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SEPARATION AND CHARACTERIZATION OF COAL DERIVED COMPONENTS

Quarterly Report for the Period July 1—September 30, 1983

By
R. J. Hurtubise
H. F. Silver

Work Performed Under Contract No. AC22-83PC60015

University of Wyoming
Laramie, Wyoming

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Separation and Characterization of Coal Derived Components

R. J. Hurtubise and H. F. Silver
University of Wyoming
Laramie, Wyoming 82071

Quarterly Report

Prepared for

Pittsburgh Energy Technology Center
Department of Energy
Pittsburgh, Pennsylvania

Abstract

The field-ionization mass spectral hydrocarbon data from F-45 (Wyodak coal-derived SRC) and F-51 (Kentucky 9/14 coal-derived SRC) were recalculated so the various hydrocarbon fractions could be compared directly on a weight percent basis. A computer program was developed which allows the field-ionization mass spectral hydrocarbon data to be compared in a three dimensional fashion. This approach provides for a rapid general comparison of all the field-ionization hydrocarbon data. The solubility of preasphaltenes was tested in several solvents. The preasphaltenes-2 were found to be largely soluble in pyridine:chloroform 9:1(v/v) or 7:3(v/v) and pyridine:chloroform:tetrahydrofuran 7:1:2(v/v/v). Experiments were carried out in which Chromasorb T was tested as a replacement for Fluoropak in the Fluoropak-basic alumina procedure. The results indicated Chromasorb T would be an adequate substitute for Fluoropak, but additional experiments will be run to confirm this. The chromatographic characteristics of numerous hydroxyl aromatics, nitrogen heterocycles, and aromatic amines were obtained on several normal-phase and reversed-phase high-performance liquid chromatographic systems.

Table of Contents

Abstract

A. Comparison of Field-Ionization Mass Spectrometry (FIMS) Hydrocarbon Results from F-45 (Wyodak Coal-Derived SRC) and F-51 (Kentucky 9/14 Coal-Derived SRC)

In the previous quarterly report, field ionization mass spectra from F-51 and F-45 were presented for preasphaltene and hydrocarbon fractions. The FIMS results of the hydrocarbon fractions were discussed in detail. However, as explained in the previous quarterly report, the FIMS data for the hydrocarbon fractions from F-45 and F-51 could not be compared on a direct wt% basis because the wt% values were different for a given pair of hydrocarbon fractions. The results reported earlier for the hydrocarbons were compared on a mole % basis. However, the FIMS data from SRI International could be recalculated so a direct comparison could be made between spectra on a wt% basis. This conclusion was reached after discussions with Dr. Buttrill of SRI International and Dr. Scheppele of Bartlesville Energy Technology Center. All of the FIMS hydrocarbon results reported in the previous quarterly report were recalculated and reevaluated so comparisons between hydrocarbon fractions from F-45 and F-51 could be compared on a wt% basis. The remainder of this section discusses the calculations used in the conversion of mole % data to wt% data, and the results analyzed for the hydrocarbons in F-51 and F-45.

It has been reported by Yoshida et al. (1) that the actual weights of components in a fraction analyzed by FIMS can be calculated by Equation 1.

$$m_i(\text{actual}) = W \times (M_i I_i) / \Sigma_i M_i I_i \qquad (1)$$

where m_i(actual) = actual weight of component i

W = weight of fraction

M_i = mass of i

I_i = intensity of a mass spectral peak

Equation (1) can be modified to give Equation 2, which gives $wt\%_i$.

$$wt\%_i = (wt\%_{total})(M_iI_i/\Sigma_iM_iI_i) \tag{2}$$

where $wt\%_i$ is the weight percent of an individual hydrocarbon and $wt\%_{total}$ is the weight percent of the entire hydrocarbon fraction

The number average molecular weight (MW_n) is defined by Equation 3.

$$MW_n = {}_iM_iI_i/\Sigma_iI_i \tag{3}$$

Values for MW_n and Σ_iI_i are supplied with the data from SRI International; thus $\Sigma_iM_iI_i$ can be found from Equation 3. Also, as reported by SRI International,

Equation 4 is valid.

$$RI_i = (I_i)(10{,}000)/\Sigma_iI_i \tag{4}$$

where RI_i = relative intensity of a mass spectral peak

Equation 2, 3, and 4 can be combined to give Equation 5.

$$wt\%_i = (wt\%_{total})(M_i \times RI_i/10{,}000 \times MW_n) \tag{5}$$

Because some of the hydrocarbon fractions run by FIMS were not completely volatile, it was necessary to correct the wt% values in Equation 5. Thus, the equation used to calculate wt% of the individual hydrocarbons in F-45 and F-51 is given by Equation 6.

$$wt\%_i = (wt\%_{total})(\text{fractional volatility})(M_i \times RI_i/10{,}000 \times MW_n) \tag{6}$$

A computer program based on the above equations and used in processing the FIMS data was written by Mr. Todd Allen of our research group. Using the new computer program, the mole % data for the hydrocarbon fractions from F-45 and F-51 were converted to wt% values. Sixteen tables of computer data were obtained; however, this data is not presented in the report.

