0.3		0.3

TABLE XXXIV

CARBON-NUMBER DISTRIBUTION OBTAINED BY LV/EI/MS FOR $C_NH_{2N+Z}NS$ AROMATIC COMPOUNDS PRESENT IN ASPHALTENE BASE FRACTION E

Z(N,S)	Weight Percents (x 10^3) for Carbon Number														
Series	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Total
-9	0.9															0.9
-11			0.4													0.4
-13					0.3											0.3
-15				1.0	1.3	1.7										4.0
-17							0.5								1.0	1.5
-19								0.3								0.3
-21								0.4	1.2	1.6						3.2
-23																0.0
-25										0.7	1.0					1.7
-27											0.2					0.2
-29														0.5		0.5

aromatic neutrals by LV/EI/MS are presented in Tables VII-IX. Carbon-number distributions obtained for the oil acids and various asphaltene acid fractions by FI/MS are presented in Tables X-XXIII. The data in these tables were calculated making the assumption $S(M_j) = 1$ in all cases. Corresponding distributions obtained for asphaltene acid fraction C by LV/EI/MS are presented in Tables XXIV and XXV. Carbon-number distributions obtained for the oil bases and both asphaltene base fractions by FI/MS are presented in Tables XXVI-XXX. The assumption of unit FI relative mole sensitivities was made in the calculation of these carbon-number distributions. Corresponding carbon-number distributions obtained for asphaltene base fraction E by LV/EI/MS are presented in Tables XXXI-XXXIV.

Discussion

The compositional data obtained from mass spectrometric analysis of the oil and asphaltene aromatic neutral fraction are summarized in Tables XXXV and XXXVI. The range in carbon numbers in columns 3, 6, and 9, the range in molecular weights shown in columns 4, 7, and 10, and the weight percents of the total liquid accounted for each group type given in columns 2, 5, and 8 are listed as a function of specific Z series for both the oil and asphaltene aromatic neutrals. The results in columns 5 through 7 and in columns 8 through 10 in both tables were obtained by FI/MS and LV/EI/MS, respectively.

The data in Tables XXXV and XXXVI demonstrate excellent agreement between the Exxon and OSU mass spectrometric analyses. As seen in Table XXXV, both analyses show that the asphaltene neutrals contain hydrocarbons in the -6 through -36 Z series. The agreement between

TABLE XXXV

SUMMARY DATA FOR C_NH_{2N+Z} AROMATIC HYDROCARBON TYPES

	Oils[a]			Asphaltenes[a]			Asphaltenes[b]		
	wt.%	Range In		wt.%	Range In		wt.%	Range In	
-Z	x 10^1	N	MW	x 10^1	N	MW	x 10^1	N	MW
6	7.5	9-29	120-400	3.6	7-31	92-428	4.1	7-35	92-484
8	10.1	10-29	132-398	4.8	9-37	118-510	7.6	9-41	118-566
10	8.8	9-30	116-410	5.6	9-40	116-550	6.7	9-40	116-550
12	20.3	10-30	128-408	10.9	10-40	128-548	12.2	10-43	128-590
14	13.8	12-30	154-406	9.7	12-40	154-546	9.8	12-41	154-560
16	10.6	12-30	152-404	9.8	12-40	152-544	11.0	12-41	152-558
18	11.6	14-30	178-402	12.2	14-40	178-542	12.6	14-41	178-556
20	4.1	15-30	190-400	8.6	15-40	190-540	8.8	15-44	190-596
22	4.6	16-30	202-398	12.0	16-41	202-552	12.5	16-40	202-538
24	1.9	18-31	228-410	8.4	18-41	228-550	7.6	18-42	228-564
26	1.4	18-31	226-408	9.5	18-41	226-548	9.1	19-42	230-562
28				5.2	20-39	252-518	4.0	20-42	252-560
30				6.9	22-40	278-530	9.4	22-42	278-558
32				3.0	22-39	276-514	1.8	23-43	290-570
34				3.5	22-41	274-540	0.5	24-40	302-526
36				1.5	24-41	300-538	0.3	24-43	300-566
38							0.3	26-41	326-536
40							0.2	28-39	352-508
42							0.04	29-39	364-506
Total	94.6			115.1			118.5		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

TABLE XXXVI

SUMMARY DATA FOR $C_NH_{2N+Z}O$ AROMATIC COMPOUND TYPES

		Oils[a]			Asphaltenes[a]			Asphaltenes[b]		
		Wt.% x 10^1	Range In		Wt.% x 10^1	Range In		Wt.% x 10^1	Range In	
-Z(O)	Parent Formula		N	MW		N	MW		N	MW
8	C_8H_8O	1.2	10-17	148-246	1.8	8-19	120-274	3.7	8-38	120-540
10	C_8H_6O	2.4	9-17	132-244	2.7	8-35	118-496	3.8	9-41	132-580
12	$C_{10}H_8O$	2.0	11-20	158-284	3.2	10-32	144-452	3.0	10-42	144-592
14	$C_{12}H_{10}O$	0.4	15-17	212-240	2.5	12-31	170-436	2.7	12-41	170-576
16	$C_{12}H_8O$	3.0	12-20	168-280	5.4	12-39	168-546	4.3	12-41	168-574
18	$C_{14}H_{10}O$	1.8	14-23	194-320	5.1	14-38	194-530	3.7	14-37	194-516
20	$C_{14}H_8O$				5.1	15-38	206-528	3.3	15-39	206-542
22	$C_{16}H_{10}O$				3.5	16-27	218-372	3.5	16-40	218-554
24	$C_{17}H_{10}O$				3.9	18-36	230-496	3.0	17-40	216-552
26	$C_{18}H_{10}O$				3.6	18-39	242-536	2.6	18-41	242-564
28	$C_{20}H_{12}O$				3.0	20-40	268-548	2.1	20-40	268-548
30	$C_{21}H_{12}O$				2.0	21-40	280-546	1.5	21-42	280-574
32	$C_{22}H_{12}O$				1.4	23-39	306-530	1.0	23-39	306-530
34	$C_{24}H_{14}O$							0.6	24-39	318-528
36	$C_{24}H_{12}O$							0.4	24-35	316-470
Total		10.8			43.2			39.2		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

the two analyses in regard to the range in both carbon number and molecular weight is excellent. The weight percents at each carbon number in each specific Z series and the weight percents obtained by FI/MS for each specific Z series are in good agreement with the values obtained by LV/EI/MS. Furthermore, the dependence of the difference in weight percents obtained by the two techniques on hydrocarbon type is qualitatively consistent with the assumption of unit relative mole sensitivities made in mathematical analysis of the FI/MS data. Field ionization molecular-ion intensities for both the oil and asphaltene neutrals were also converted to weight percents including FI relative mole sensitivities. Relative mole sensitivities were reasonably assumed to be constant within each Z series (23). For the hydrocarbon Z(H) series present in the asphaltene neutrals, Table XXXVII compares the weight percents calculated from the FI/MS ion intensities assuming unit relative mole sensitivities (see column 2) and including relative mole sensitivites for each Z(H) series (see column 3) and from the LV/EI/MS molecular-ion intensities (see column 4). Comparison of the results in columns 2 and 3 with the corresponding entries in column 4 reveals, as expected, that inclusion of FI relative mole sensitivites improves the already good agreement between the two analyses. It should be noted that minor amounts of -38, -40, and -42 Z series hydrocarbons were observed in the asphaltene neutrals by LV/EI/MS but not by FI/MS. This result undoubtedly reflects the enhanced sensitivity of the MS-50 over that of the 21-110.

In addition to $C_NH_{2N+Z(H)}$ and $C_NH_{2N+Z(O)}O$ compound types, the LV/EI/MS analysis found minor amounts of $C_NH_{2N+Z(S)}S$ compounds in the asphaltene neutrals. The observation of $C_NH_{2N+Z(S)}S$ molecular ions

TABLE XXXVII

A COMPARISON OF THE QUANTITATIVE DATA OBTAINED FOR THE ASPHALTENE AROMATIC HYDROCARBON TYPES

Z Series	OSU Results		Exxon Results
	Wt. % x 10[1a]	Wt. % x 10[1b]	Wt. % x 10[1]
-6	3.6	5.5	4.1
-8	4.8	6.8	7.6
-10	5.6	7.6	6.7
-12	10.9	13.1	12.2
-14	9.7	10.8	9.8
-16	9.8	10.7	11.0
-18	12.2	12.6	12.6
-20	8.6	8.1	8.8
-22	12.0	11.6	12.5
-24	8.4	7.8	7.6
-26	9.5	8.4	9.1
-28	5.2	4.3	4.0
-30	6.9	5.6	9.4
-32	3.0	2.6	1.8
-34	3.5	2.7	0.5
-36	1.5	1.2	0.3
Total	115.1	119.4	118.0

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[a] Calculations assume unit relative mole sensitivites.

[b] Calculations assume relative mole sensitivites constant within a Z series.

in the LV/EI/MS and the failure to detect such species in both the FI/MS and 70-eV EI/MS is consistent with the difference in resolution capabilities between the AEI MS-50 and the CEC 21-110B. As seen in Table IX the carbon-number distribution reveals that the $C_NH_{2N+Z(S)}S$ compounds in the asphaltene neutrals account for 0.8% of the total liquid.