Table 1 summarizes the wt% values obtained for the hydrocarbons from F-45 and F-51 and also relates the wt% values to the various Z series. The general formula that defines the Z term is given by C_nH_{2n+Z}. These data are compared more readily in graphical form, as in Figures 1-9. In Figures 10-18, plots of wt% versus mass are presented for the various Z series in the saturate and double bond fractions from F-45 and F-51. As explained in the previous quarterly report, the conclusions for the data in that report were tentative because the wt% values for a given pair of fractions were not the same. The data for F-45 and F-51 in Table 1 and Figures 1-18 can be compared directly because all the results are based on wt%. Specifically the wt% is based on the weight of the particular SRC sample. Below are some of the conclusions which can be made from the information in Table 1 and Figures 1-18. These conclusions are more reliable than the conclusions reached in the last quarterly report because comparisons were made directly between F-45 and F-51 fractions on the basis of wt%.

Saturates (Figures 1 and 10)

a) The Wyodak SRC sample contains 3.1 times more saturates that the Kentucky sample.

b) The Wyodak SRC sample has more material in every Z series compared to the Kentucky sample (Figure 1).

c) In the +2, 0, and -2 Z series, the maxima are shifted to higher molecular weights in the Kentucky SRC sample (Figure 10).

Table 1. Wt% of Various Z Series in Hydrocarbon Fractions from F-45 and F-51

Wt % in SRC

	saturates		3d.b.		5d.b.		6d.b.		7d.b.		8d.b.		9d.b.		10-11 d.b.		12+ d.b.	
Z	W	K	W	K	W	K	W	K	W	K	W	K	W	K	W	K	W	K
+2	.047	.027																
0	.043	.023																
-2	.039	.016																
-4	.042	.013																
-6	.051	.018	.015	.022														
-8	.067	.019	.027	.032														
-10	.057	.011	.023	.028														
-12			.018	.031	.087	.045	.015	.039										
-14			.015	.030	.19	.14	.039	.045										
-16			.009	.020	.13	.15	.069	.087	.050	.051								
-18			.008	.014	.073	.087	.048	.098	.12	.29								
-20					.046	.052	.043	.087	.33	.38	.089	.089						
-22					.031	.034	.032	.067	.38	.29	.51	.40	.058	.069				
-24					.022	.024	.019	.050	.21	.17	.31	.32	.20	.13				
-26									.12	.11	.21	.22	.21	.16	.15	.084		
-28									.070	.065	.12	.12	.18	.17	.37	.15		
-30											.073	.077	.14	.14	.38	.18		
-32											.059	.068	.092	.098	.41	.18	.26	.19
-34													.059	.073	.31	.15	.31	.22
-36															.24	.11	.32	.23
-38															.16	.084	.34	.22
-40																	.30	.20
-42																	.28	.20
-44																	.24	.18