As seen in Table XXXV, both the oils and asphaltenes contain appreciable quantities of -6 through -26 (H) aromatic hydrocarbons. Except for the -6(H) and -8(H) series, the carbon-number distributions for these Z series commence at the same molecular weights in both fractions but extend to higher molecular weights in the asphaltenes than in the oils. The fact that the -6(H) and -8(H) series commence at 1 and 2 carbon numbers lower in the asphaltenes than in the oils, respectively, is an interesting result which does not appear to be consistent with a separation based upon solubilities. The appreciable overlap in compositions of both fractions is consistent with the observation that the asphaltene neutrals are *ca.* 88% pentane soluble upon removal of the acidic and basic components. These hydrocarbon types in the oils and asphaltenes account for 9.5 and 9.8%, respectively, of the total liquid.

Both the oil and asphaltene neutrals contain appreciable amounts of naphthalenes, -12(H), acenaphthenes, -14(H), fluorenes/acenaphthylenes, -16(H), and phenanthrenes, -18(H). The asphaltenes also contain an appreciable amount of pyrenes/fluoranthenes, -22(H). Compounds in the -6(H) series are reasonably attributed to benzene and its alkylated derivatives. Compounds in the -8(H) and -10(H) series are likely to be indane and indene and homologs, respectively. The oils and asphaltenes contain aromatic hydrocarbons possessing from 1 through 4 and 1 through 7 aromatic rings, respectively.

The carbon-number distributions in Tables IV, V, and VII for the aromatic hydrocarbons in the oils and asphaltenes are characterized by the occurrence of the maximum weight percent in the early part of each Z(H) series distribution. In this regard it should be noted that the COED process involves multi-stage pyrolysis. Thus, for aromatic hydrocarbon types, the dependence of the weight percents on carbon number for the COED liquid parallels the dependence observed for liquids obtained from other coal pyrolysis processes (17,26). It is interesting to note that the weight percents for $C_{24}H_{18}$, $C_{25}H_{24}$, and $C_{26}H_{30}$ in the -30(H), -26(H), and -22(H) Z series, respectively, are larger than would have been expected. As seen in Table VII, the same result was obtained in the LV/EI/MS analysis. Although the origin of this phenomenon is unclear, it could conceivably reflect either the perferential formation of these compounds or the resistance of these compounds to hydrogenation/pyrolysis in the liquefaction process.

The data in Table XXXVI show that both the oils and asphaltenes contain compounds in the -8 through -18 Z(O) series. The carbon-number distributions for the -8(O), -10(O), -12(O), and -14(O) Z series commence at lower molecular weights in the asphaltenes than in the oils. However, the Z(O) series extend to higher molecular weights in the asphaltenes than in the oils. This result parallels that obtained for the aromatic hydrocarbons. It should be noted that the weight percents obtained for the $C_NH_{2N+Z(O)}O$ compounds by FI/MS and LV/EI/MS are in good agreement. The LV/EI/MS analysis reveals the presence of minor amounts of -34(O) and -36(O) compounds in the asphaltene neutrals. It is important to note that the oxygen compounds in the oil and asphaltene neutrals comprise 1.1% and 4.3% of the total liquid, respectively. This result is reasonable in that greater amounts of heteroatom-containing compounds would be expected to be present in the asphaltene fractions and not the oils.

The IR spectra of the oil and asphaltene neutrals, Figures 5 and 6, show almost no absorptions in the spectral region 3200-3600 cm^{-1}. This result indicates that the oxygen-containing compounds in the neutral fractions are not characterized by the presence of OH groups. Weak absorptions at ca. 1700 cm^{-1} were observed in both spectra. These could be indicative of the presence of minor amounts of ketones/aldehydes. Identification of the other absorption bands is well known (19-21). The absorptions at 2860, 2950, and 3050 cm^{-1} can be ascribed to aliphatic CH and aromatic CH stretching. The band at 1600 cm^{-1} is characteristic of ring aromatic C=C. Water bands at 3620-3695 cm^{-1} are observed in the matrix-isolation spectrum of the oil neutrals. Based on the IR data and the parent formulas in Table XXXVI, the $C_NH_{2N+Z(O)}O$ compounds in the neutral fractions are principally comprised of furans. Furthermore, comparison of the Z(H) values in Table XXXV with the Z(O) values in Table XXXVI suggests that the furans are phenomenologically derived from the aromatic hydrocarbons by replacement of a ring CH_2 by O.

Appreciable amounts of dihydrobenzofurans, -8(O), benzofurans, -10(O), naphthenobenzofurans, -12(O), dibenzofurans, -16(O), and acenaphthenofurans, -18(O), are present in both the oil and asphaltene neutrals. The oils and asphaltenes contain aromatic oxygen-containing compounds possessing from 2 through 3 and 2 through 7 aromatic rings, respectively.

As seen in Table IV, the carbon-number distributions for the $C_NH_{2N+Z(O)}O$ compounds in the oil neutrals are relatively short and reach a maximum near the center of each Z(O) series distribution. The carbon-number distributions for the $C_NH_{2N+Z(O)}O$ compounds in the asphaltene neutrals, Tables VI and VIII, are characterized by the occurrence of maximums in the beginning of the distribution. The origin of the differences in these Z(O) distributions is not clear. Furthermore, the former contrasts with the result obtained for the oil aromatic hydrocarbons and the latter parallels the distribution of weight percents in each Z(H) series for the asphaltene neutrals. It is tempting to ascribe the difference in the distribution of weight percents of the various Z(O) compound types in the oil and asphaltene neutrals to the chemistry associated with the COED process. However, the fact that considerable overlap exists in the neutral aromatic Z(O) compounds between the oils and asphaltenes precludes this conclusion because the results could reflect phenomena associated with solvent extraction.

The compositional data obtained for the acids containing either one or two oxygens in the oil and four asphaltene acid fractions are summarized in Tables XXXVIII and XXXIX, respectively. The data for asphaltene fraction C demonstrate good agreement between the Exxon and OSU mass spectrometric analyses. Both analyses show that asphaltene acid fraction C contains compounds in the -6 through -34 Z(O) series. These compounds comprise 25.3% of the total liquid as determined by FI/MS and 21.4% of the total liquid as determined by LV/EI/MS. Compound types in the -6 through -34 $Z(O_2)$ series were also observed in acid

TABLE XXXVIII

SUMMARY DATA FOR $C_NH_{2N+Z}O$ AROMATIC ACIDS

		Oils[a]			Asphaltene Fraction A[a]			Asphaltene Fraction B[a]		
	Parent	Wt.%	Range In		Wt.%	Range In		Wt.%	Range In	
-Z(O)	Formula	x 10^1	N	MW	x 10^1	N	MW	x 10^1	N	MW
6	C_6H_6O	13.5	6-23	94-332	5.8	6-11	94-164	0.1	6-10	94-150
8	$C_9H_{10}O$	10.1	9-24	134-344	0.7	9-13	134-190	0.6	9-14	134-204
10	C_9H_8O	4.5	9-24	132-342	1.7	9-16	132-230	0.2	9-14	132-202
12	$C_{10}H_8O$	4.5	10-24	144-340	5.8	10-18	144-256	0.3	10-15	144-214
14	$C_{12}H_{10}O$	4.2	12-24	170-338	1.6	12-15	170-212	0.4	12-18	170-254
16	$C_{12}H_8O$	2.9	12-24	168-336	2.8	12-18	182-252	0.4	12-19	182-266
18	$C_{14}H_{10}O$	4.1	14-24	194-334	3.4	14-21	194-292	0.2	14-22	194-306
20	$C_{15}H_{10}O$	1.4	15-24	206-332	2.6	15-22	206-304	0.2	15-21	206-290
22	$C_{16}H_{10}O$	1.3	16-25	218-344	2.1	16-22	218-302	0.8	16-24	218-330
24	$C_{17}H_{10}O$				1.9	17-24	230-328	0.3	17-24	230-328
26	$C_{18}H_{10}O$				2.5	18-24	242-326	0.2	19-25	256-340
28	$C_{20}H_{12}O$				2.2	20-26	268-352	0.2	20-27	268-366
30	$C_{21}H_{12}O$				1.5	21-26	280-350	0.1	22-29	294-392
32	$C_{22}H_{12}O$				0.9	22-27	292-362	0.1	24-27	320-362
34	$C_{24}H_{14}O$									
36	$C_{24}H_{12}O$									
Total		46.5			35.5			4.1		

[a] Results from FI/MS analysis.

TABLE XXXVIII (Continued)

		Asphaltene Fraction C[a]			Asphaltene Fraction C[b]			Asphaltene Fraction D[a]		
-Z(O)	Parent Formula	Wt.% x 10^1	Range In N	Range In MW	Wt.% x 10^1	Range In N	Range In MW	Wt.% x 10^1	Range In N	Range In MW
6	C_6H_6O	4.4	6-14	94-206	5.9	6-14	94-206	0.06	6-13	94-192
8	$C_9H_{10}O$	3.4	9-15	134-218	2.2	8-16	120-232	0.04	9-16	134-232
10	C_9H_8O	1.4	9-16	132-230	0.8	9-19	132-272	0.08	9-16	132-230
12	$C_{10}H_8O$	1.2	10-17	144-242	1.1	10-21	144-298	0.08	10-18	144-256
14	$C_{12}H_{10}O$	1.5	12-18	170-254	1.0	12-21	170-296	0.05	12-18	170-254
16	$C_{12}H_8O$	3.3	13-20	182-280	1.9	13-26	182-364	0.07	13-20	182-280
18	$C_{14}H_{10}O$	1.9	14-21	194-292	1.3	14-29	194-404	0.06	14-23	194-320
20	$C_{15}H_{10}O$	1.4	15-22	206-304	1.2	14-29	192-402	0.06	15-23	206-318
22	$C_{16}H_{10}O$	2.1	16-25	218-344	2.0	16-29	218-400	0.08	16-25	218-344
24	$C_{17}H_{10}O$	1.5	17-25	230-342	1.4	17-31	230-426	0.07	18-26	244-356
26	$C_{18}H_{10}O$	1.3	18-26	242-354	1.1	18-32	242-438	0.05	19-26	256-354
28	$C_{20}H_{12}O$	0.9	20-26	268-352	0.7	20-31	268-422	0.04	20-26	268-352
30	$C_{21}H_{12}O$	0.6	24-26	322-350	0.5	21-31	280-420	0.05	22-28	294-378
32	$C_{22}H_{12}O$	0.2	24-26	320-348	0.2	22-33	292-446	0.02	22-26	292-348
34	$C_{24}H_{14}O$	0.2	25-27	332-360	0.1	24-33	318-444	0.01	25-27	332-360
36	$C_{24}H_{12}O$				0.1	24-30	316-400			
Total		25.3			21.5			0.8		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

TABLE XXXIX

SUMMARY DATA FOR $C_NH_{2N+Z}O_2$ AROMATIC ACIDS

		Oils[a]			Asphaltene Fraction A[a]			Asphaltene Fraction B[a]		
-Z(O_2)	Parent Formula	Wt.% x 10^1	Range In N	Range In MW	Wt.% x 10^1	Range In N	Range In MW	Wt.% x 10^1	Range In N	Range In MW
6	$C_6H_6O_2$	1.7	6-11	110-180	7.6	6-13	110-208	1.2	6-13	110-208
8	$C_9H_{10}O_2$	1.5	9-22	150-332	1.1	7-13	122-206	0.2	7-11	122-178
10	$C_9H_8O_2$	2.9	9-23	148-344	2.9	9-16	148-246	0.5	9-16	148-246
12	$C_{10}H_8O_2$	1.8	10-23	160-342	0.8	10-14	160-216	0.4	10-16	160-244
14	$C_{12}H_{10}O_2$	2.4	12-23	186-340	4.5	11-19	172-284	0.3	11-16	172-242
16	$C_{12}H_8O_2$	3.2	12-23	184-338	9.8	12-20	184-296	0.4	12-20	184-296
18	$C_{14}H_{10}O_2$	3.5	14-23	210-336	5.0	14-23	210-336	0.3	14-21	210-308
20	$C_{15}H_{10}O_2$				2.1	15-24	222-348	0.3	15-23	222-334
22	$C_{16}H_{10}O_2$				2.9	16-25	234-360	0.3	16-24	234-346
24	$C_{17}H_{10}O_2$				2.5	17-26	246-372	0.3	17-23	246-330
26	$C_{18}H_{10}O_2$				2.2	18-26	258-370	0.2	18-25	258-356
28	$C_{20}H_{12}O_2$				1.4	20-27	284-382	0.2	20-27	284-382
30	$C_{21}H_{12}O_2$				0.9	21-27	296-380	0.1	21-27	296-380
32	$C_{22}H_{12}O_2$				0.9	22-28	308-392	0.1	22-26	308-364
34	$C_{24}H_{14}O_2$				0.4	24-29	334-404	0.04	24-26	334-362
36	$C_{24}H_{12}O_2$				0.2	25-28	346-388	0.1	24-27	332-374
Total		17.0			45.2			4.9		

[a] Results from FI/MS analysis.

TABLE XXXIX (Continued)

		Asphaltene Fraction C[a]			Asphaltene Fraction C[b]			Asphaltene Fraction D[a]		
		Wt.%	Range In		Wt.%	Range In		Wt.%	Range In	
$-Z(O_2)$	Parent Formula	x 10^1	N	MW	x 10^1	N	MW	x 10^1	N	MW
6	$C_6H_6O_2$	0.2	6-10	110-166	0.2	6-10	110-166	0.04	6-11	110-180
8	$C_9H_{10}O_2$	0.2	9-13	150-206	0.1	9-13	150-206	0.04	8-12	136-192
10	$C_9H_8O_2$	0.7	9-14	148-218	0.8	9-18	148-274	0.04	9-16	148-246
12	$C_{10}H_8O_2$	0.4	10-16	160-244	0.3	10-18	160-272	0.05	10-18	160-272
14	$C_{12}H_{10}O_2$	0.5	12-19	186-284	0.2	12-22	186-326	0.04	12-18	186-270
16	$C_{12}H_8O_2$	1.2	12-19	184-282	1.1	12-26	184-380	0.05	13-19	198-282
18	$C_{14}H_{10}O_2$	1.2	14-21	210-308	0.9	14-28	210-406	0.09	14-21	210-308
20	$C_{15}H_{10}O_2$	1.1	16-23	236-334	0.9	15-28	222-404	0.05	17-22	250-320
22	$C_{16}H_{10}O_2$	1.3	16-23	234-332	1.1	16-28	234-402	0.05	16-24	234-346
24	$C_{17}H_{10}O_2$	1.6	17-26	246-372	1.2	18-32	260-456	0.09	17-26	246-372
26	$C_{18}H_{10}O_2$	0.9	19-26	272-370	1.0	19-31	272-440	0.06	20-26	286-370
28	$C_{20}H_{12}O_2$	0.5	20-26	284-368	0.6	20-32	284-452	0.05	20-25	284-354
30	$C_{21}H_{12}O_2$	0.5	22-26	310-366	0.6	22-32	310-450	0.03	22-25	310-352
32	$C_{22}H_{12}O_2$	0.4	25-27	350-378	0.4	22-32	308-448	0.04	23-27	322-378
34	$C_{24}H_{14}O_2$	0.04	25	348	0.2	24-33	334-460	0.01	24	334
36	$C_{24}H_{12}O_2$				0.02	25-33	346-458	0.01	25-26	346-360
Total		10.7			9.6			0.7		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

fraction C by both analyses. These compound types make up 10.7% of the total liquid as determined by FI/MS and 9.6% of the total liquid as determined by LV/EI/MS. Minor amounts of -36(O) and -36(O_2) compounds were observed in the LV/EI/MS analysis of asphaltene acid fraction C. These specific Z series were not observed in the FI/MS of this fraction. The data in Tables XXXVIII and XXXIX also reveal that the two analyses of acid fraction C differ slightly in terms of the total number of carbons in a given specific Z series, i.e., the molecular weight range for a compound class. However, inspection of the carbon-number distributions in Tables XXIV and XXV reveals that this difference reflects very low intensity molecular ions and, hence, represents compounds which account for only 0.3% of the total liquid. Consequently, it is not surprising that the two analyses are in good agreement in regard to the total weight percent of each Z(O) and Z(O_2) series. Summary data for additional compound types present in the acid fractions are presented in Table XXXX. In addition to these compounds, both mass spectrometric analyses detected trace quantities of hydrocarbon contaminents in all acid fractions.

The data in Tables XXXVIII and XXXIX reveal that both the oils and the asphaltene acid fractions contain compounds in the -6 through -22 Z(O) series and -6 through -18 Z(O_2) series, respectively. This result and the absence of compounds in the oils containing either 3 or 4 oxygens suggests that introduction of additional oxygens reduces the maximum ring number for contamination during the solvent separation.

It should be noted that the carbon-number distributions of the Z(O) and Z(O_2) series common to both the oils and asphaltene fractions start at the same molecular weights in both fractions but extend to

TABLE XXXX

SUMMARY DATA FOR OTHER ACIDIC COMPOUNDS

Fraction	General Formula	Z Series	Wt. % x 10^1
Oils[a]	$C_NH_{2N+Z}N$	-15 (N)	1.1
Asphaltene Fraction A[a]	$C_NH_{2N+Z}O_3$	-16 through -32 (O_3)	10.0
	$C_NH_{2N+Z}O_4$	-16,-18,-26, and -28 (O_4)	3.2
Asphaltene Fraction B[a]	$C_NH_{2N+Z}O_3$	-14 through -30 (O_3)	1.1
	$C_NH_{2N+Z}O_4$	-18 through -28 (O_4)	0.4
Asphaltene Fraction C[b]	$C_NH_{2N+Z}N$	-5 through -21 (N)	0.6
	$C_NH_{2N+Z}O_3$	-6 through -36 (O_3)	1.5
	$C_NH_{2N+Z}O_4$	-6 through -34 (O_4)	0.7
	$C_NH_{2N+Z}NO$	-5 through -33 (NO)	1.2
Asphaltene Fraction D[a]	$C_NH_{2N+Z}O_3$	-16 through -32 (O_3)	0.2
	$C_NH_{2N+Z}O_4$	-18 through -28 (O_4)	0.05
	$C_NH_{2N+Z}NO$	-5,-9,-11,-15 through -19 (NO)	0.4

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

higher molecular weights in the oils than in the asphaltene fractions. This is especially evident in the -6 through -14 Z(O) series and the -8 through -14 $Z(O_2)$ series. This result is opposite to that observed in the aromatic neutral fraction. It is not obvious how this result can be reconciled with a separation of acids according to their solubilities in pentane and benzene.