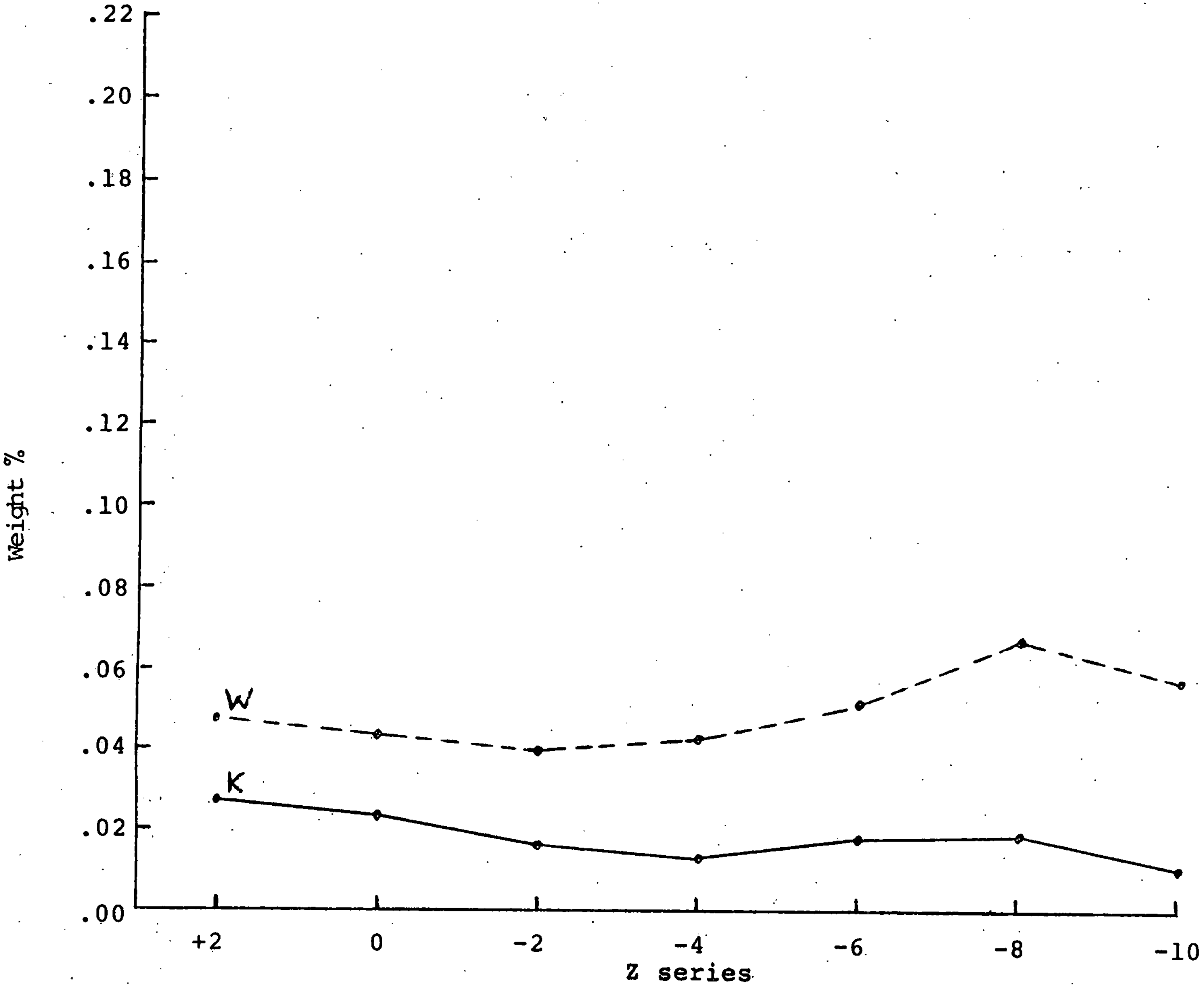


Figure 1. Wt% in SRC vs. Z series for saturates isolated from Wyodak and Kentucky SRC.