As seen in Figures 7 through 11, the IR spectra of the oil and asphaltene acid fractions exhibit a strong absorption band at 3600 cm^{-1} attributable to phenolic O-H stretch. The absence of both a strong absorption in the region 1700-1750 cm^{-1} and a broad band in the 2800-3300 cm^{-1} region of the oil acid fraction and asphaltene acid fractions A, C, and D excludes carboxylic acids as major contributors to acids containing two or more oxygens. Therefore, it is reasonable to conclude that these acid fractions are characterized by aromatic compounds possessing 1 through 4 hydroxyl groups bonded to a ring carbon. Comparison of both the molecular formulas and specific Z values in Tables XXXVIII, XXXIX, and XXXX with the corresponding data in Table XXXV, suggests that the phenols can be viewed as being derived from the aromatic hydrocarbons by substitution of 1 through 4 hydroxyl groups for aromatic hydrogens.

The IR spectrum of asphaltene acid fraction B exhibits both a band at _ca_. 1700 cm^{-1} and a broad band at _ca_. 2800-3500 cm^{-1} characteristic of carboxylic acids. Furthermore, FI/MS of asphaltene acid fraction B confirms the existence of molecular ions at m/e 122 and 136 in the $-8(O_2)$ Z series as well as a molecular ion at m/e 172 in the $-14(O_2)$ Z series. Benzoic acid molecular ions and variously methylated homologs could account for the ions at m/e 122 and 136, respectively.

Although the $-8(O_2)$ Z series also contains dihydroxyindanes and dihydroxytetralines, the parent members of these compound series have molecular weights of 150 and 164, respectively. The $-14(O_2)$ Z series contains compounds such as dihyroxyacenaphthalenes and dihydroxytetrahydrophenanthrenes. The former series commences at mass 186 and the latter one at mass 214. Naphthalenoic acid, however, has a molecular weight of 172. Thus, the molecular ions possessing the formulas $C_7H_6O_2$, $C_8H_8O_2$, and $C_{11}H_8O_2$ and the IR data for asphaltene acid fraction B suggests the presence of carboxylic acids. It should also be noted that FI/MS confirms the presence of molecular ions at m/e 122 and 172 in asphaltene acid fraction A and m/e 136 in asphaltene fractions A and D. The absorption in the region 3100-3500 cm^{-1} of the partial IR spectra of the matrix-isolated oil acids and asphaltene acid fractions A and D in Figures 7, 8, and 10 could be construed as supporting the presence of carboxylic acids in these fractions. However, ions at m/e 122, 136, and 172 were not observed in the FI/MS of the oil acids and asphaltene acid fraction C. Thus, the absorptions in the 3100-3500 cm^{-1} region of these IR spectra are equally well-explained by the presence of intermolecularly hydrogen-bonded phenols. Therefore, the IR spectra of asphaltene acid fractions A and D, unlike the IR spectrum of acid fraction B, neither confirm nor exclude the presence of benzoic and naphthalenoic acids in the former and singly methylated benzoic acids in the latter. The carbon-number distributions in Tables XII, XV, and XXI indicate that benzoic acid in fractions A and B account for 0.01%, singly methylated benzoic acids in fractions A, B, and D account for 0.01%, and naphthalenoic acids in fractions A and B contribute 0.06% of the total coal liquid. Thus, the total amount of carboxylic acids is indicated to be *ca.* 0.08% of the total liquid. To our knowledge this represents one of the first observations of carboxylic acids in coal-derived liquids. Either the chemistry associated with the COED process, the nature of the feed coal, or the breakdown of the A-29 resin during the separation procedure could explain the origin of these acids. Although the last phenomenon cannot be eliminated as an explanation, the failure to observe carboxylic acids in asphaltene acid fraction C, in the oil acids, and in the acid fraction from other coal-derived liquid separations conducted in our laboratory (17) appear to render it somewhat tenuous.

As shown in Table XXXX, aromatic compounds containing both nitrogen and nitrogen plus oxygen are present in the various acid fractions. It should be noted that the resolution (20,000), at which 70-eV EI/MS were acquired, is not sufficient to resolve either $C_{N-1}{}^{13}CH_{2N+Z(O)}O$ molecular ions from $C_NH_{2N+Z(N,O)}NO$ molecular ions or $C_{N-1}{}^{13}CH_{2N+Z(O_3)}O_3$ molecular ions from the $C_NH_{2N+Z(N)}N$ molecular ions. However, the existence of both $C_NH_{2N+Z(N,O)}NO$ and $C_NH_{2N+Z(N)}N$ compounds in the acid fractions is demonstrated by the ratio of the intensities of the appropriate even and odd mass ions in the FI/MS of the various acid fractions. It should be noted that isotope corrections were included in the conversion of FI/MS ion intensities to weight percents.

Based on the chemistry associated with ion-exchange chromatography (16,17) and the molecular formulas for at least the first homologs in the lower valued Z(N) series, the nitrogen-containing aromatic compounds are reasonably ascribed to the presence of pyrroles, e.g., carbazoles. Absorption bands in the 3470 cm^{-1} region are characteristic of pyrrolic NH (6,21). The broad bands in the 2800-3500 cm^{-1} region of the KBr spectrum of asphaltene acid fraction B (see Figure 9) and of the matrix-isolation spectrum of asphaltene acid fraction C (see Figure 10) and the nondescript nature of the 3400 cm^{-1} region in the solution spectrum of asphaltene acid fraction D (see Figure 11) preclude any conclusions concerning either the presence or the absence of pyrroles in these fractions. However, the partial matrix-isolation spectra of the oil acids and asphaltene acid fraction A in Figures 7 and 8, respectively, reveal resolved absorption bands in the region around 3470 cm^{-1} superimposed on the broad 2800-3500 cm^{-1} absorption band. As seen in Figure 5, the matrix-isolation IR spectrum of the oil neutrals does not exhibit absorptions in the 3470 cm^{-1} region. In contrast, Figure 12 reveals the presence of a band in the 3400-3500 cm^{-1} region of the matrix-isolation spectrum of the oil bases. Comparison of Figures 7 and 8 with Figure 12 shows that the structure of the 3400-3500 cm^{-1} absorptions in the former two is somewhat different than in the latter one. It appears unlikely that these absorptions reflect only the presence of intermolecular hydrogen bonding between water molecules trapped in the matrix because, as seen in Figure 5, they are absent in the corresponding spectrum of the oil neutral fraction. Consequently, absorptions at 3475 and 3480 cm^{-1} in the IR spectra in Figures 7 and 8 may be construed as providing some evidence supporting the presence of pyrroles. Based on Figure 12, it is thus conceivable that some pyrroles are also present in at least the oil base fraction. The data clearly preclude any assessment of the extent to which the NO-containing acids derive contributions from pyrroles containing either a phenolic group or a furan ring.

The carbon-number distributions of the acid fractions (Tables X through XXIII) are much shorter in comparison to the corresponding distributions for the neutral fractions. The distributions are also characterized by the occurrence of maximums in the beginning of the distribution.

Tables XLI and XLII summarize the compositional data obtained for the nitrogen and nitrogen plus oxygen containing bases, respectively, present in the oils and both asphaltene base fractions. These compound types represent the major contributors to the composition of the various base fractions. Additional compound types found in the base fractions are listed in Table XLIII.

Compositional data obtained for asphaltene fraction E by both FI/MS and LV/EI/MS are reported in Tables XLI and XLII. The two analyses are in reasonable agreement in regard to both carbon number range and molecular weight range for both Z(N) and Z(N,O) bases. Furthermore, inspection of the carbon-number distributions in Tables XXVII, XXVIII, XXXI, and XXXII reveal that the differences reflect the presence of low-intensity molecular ions at higher m/e values in the LV/EI/MS than in the FI/MS. Consequently, the excellent agreement in the weight percents for the various Z(N) and Z(N,O) series obtained by the two analyses is not an artifact.

The data in Tables XLI and XLII reveal that both the oils and asphaltene fractions contain aromatic compound types in the -5 through -25 Z(N) series and -7 through -19 Z(N,O) series, respectively. This result suggests that introduction of an oxygen to the aromatic nitrogen-containing bases reduces the maximum ring number for contamination during the solvent separation. The observation that the oils contain

TABLE XLI

SUMMARY DATA FOR $C_NH_{2N+Z}N$ AROMATIC BASES

		Oils[a]			Asphaltene Fraction E[a]			Asphaltene Fraction E[b]			Asphaltene Fraction F[a]		
			Range In			Range In			Range In			Range In	
-Z(N)	Parent Formula	Wt.% x 10^1	N	MW	Wt.% x 10^1	N	MW	Wt.% x 10^1	N	MW	Wt.% x 10^1	N	MW
5	C_5H_5N	0.3	8-19	121-275	0.2	8-19	121-275	0.4	7-21	107-303	0.1	8-18	121-261
7	C_8H_9N	0.5	8-18	119-259	0.3	8-20	119-287	0.3	8-22	119-315	0.07	8-20	119-287
9	C_8H_7N	0.6	8-20	117-285	0.3	8-19	117-271	0.3	8-26	117-369	0.08	8-20	117-285
11	C_9H_7N	2.3	9-25	129-353	1.3	9-23	129-325	1.1	9-26	129-367	0.2	9-23	129-325
13	$C_{11}H_9N$	1.1	11-24	155-337	0.7	11-28	155-393	0.6	11-28	155-393	0.2	11-25	155-351
15	$C_{11}H_7N$	0.8	12-25	167-349	0.5	12-23	167-321	0.6	12-27	167-377	0.2	12-23	167-321
17	$C_{13}H_9N$	0.8	13-21	179-291	0.8	13-28	179-389	0.9	13-27	179-375	0.3	13-25	179-347
19	$C_{14}H_9N$	0.6	14-26	191-359	0.4	14-28	191-387	0.3	14-28	191-387	0.2	17-27	233-373
21	$C_{15}H_9N$	0.7	16-26	217-357	0.8	15-28	203-385	0.6	15-28	203-385	0.3	15-29	203-399
23	$C_{16}H_9N$	0.5	16-25	215-341	0.5	17-29	229-397	0.4	17-30	229-411	0.3	16-29	215-397
25	$C_{17}H_9N$	0.3	18-26	241-353	0.2	18-29	241-395	0.3	18-30	241-409	0.1	18-29	241-395
27	$C_{19}H_{11}N$				0.3	19-29	253-393	0.3	19-29	253-393	0.2	19-29	253-393
29	$C_{21}H_{13}N$				0.3	21-29	279-391	0.2	21-29	279-391	0.1	21-29	297-391
31	$C_{21}H_{11}N$				0.2	21-29	277-389	0.2	22-28	291-375	0.1	21-29	277-389
33	$C_{23}H_{13}N$				0.2	23-30	303-401	0.1	23-29	303-387	0.05	23-30	303-401
35	$C_{23}H_{11}N$				0.1	23-30	301-399	0.04	23-29	301-385	0.06	23-30	301-399
37	$C_{25}H_{13}N$				0.03	28-32	269-425	0.02	25-30	327-397	0.05	25-30	327-397
39	$C_{27}H_{15}N$				0.03	27-30	353-395	0.01	27-30	353-395	0.01	27-30	353-395
41	$C_{27}H_{13}N$							0.01	27-29	351-379			
Total		8.5			7.2			6.7			2.6		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

TABLE XLII

SUMMARY DATA FOR $C_NH_{2N+Z}NO$ AROMATIC BASES

		Oils[a]			Asphaltene Fraction E[a]			Asphaltene Fraction E[b]			Asphaltene Fraction F[a]		
		Wt.%$_1$	Range In		Wt.%$_1$	Range In		Wt.%$_1$	Range In		Wt.%$_1$	Range In	
-Z(NO)	Parent Formula	x 10^1	N	MW	x 10^1	N	MW	x 10^1	N	MW	x 10^1	N	MW
7	C_7H_7NO	0.5	7-22	121-331	0.1	7-15	121-233	0.1	8-17	135-261	0.04	7-15	121-233
9	C_7H_5NO	0.7	9-23	147-343	0.2	8-16	133-245	0.2	8-20	133-301	0.07	8-15	133-231
11	$C_{10}H_9NO$	0.5	10-23	159-341	1.8	10-19	159-285	1.2	10-22	159-327	0.1	10-18	159-271
13	$C_{10}H_9NO$	0.3	12-24	185-353	0.2	11-18	171-269	0.2	11-25	171-367	0.1	11-18	171-269
15	$C_{11}H_7NO$	0.7	11-23	169-337	0.4	12-20	183-295	0.2	12-27	183-393	0.2	11-21	169-309
17	$C_{13}H_9NO$	0.7	14-24	209-349	0.6	13-22	195-321	0.4	14-27	209-391	0.2	13-22	195-321
19	$C_{13}H_7NO$	1.0	14-25	207-361	0.3	13-21	193-305	0.2	15-27	221-389	0.1	13-23	193-333
21	$C_{15}H_9NO$				0.3	15-22	219-317	0.3	15-27	219-387	0.2	17-24	247-345
23	$C_{16}H_9NO$				0.2	17-26	245-371	0.2	17-27	245-385	0.1	17-24	245-343
25	$C_{18}H_{11}NO$				0.2	18-26	257-369	0.3	18-28	257-397	0.06	18-26	257-369
27	$C_{19}H_{11}NO$				0.2	20-26	283-367	0.3	20-28	283-395	0.1	18-27	255-395
29	$C_{20}H_{11}NO$				0.03	21-25	295-351	0.2	20-28	281-393	0.04	20-28	281-393
31	$C_{21}H_{11}NO$				0.01	23-26	321-363	0.2	20-28	279-391	0.03	24-28	335-391
33	$C_{23}H_{13}NO$				0.02	24-25	333-347	0.1	23-28	319-389	0.02	24-28	333-389
35	$C_{23}H_{11}NO$				0.03	24-25	331-345	0.04	23-28	317-387	0.03	23-29	317-401
37	$C_{24}H_{11}NO$							0.02	24-28	329-385			
39	$C_{26}H_{13}NO$							0.01	26-29	355-397			
41	$C_{27}H_{13}NO$							0.01	27	367			
Total		4.4			4.7			4.2			1.4		

[a] Results from FI/MS analysis. [b] Results from LV/EI/MS analysis.

TABLE XLIII

SUMMARY DATA FOR OTHER BASIC COMPOUNDS

Fraction	General Formula	Z Series	Wt. % x 10^1
Oils	$C_NH_{2N+Z}NO_2$	$-11(NO_2)$	0.05
Asphaltenes	$C_NH_{2N+Z}NO_2$	-5 through $-37(NO_2)$	0.76
	$C_NH_{2N+Z}NS$	-9 through $-29(NS)$	0.13
	$C_NH_{2N+Z}NO_3$, $C_NH_{2N+Z}NS_2$, $C_NH_{2N+Z}NSO$ $C_NH_{2N+Z}NSO_2$ and $C_NH_{2N+Z}NS_2O$		Trace

compounds in the -11 $Z(N,O_2)$ series only as opposed to the asphaltenes which contain compounds in the -5 through -37 $Z(N,O_2)$ series, supports this conclusion. The carbon-number distributions for the Z(N) series, common to both the oils and asphaltenes, commence at about the same molecular weights in both fractions but extend to slightly higher molecular weights in the asphaltenes than in the oils. In contrast to this result, the carbon-number distributions for the Z(N,O) series, common to both the oils and asphaltenes, commence at about the same molecular weights in both fractions but extend to slightly higher molecular weights in the oils than in the asphaltenes.

As previously noted, the absorptions above 3600 cm^{-1} in the matrix-isolation spectrum of the oil bases (see Figure 12) can be ascribed to intermolecularly hydrogen-bonded water molecules. Therefore, the 2500-3600 cm^{-1} region of the IR spectra in Figures 12-14 show no evidence for the presence of OH groups in any of the base fractions. As previously noted, the IR spectrum of the oil bases in Figure 12 exhibits absorptions in the 3470 cm^{-1} region which could be indicative of the presence of pyrroles. It should be noted that a weak absorption at *ca.* 3350 cm^{-1} observed in the IR spectrum of asphaltene fraction E (see Figure 13) could be interpreted as providing tenuous evidence for the presence of basic NH. Absorptions at *ca.* 1700 cm^{-1} in the spectra of all three base fractions indicate the presence of carbonyl groups.

Based on the IR spectra, the method of separation, and the molecular formulas for the first homologs in at least the lower Z(N) and Z(N,O) series, these compound types are principally comprised of azaaromatics. The former and latter compound types can be phenomenologically viewed as arising from replacement of an aromatic-ring CH in the hydrocarbons and furans, respectively, by nitrogen. The Z(N) compound types present in both the oils and asphaltenes possess from 1 through 5 and 1 through 7 aromatic rings, respectively. The Z(NO) compounds present in both the oils and asphaltenes possess from 2 through 4 and 2 through 5 aromatic rings, respectively.

CHAPTER III

SUMMARY AND CONCLUSIONS

In summary, the data in Tables XXXV, XXXVI, and XXXVIII through XLIII demonstrate that the asphaltenes contain higher molecular weight specific Z series, higher molecular weight homologs in most cases, and different compound types than do the oils. However, the results also show that compound types are observed in both the oils and asphaltenes which are equivalent in molecular formula and, hence, assumably in molecular structure. This result suggests that a number of physical/chemical phenomena, such as coprecipitation, molecular inclusions, and intermolecular electronic interactions, are involved in the use of simple solvent extraction to isolate oils and asphaltenes.

Oils and asphaltenes, which constitute a partial characterization of coal liquids according to solvent extractions, have generally been considered to be key intermediates in the mechanism of coal liquefaction. However, the results in Tables XXXV through XLIII demonstrate that a simple solvent extraction does not produce oil and asphaltene fractions possessing unique compositions. Furthermore, as demonstrated by the weight percents in these Tables, the overlap in compositions is appreciable. In contrast, a true separation according to solubility would result in oil and asphaltene fractions essentially comprised of either unique compound types (Z series) or unique homologs (carbon-number distributions) for corresponding Z series, or both.