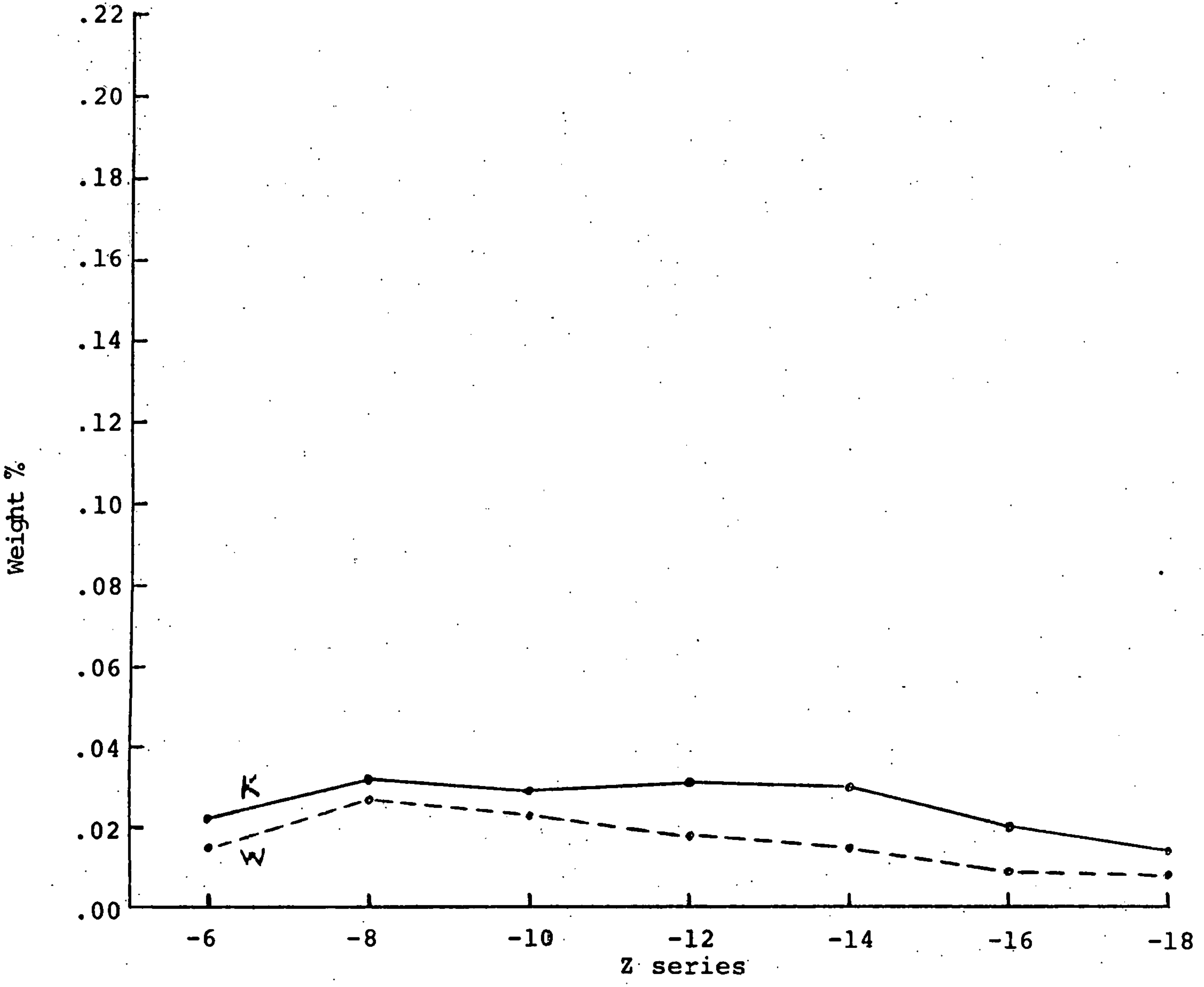


Figure 2. Wt% in SRC vs. Z series for three double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