The consequence of the above consideration for the characterization of coal liquids by simple solvent separation is illustrated using the results for aromatic hydrocarbons. Consistent with a true solubility separation, the weight percents of the homologs of the various aromatic hydrocarbon Z series in the asphaltene neutrals which are common to those in the oil neutrals were added to the corresponding values for the latter. The results so obtained are summarized in Table XLIV. Of the total aromatic hydrocarbons in the COED liquid which are recovered by benzene, the data in Table XXXV lead to the conclusion that *ca*. 55% are characterized as being asphaltene. In contrast, the data in Table XLIV lead to the conclusion that only *ca*. 16% should be classified as being asphaltene. Furthermore, the fact that 88% of the asphaltene neutrals are pentane soluble in combination with the data in Table II suggests that only 8% of the hydrocarbons belong to the asphaltenes. In addition, the data in Tables XXXV and XLIV lead to significantly different conclusions concerning the average molecular weights of the hydrocarbon types and the average hydrocarbon structure present in the oils and asphaltenes. Tables XLV and XLVI show data similarly obtained for $C_NH_{2N+Z(O)}O$ acids and $C_NH_{2N+Z(N)}N$ bases, respectively. Data presented in Tables XXXVIII and XLI lead to the conclusions that 59% of the total $C_NH_{2N+Z(O)}O$ acids in the COED liquid and 54% of the total $C_NH_{2N+(N)}N$ bases in the COED liquid, respectively, are characterized as being asphaltenes. In contrast, the data in Tables XLV and XLVI lead to the conclusions that only 13% of the total $C_NH_{2N+Z(O)}O$ acids and 12%

TABLE XLIV

SUMMARY DATA FOR C_NH_{2N+Z} AROMATIC HYDROCARBONS CHARACTERISTIC OF OILS AND ASPHALTENES

	Oils			Asphaltenes		
	Wt.%	Range In		Wt.%	Range In	
-Z	x 10^1	N	MW	x 10^1	N	MW
6	10.7	9-29	120-400	0.04	30-31	414-428
8	14.7	10-29	132-398	0.2	30-37	412-510
10	13.5	9-30	116-410	0.9	31-40	424-550
12	30.4	10-30	128-408	0.9	31-40	422-548
14	21.9	12-30	154-506	1.6	31-40	420-546
16	18.6	12-30	152-404	1.7	31-40	418-544
18	21.7	14-30	178-402	1.8	31-40	416-542
20	10.6	14-30	190-400	2.1	31-40	414-540
22	14.9	16-30	202-398	1.7	31-41	412-552
24	8.9	18-31	228-410	1.3	32-41	424-550
26	9.5	18-31	226-408	1.4	32-41	422-548
28				5.2	20-39	252-518
30				6.9	22-40	278-530
32				3.0	22-39	276-514
34				3.5	22-41	274-540
36				1.5	24-41	300-538
Total	175.4			33.7		

TABLE XLV

SUMMARY DATA FOR $C_NH_{2N+Z}O$ AROMATIC ACIDS CHARACTERISTIC OF OILS AND ASPHALTENES

	Oils			Asphaltenes		
	Wt.%	Range In		Wt.%	Range In	
-Z(O)	x 10^1	N	MW	x 10^1	N	MW
6	23.9	6-23	94-332			
8	14.8	9-24	134-344			
10	7.9	9-24	132-342			
12	11.9	10-24	144-340			
14	7.8	12-24	170-338			
16	9.5	12-24	168-336			
18	9.7	14-24	194-334			
20	5.7	15-24	206-332			
22	6.4	16-25	218-344			
24				3.8	17-26	230-356
26				4.1	18-26	242-354
28				3.3	20-27	268-366
30				2.3	21-29	280-392
32				1.2	22-27	292-362
34				0.2	25-27	332-360
Total	97.6			14.9		

TABLE XLVI

SUMMARY DATA FOR $C_NH_{2N+Z}N$ AROMATIC BASES CHARACTERISTIC OF OILS AND ASPHALTENES

	Oils			Asphaltenes		
	Wt.%	Range In		Wt.%	Range In	
-Z(N)	x 10^1	N	MW	x 10^1	N	MW
5	0.6	8-19	121-275			
7	0.8	8-18	119-259	0.1	19-20	273-287
9	1.0	8-20	117-285			
11	3.8	9-25	129-353			
13	2.0	11-24	155-337	0.1	25-28	351-393
15	1.5	12-25	167-349			
17	1.8	13-21	179-291	0.1	22-28	305-389
19	1.2	14-26	191-359	0.01	27-28	373-387
21	1.9	16-26	217-357	0.03	27-29	371-399
23	1.2	16-25	215-341	0.1	26-29	355-397
25	0.6	18-26	241-353	0.03	27-29	367-395
27				0.5	19-29	253-393
29				0.4	21-29	279-391
31				0.3	21-29	277-389
33				0.3	23-30	303-401
35				0.2	23-30	301-399
37				0.1	25-32	327-425
39				0.04	27-30	353-395
Total	16.4			2.3		

of the total $C_NH_{2N+Z(N)}N$ bases, respectively, should be classified as being asphaltene. It is not unreasonable to expect that such differences in chemical composition will have major consequences for the elucidation of the reaction networks occurring in coal liquefaction and for the determination of other kinetic parameters as a function of catalyst and reaction conditions.

The data presented in Tables XXXV, XXXVI, and XXXVIII through XLIII also suggest that introduction of successive number of oxygens to the various aromatic compound types tends to reduce the maximum ring number for contamination during the solvent separation. This conclusion is supported by data obtained for the acids, bases, and neutrals.

It should be noted that the suitability of ion-exchange chromatography to the separation of coal liquids has been questioned (27-29). In this regard, the present results support the contention of Ruberto, Jewell, and Cronauer (30) that the general and stepwise SARA procedure is suitable for the separation of coal-derived liquids.

It is also important to note that the detailed analysis of the liquefaction of coal in hydrogen-donor and non-donor solvents question the suitability of describing the mechanism of coal liquefaction in terms of oils, asphaltenes, and preasphaltenes (31). In addition, the sequence of solvent extraction has been shown recently to have a significant effect on the yields of solubility fractions (32). Finally, detailed spectroscopic characterization of total coal liquids has shown that compound types equivalent in molecular formula are observed in both oils and asphaltenes (6). Consequently, these results and the results of this study taken together demonstrate that the use of the yields of the oils and asphaltenes obtained by simple solvent extraction to deduce the effect of 1) variation in reaction conditions and catalyst on the mechanism and kinetics of coal liquefaction, and 2) alteration in process conditions on the quality of the coal liquid lead to erroneous conclusions unless the yields are corrected for overlapping distributions. Consequently, detailed molecular analysis of solubility fractions is an essential requirement for indepth study of the chemistry of coal liquefaction and for correct evaluation of process effectiveness. Alternatively, the fractions obtained by simple solvent extraction could be subjected to detailed fractionation (10,13,14).

CHAPTER IV

EXPERIMENTAL

Separations

Coal Liquid Extraction

A soxhlet extractor was used to obtain oils, asphaltenes, and a residue. The soxhlet extractor was loaded so that it contained a layer each of glass, wool, sand, and diatomaceous earth. A thimble containing 19 grams of the COED coal liquid was placed on this bed and exhaustively extracted with pentane. The extraction was continued until a clear layer of pentane was obtained. This required one week. The oils were then recovered by first evaporating most of the solvent with a roto-evaporator. The remaining solvent was removed by passing a stream of dry N_2 into the flask. This process was continued until a constant weight was obtained. The oils were then washed with pentane until five clear washes were obtained. The pentane washings were combined and the oils recovered using a roto-evaporator. The residue from the pentane washings was dried and weighed. The soxhlet extractor was then filled with benzene and the thimble, which had been removed from the column and dried in an oven for about an hour, was immersed in the benzene on top of the column. The thimble was exhaustively extracted with benzene until a clear layer of solvent was obtained. This required two weeks. The asphaltenes were recovered by evaporating the solvent with a roto-evaporator and weighing to a constant weight. This sample was then added to the residue obtained in the pentane washing of the oils to give the total asphaltene sample. The thimble was removed from the column, dried in an oven for about an hour, and weighed to obtain the weight of the pentane insoluble/benzene insoluble residue.

Separation of Oils

Separation of Oil Acids. The chromatographic column is illustrated in Figure 15. The column is 1.4 cm in diameter (i.d.) and 119 cm in length. The temperature of the resin was controlled by circulating water through the outside jacket. The recycling arrangement permits continuous elution of the sample without use of large quantities of solvent or regulation of the reflux rate.

Amberlyst A-29 anion-exchange resin (Rohm and Haas, Inc.) was activated as follows. Methanolic HCl solution was prepared by mixing 10 volumes of concentrated HCl with 90 volumes of absolute methanol. Methanolic potassium hydroxide solution was prepared by adding 90 ml of methanol to 10 grams of potassium hydroxide. A volume of the resin was placed in a column and the resin was washed with a volume of methanolic HCl solution equivalent to 6 times the volume of resin taken. The resin was then washed with deionized water until the washings were neutral. The resin was then removed from the column, placed in a soxhlet extractor and then extracted with methanol, benzene, and pentane, in that order. The time for each extraction was 24 hours. After the three extractions, the resin was vacuum dried.