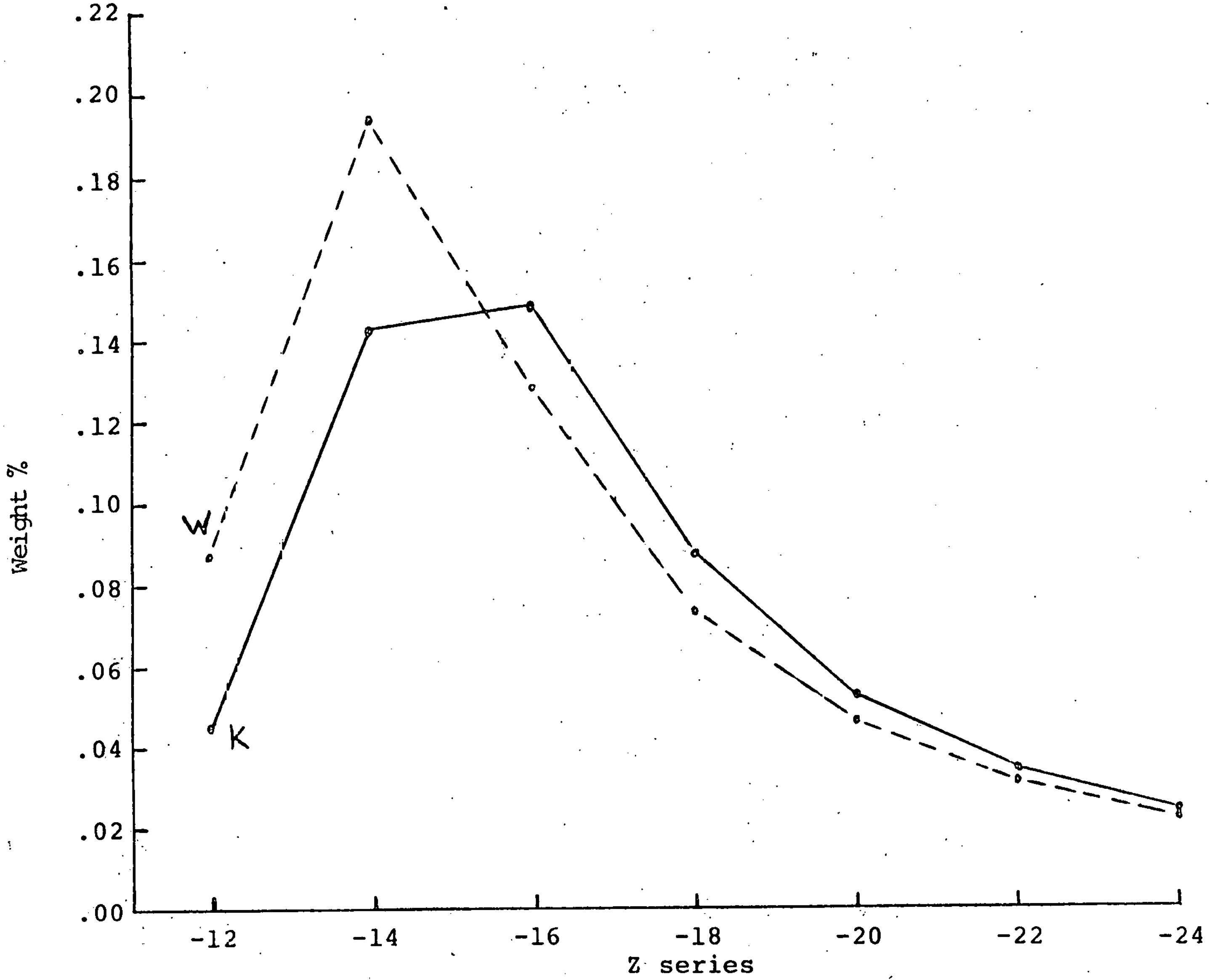


Figure 3. Wt% in SRC vs. Z series for five double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

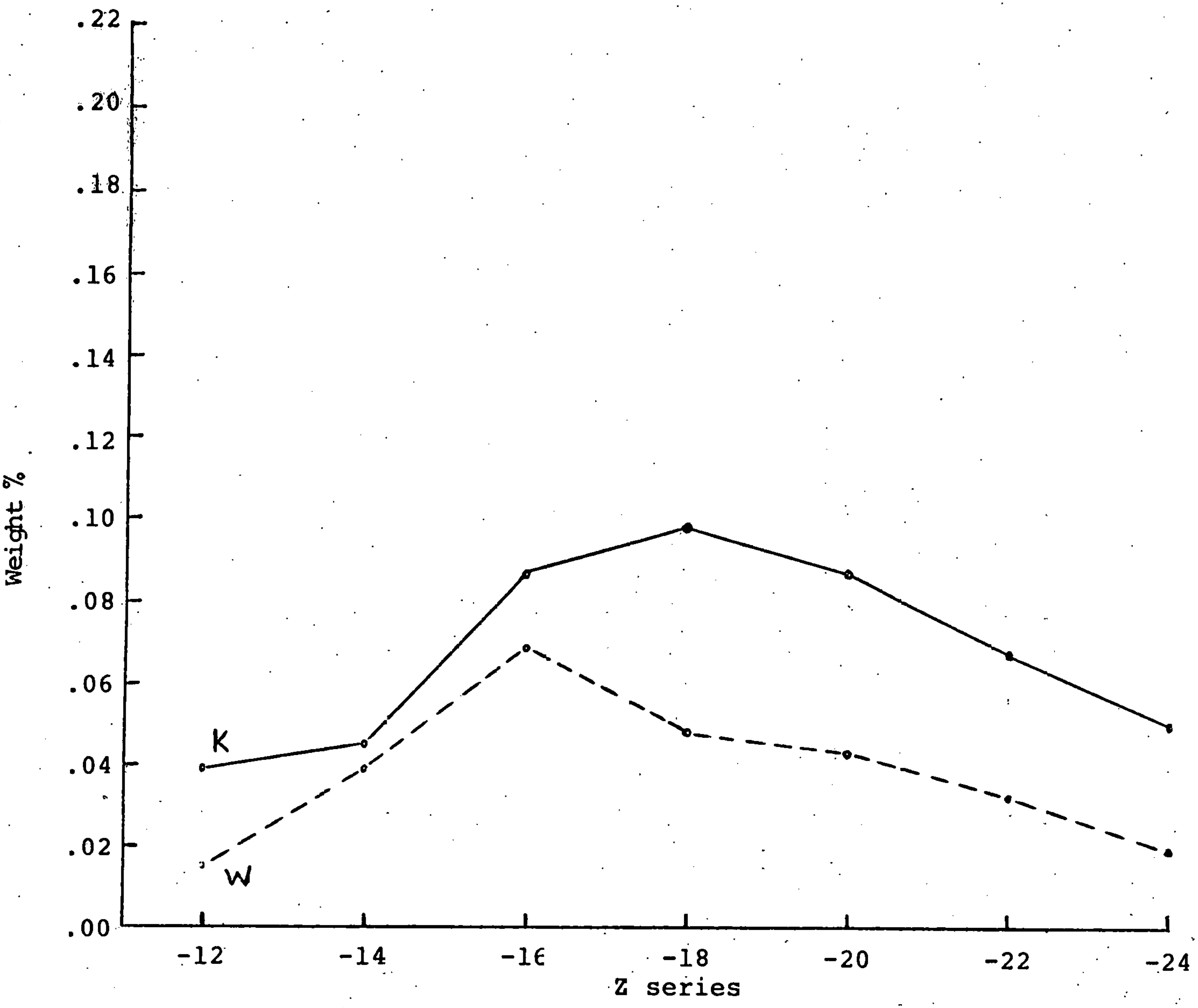


Figure 4. Wt% in SRC vs. Z series for six double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