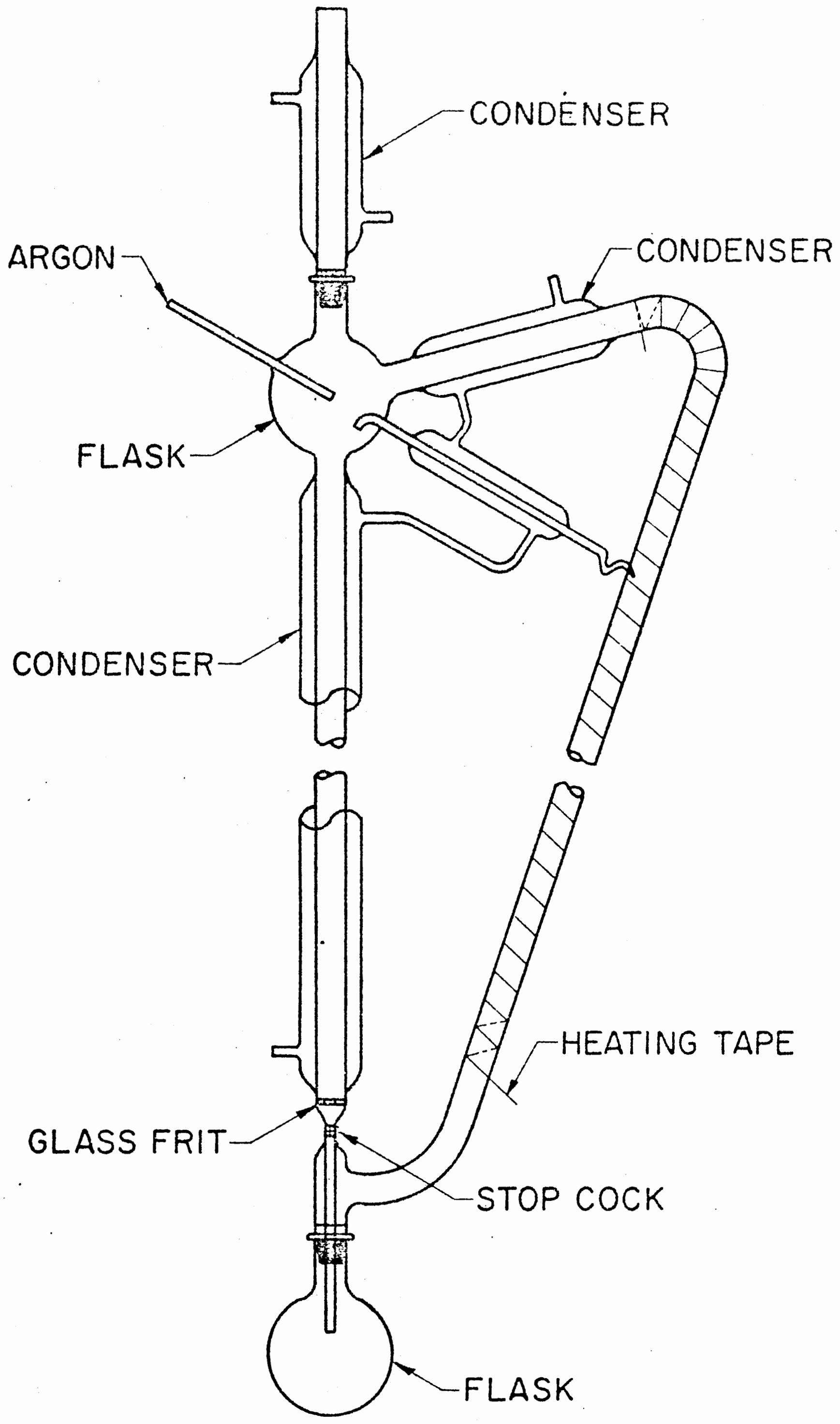

Figure 15. Recycling Chromatographic Column

The chromatographic column in Figure 15 was filled with pentane. A slurry of anion-exchange resin in pentane was then added to the column. A vibrator was used to settle and pack the resin. The resin was then extracted with recycled pentane under an argon atmosphere for 10 hours.

A 5-gram sample of the oils was dissolved in 25 ml of pentane and the resulting solution was quantitatively transferred to the column of ion-exchange resin. The solvent reservoir was then filled with pentane and the column was set up for elution at a rate of about 6-10 drops per minute. The elution of the non-adsorbed material was followed by monitoring the fluorescence of the eluent below the bed of resin. Elution of the non-adsorbed material required approximately 48 hours. The acids were then removed as follows. The upper solvent reservoir was filled with benzene and a flask containing benzene was fitted to the bottom of the column (see Figure 15). The elution of the resin bed with benzene lasted 24 hours. Elution with benzene removes any weakly acidic components adsorbed to the resin. At this point, a flask containing absolute methanol was fitted to the bottom of the column and a glass tube with a fritted end was inserted through the top condenser of the column so that gaseous CO_2 could be bubbled into the methanol in the upper solvent reservoir. The methanol saturated with CO_2 was then used to elute the strong acids from the resin. The removal of acids was followed by monitoring the fluorescence of the eluent with a UV lamp. The solvent was removed from both samples with a roto-evaporator until a constant weight was achieved. The acids removed from the resin using benzene and methanol/CO_2 were combined to yield a total acid fraction.

Separation of Oil Bases. The chromatographic column used is illustrated in Figure 15. Amberlyst 15 (Rohm and Haas, Inc.) was activated as follows. A volume of the resin was placed in a column and the resin washed with a volume of methanolic potassium hydroxide equivalent to 6 times the volume of resin taken. The rate of elution of the methanolic potassium hydroxide solution was controlled by the heat generated by the discharging of the resin. The resin was then washed with deionized water until the washings were neutral. The resin was then washed with a volume of methanolic HCl solution equivalent to 6 times the volume of resin taken. Again, the rate of elution for the methanolic HCl solution was controlled by the exothermicity of reaction. The resin was then washed with deionized water until the washings were neutral. The resin was removed from the column and placed in a soxhlet extractor. The resin was then subjected to extraction using methanol, benzene, and pentane. The time for each extraction was 24 hours. After the three extractions, the resin was vacuum dried.

The chromatographic column in Figure 15 was filled with pentane. A slurry of cation-exchange resin in pentane was then added to the column. A vibrator was used to settle and pack the resin. The resin was then extracted with recycled pentane under an argon atmosphere for 10 hours.

The oils minus the acids (obtained from the previous separation) were introduced onto the cation-exchange resin as previously described. Elution of non-basic material was identical to elution of non-acidic material described previously. After elution of the non-basic material, the weakly adsorbed bases were removed from the resin by elution with benzene for 24 hours. A flask containing 500 ml of a 2% by volume solution of isopropylamine in methanol was then fitted to the bottom of the column and the resin slowly discharged. The flow of the isopropylamine/methanol solution through the resin and the flow of water through the chromatographic-column jacket was adjusted in order to control the exothermicity produced by discharging the ion-exchange resin. Removal of the bases was followed by monitoring the fluorescence of the eluent with a UV light. The solvent was removed from the samples with a roto-evaporator until a constant weight was obtained. The bases removed by elution with benzene and the bases removed by elution with isopropylamine/methanol were combined to yield a total base fraction.

Separation of Oil Aromatic Neutrals. The oil neutrals (oils minus acids and bases) were separated into aromatic and saturate concentrates as follows. A 1.75 x 116 cm column was packed with 200 grams of activated silica gel. A sample of the oil neutrals was dissolved in 25 ml of pentane and quantitatively charged to the column. The resin was then eluted with pentane. After the first 150 ml of the eluate had been recovered, 50 ml aliquots were collected and analyzed for ultraviolet absorbance at 270 nm until the absorbance equalled 0.05. At that point the elution was stopped and the eluates were combined. The saturates were recovered by evaporation of the pentane and brought to a constant weight.

The silica gel was then partially deactivated by eluting the column with ca. 200 ml of chloroform. This eliminated the problem of excessive heat created by the subsequent methanol elution. The column was then eluted with methanol until the eluate was colorless. The neutral aromatics were then recovered by evaporating the solvent.

Separation of Asphaltenes

Separation of Asphaltene Acids.

The chromatographic column used in the separation of the asphaltenes was identical to the column used in the separation of the oils. Amberlyst A-29 anion-exchange resin (Rohm and Haas, Inc.) was activated, extracted, and dried using the previously described procedure (see Separation of Oil Acids).

The chromatographic column in Figure 15 was filled with benzene. A slurry of anion-exchange resin in benzene was then added to the column. A vibrator was used to settle and pack the resin. The resin was then extracted with recycled benzene under an argon atmosphere for 10 hours.

An 11-gram sample of the asphaltenes was dissolved in 25 ml of benzene and the resulting solution was quantitatively transferred to the column of ion-exchange resin. The initial adsorption of asphaltenes on the resin was subject to some amount of back-diffusion into the benzene solvent at the top of the column. This problem was avoided as follows. Ten ml of benzene was added to the top flask and the fluorescence of the solvent was monitored using a UV lamp. This quantity of solvent was then allowed to run into the resin bed. A second 10 ml volume of benzene was then added, the fluorescence of the solvent measured, and run into the resin bed. This procedure was repeated until the added benzene no longer showed fluorescence. The solvent reservoir was then filled with fresh benzene and the column was set up for elution at a rate of about 6-10 drops per minute. The elution of the non-adsorbed material was followed by monitoring the fluorescence of the eluent below the glass frit in Figure 15. Since the eluent continued to show fluorescence after a period of 72 hours, a second column of anion-exchange resin was prepared. The procedure was identical to that followed in preparing the first column. The non-adsorbed material was quantitatively transferred to the second column of ion-exchange resin. The solvent reservoir was filled with fresh benzene and the column was set up for elution at a rate of about 6-10 drops per minute. The elution of the non-adsorbed material was followed by monitoring the eluent with a UV lamp. Again, the eluent continued to show fluorescence after 72 hours so a third column of anion-exchange resin was prepared. The preparation of the third column was identical to that followed for the first two columns. Elution of the non-adsorbed material from the third column required approximately 48 hours. After elution of the non-adsorbed material, the acids were removed as follows. A flask containing absolute methanol was fitted to the bottom of the column (see Figure 15). A glass tube with a fritted end was inserted through the top condenser of the column so that gaseous CO_2 could be bubbled into the methanol in the upper solvent reservoir. The methanol saturated with CO_2 was then used to elute the acids from the anion-exchange resin. The removal of the acids was followed by monitoring the fluorescence of the eluent with a UV lamp. When fluorescence was no longer observed, elution was terminated. The solvent was removed from a sample by heating at ca. 50° C under a stream of dry N_2. Solvent removal was completed by repetitive weighing and reheating at 50° C under N_2

for 30 minute intervals until the weight decrease between consecutive weighings was 0.5%. Another technique was used to remove any strong acids that remained on the first column of ion-exchange resin. The ion-exchange resin was removed from the column and discharged using aqueous 6N HCl solution. The resin was then washed with deionized water until the washings were neutral. The discharged resin was then loaded into a jacketed soxhlet extractor and extracted with a benzene/methanol azeotropic mixture until the eluent no longer fluoresced. The bulk of the solvent was removed by distillation. Benzene was then added and the resulting solution dried using $MgSO_4$, and filtered. The benzene was removed by the same technique previously described.