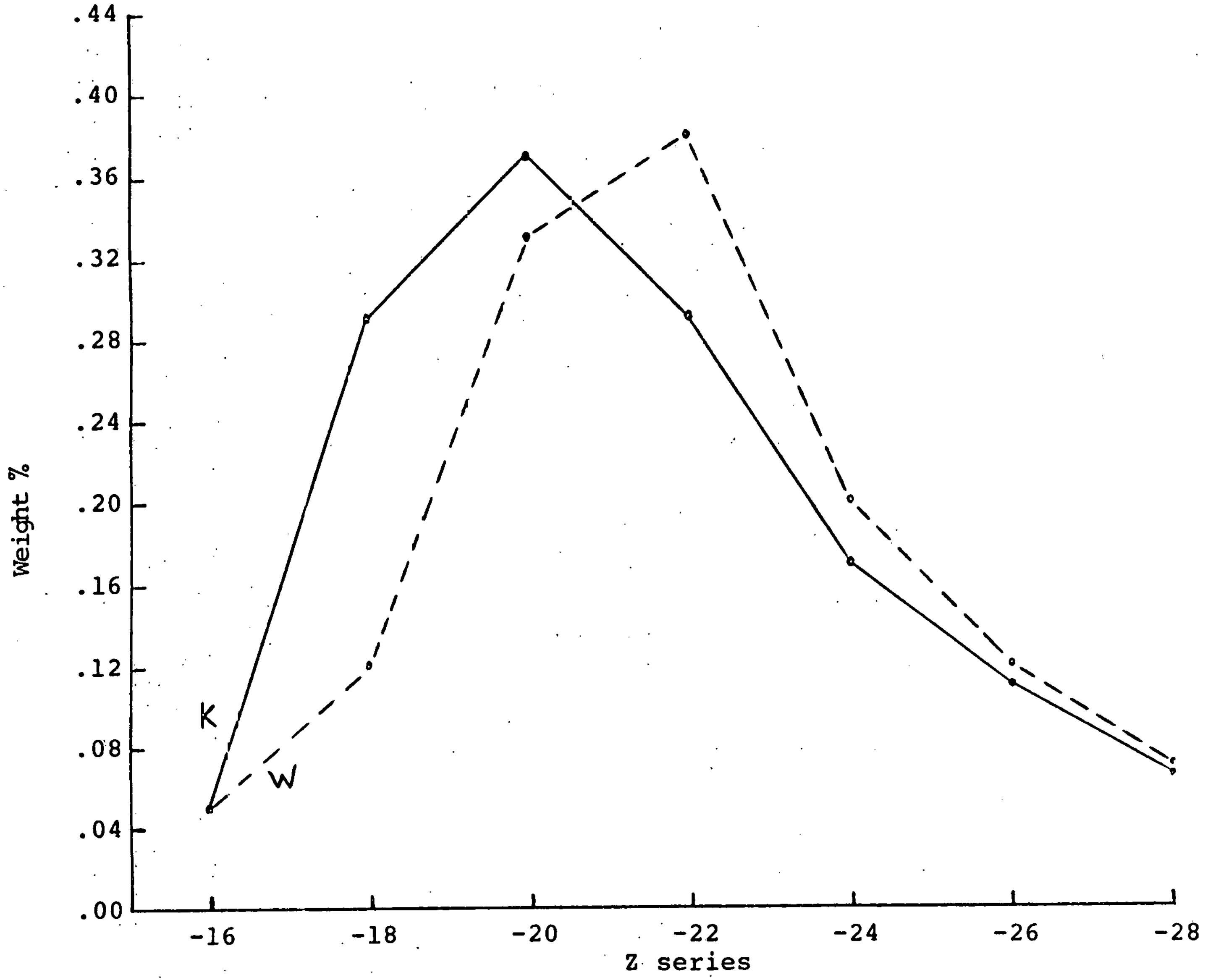


Figure 5. Wt% in SRC vs. Z series for seven double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

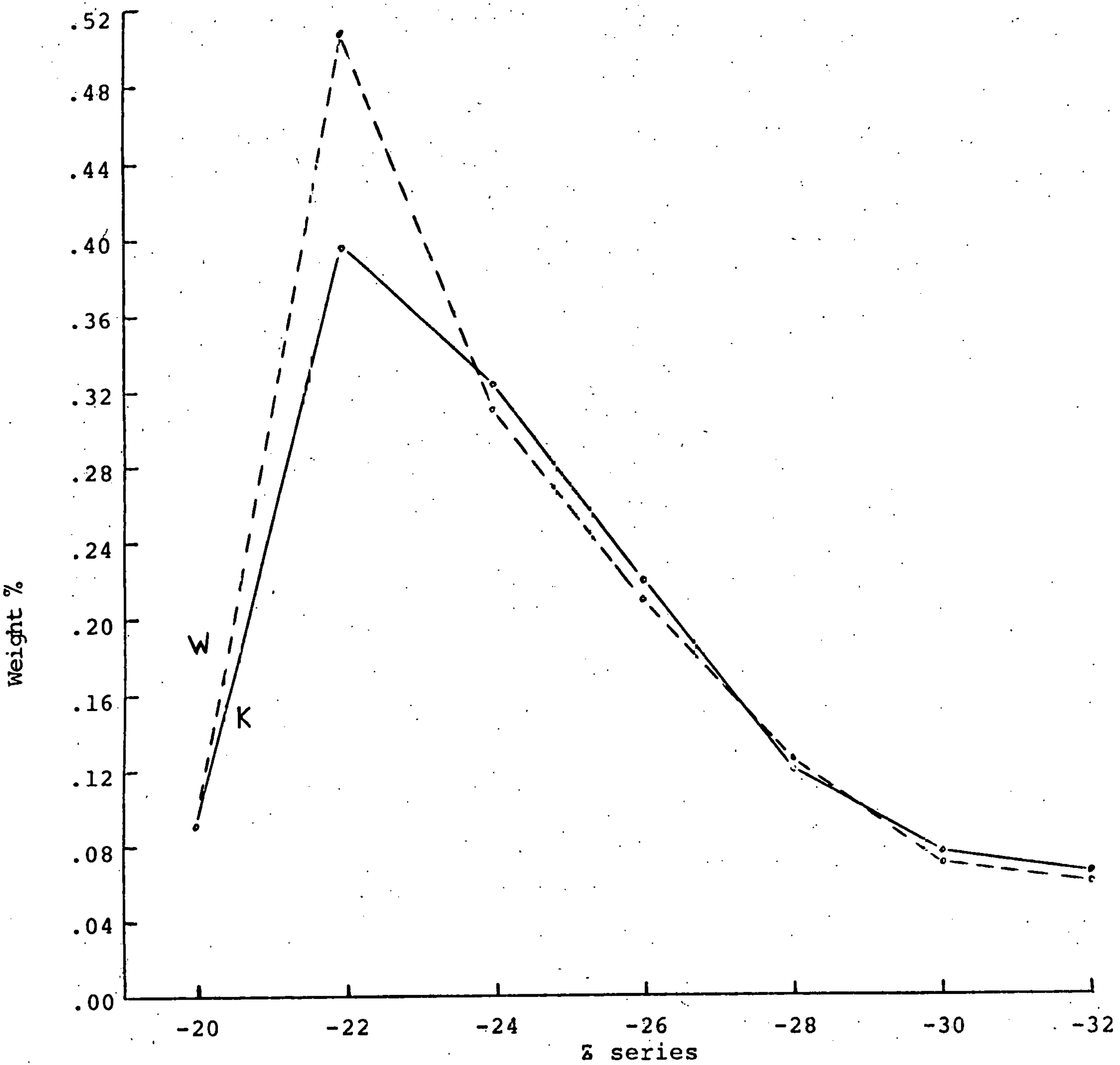


Figure 6. Wt% in SRC vs. Z series for eight double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