Separation of Asphaltene Bases. The chromatographic column used was identical to the column used in the separation of the oils. Amberlyst 15 cation-exchange resin was activated as previously described (see Separation of Oil Bases).

The chromatographic column in Figure 15 was filled with benzene. A slurry of cation-exchange resin in benzene was then added to the column. A vibrator was used to settle and pack the resin. The resin was then extracted with recycled benzene under an argon atmosphere for 10 hours.

The asphaltenes minus the acidic compondents (obtained from the previous separation) were introduced onto the ion-exchange resin as previously described. The elution of non-basic material was identical to that described in the procedure for elution of the non-acidic components.

The bases were removed by discharging the resin with 500 ml of an 8% by volume isopropylamine in methanol solution. The exothermicity from discharging the ion-exchange resin required decreased flow of the isopropylamine methanol solution and increased water flow through the chromatographic column. After the ion-exchange resin was discharged, a flask containing methanol and benzene was fitted to the bottom of the column. The benzene/methanol azeotrope was then eluted through the discharged resin. The fluorescence of the eluent was followed using a UV lamp. When fluorescence was no longer visible, elution was terminated. The bulk of the solvent was removed using a roto-evaporator. The two samples were then brought to constant weight as previously described.

Separation of Asphaltene Aromatic Neutrals. A sample of the asphaltene neutrals (asphaltenes minus the acids and bases) was contacted with pentane and centrifuged. The residue was then isolated, contacted with pentane, and centrifuged again. This procedure was repeated until the pentane washes were clear. The pentane washes were then combined, the solvent removed with a roto-evaporator, and the sample brought to a constant weight.

The pentane soluble "asphaltene" neutrals were then separated into saturate and aromatic concentrates as follows. The same column used in the separation of the oil neutrals was packed with ca. 200 grams of activated silica gel. A sample of the asphaltene neutrals was dissolved in a 25 ml of pentane and charged to the silica gel. The procedure for following the elution of the saturates and aromatics and collecting the concentrates is identical to that described in the separation of the oil neutrals.

Infrared Spectroscopy Experimental

Instrumental

All IR spectra were recorded on a grating instrument (Beckman IR 7) covering the spectral range from 600-4000 cm^{-1} at room temperature. All solution spectra were obtained using 0.5 mm matched compensating cells. Matrix-isolation spectra were obtained using KBr windows.

Sample Preparation

The solvent used for the solution spectra of both the oil and asphaltene neutrals was CCl_4. Other spectra were obtained using $CDCl_3$ as the solvent. The KBr spectrum of asphaltene fraction B was acquired using a 2 mg sample mixed with powdered KBr and pressed into a clear pellet of 1.3 cm diameter.

The technique of matrix-isolation involved sample deposition in a N_2 matrix (33). The length of time required for sample deposition ranged from 1 to 3½ hours.

Mass Spectrometry Experimental

Instrumental

All field-ionization and 70-eV high-resolution electron impact mass spectra were obtained on a CEC 21-110B double-focusing mass spectrometer equipped with a modified combination FI/EI ion source and standard electron-impact ion source, respectively (17). Field-ionization emitters were cut from uncoated stainless-steel razor blades and conditioned in the ion source in the presence of acetone. Field-ionization spectra were obtained with an emitter potential of 5.8 LV and a counter-electrode potential of +800 to -800 V.

High-resolution 70-eV EI mass spectra were recorded on Ilford Q2 photographic plates. Perfluorokerosene was used as the internal standard. Line positions recorded on the photographic plates were read with a Grant Instruments Comparitor-Densitometer.

Low-resolution FI spectra were acquired using an AEI DS-50S data acquisition system interfaced to the CEC 21-110B. High-resolution FI spectra were acquired using an oscillographic recorder. Samples were introduced into the ion source via an all-glass inlet system. An all-glass sample cup was added to the inlet system to allow for vaporization of samples at high temperatures (34). The inlet temperature and the source temperature were kept at ca. 320° C.

Sample Preparation

A small amount of sample was placed in a weighted sample vial. The weight of the sample was obtained and the sample introduced in the mass spectrometer. After the mass spectrum had been recorded, the sample vial was removed and allowed to cool in a desiccator. The sample vial was then weighed to obtain the amount of the sample that volatilized in the inlet system of the mass spectrometer.

LITERATURE CITED

(1) S. Weller, M. G. Pelipetz, and S. Friedman, Ind. Engng. Chem., **43**, 1572 (1951).

(2) B. J. Liebenberg and H. C. J. Potgleter, Fuel, **52**, 130 (1973).

(3) R. Yoshida, Y. Maekawa, T. Ishii, and G. Takeya, Fuel, **55**, 337 (1976).

(4) I. Schwager and T. F. Yen, Am. Chem. Soc., Div. Fuel Chem. Prepr., **21**, 199 (1976).

(5) F. K. Schweighardt and A. G. Sharkey, "Coal Chemistry Workshop - Preprints", Paper No. 6, Stanford Research Institute, Stanford, 1976.

(6) T. Aczel, R. B. Williams, R. J. Pancirov, and J. H. Karchmer, "Chemical Properties of Synthoil Products and Feeds", Report prepared for U.S. Energy Research and Development Administration, FE 8007, 1977.

(7) R. Yoshida, Y. Maekawa, T. Ishii, and G. Takeya, Fuel, **55**, 341 (1976).

(8) H. W. Sternberg, R. Raymond, and F. K. Schweighardt, Science, **188**, 49 (1975).

(9) I. Schwager, W. C. Lee, and T. F. Yen, Anal. Chem., **49**, 2363 (1977).

(10) I. Schwager, P. A. Formanian, and T. F. Yen, Am. Chem. Soc., Div. Pet. Chem., Prepr., **22**, 677 (1977).

(11) B. C. Bockrath, C. L. Delle Donne, and F. K. Schweighardt, Fuel, **57**, 4 (1978).

(12) A. Marzec, D. Bodzek, and T. Krzyzanowska, ACS Symp. Ser., Org. Chem. Coal, 71 (1978).

(13) I. Schwager and T. F. Yen, Fuel, **57**, 100 (1978).

(14) I. Schwager and T. F. Yen, Fuel, **58**, 219 (1979).

(15) R. T. Eddinger, J. F. Jones, and F. E. Blanc, Chem. Eng. Progr., **64**, 33 (1968).

(16) D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, *Anal. Chem.*, **44**, 1391 (1972).

(17) G. J. Greenwood, "Characterization of Coal-Derived Liquids Using Mass Spectrometry." Ph.D. Thesis, Oklahoma State University, 1977.

(18) J. F. McKay, T. E. Cogswell, J. H. Weber, and D. R. Latham, *Fuel*, **54**, 50 (1975).

(19) L. R. Snyder, *Anal. Chem.*, **41**, 314 (1969).

(20) J. C. Petersen, R. V. Barbour, S. M. Dorrence, F. A. Barbour, and R. V. Helm, *Anal. Chem.*, **43**, 1491 (1971).

(21) F. R. Borwn, S. Friedman, L. E. Makovsky, and F. K. Schweighardt, *Appl. Spectrosc.*, **31**, 241 (1977).

(22) E. Kendrick, *Anal. Chem.*, **35**, 2146 (1963).

(23) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, **48**, 2105 (1976).

(24) J. E. Dooley, S. E. Scheppele, and C. J. Thompson, "Characterizing Syncrudes from Coal", Analytical Methods for Coal and Coal Products, Ed. C. Karr, Jr., Academic Press, 1978, Chapter 32.

(25) H. E. Lumpkin and T. Aczel, *Anal. Chem.*, **36**, 181 (1964).

(26) J. L. Shultz, R. A. Friedel, and A. G. Sharkey, Jr., "Mass Spectrometric Analysis of Coal-Tar Distillates and Residues", Washington, U.S. Department of Interior, Bureau of Mines, RI 7000 (1967).

(27) L. R. Snyder and B. E. Buell, *Anal. Chem.*, **40**, 1295 (1968).

(28) M. Farcasiu, *Fuel*, **56**, 9 (1977).

(29) M. Farcasiu, *Fuel*, **57**, 576 (1978).

(30) R. G. Ruberto, D. M. Jewell, and D. C. Cronauer, *Fuel*, **57**, 575 (1978).

(31) R. C. Neavel, *Fuel*, **55**, 237 (1976).

(32) R. G. Ruberto and D. C. Cronauer, *Fuel Processing Techn.*, **2**, 215 (1979).

(33) G. Ritzhaupt and J. P. Devlin, *J. Phys. Chem.*, **81**, 521 (1977).

(34) C. Stafford, T. D. Morgan, and R. J. Brunfeldt, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 87 (1968).

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