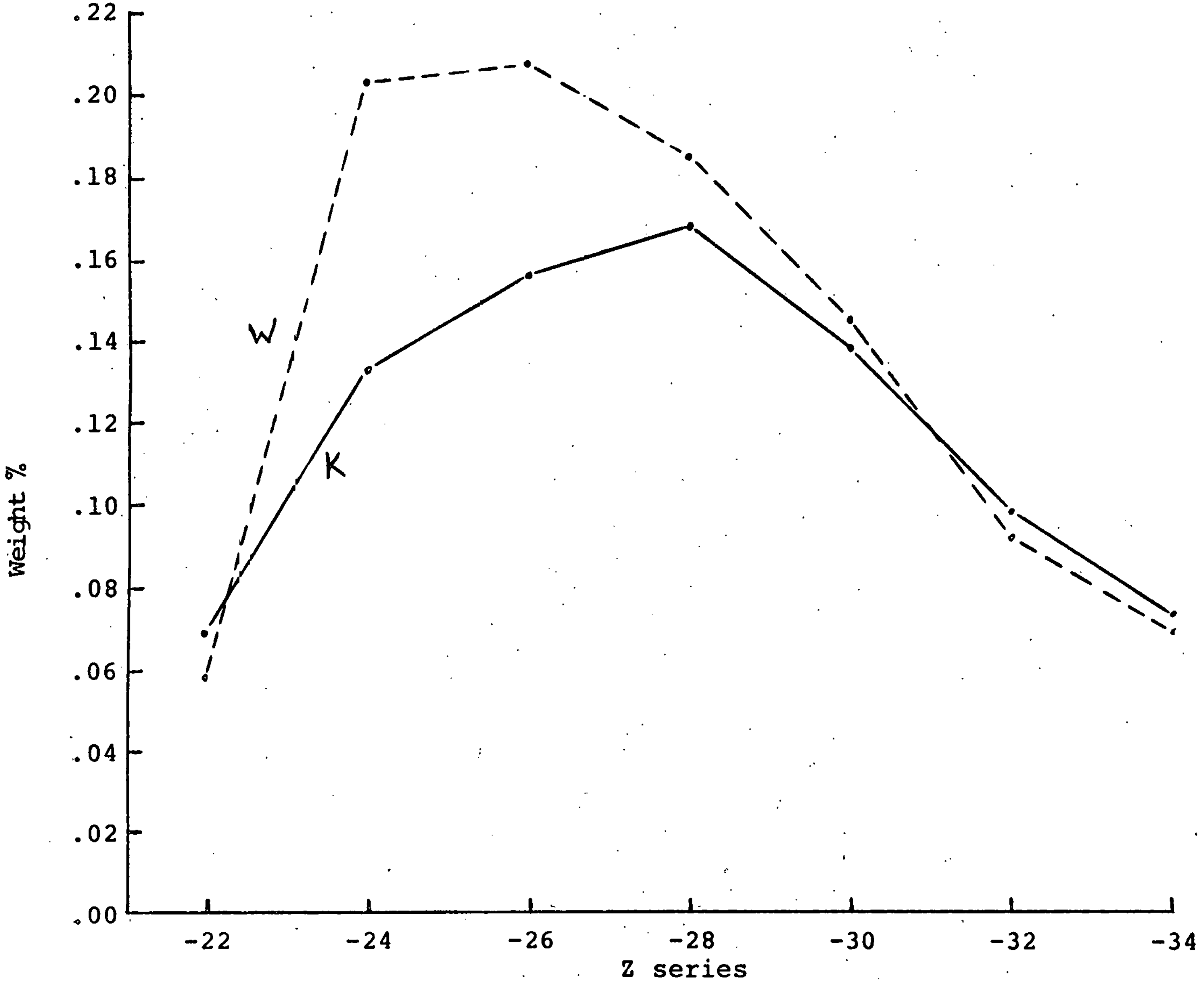


Figure 7. Wt% in SRC vs. Z series for nine double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

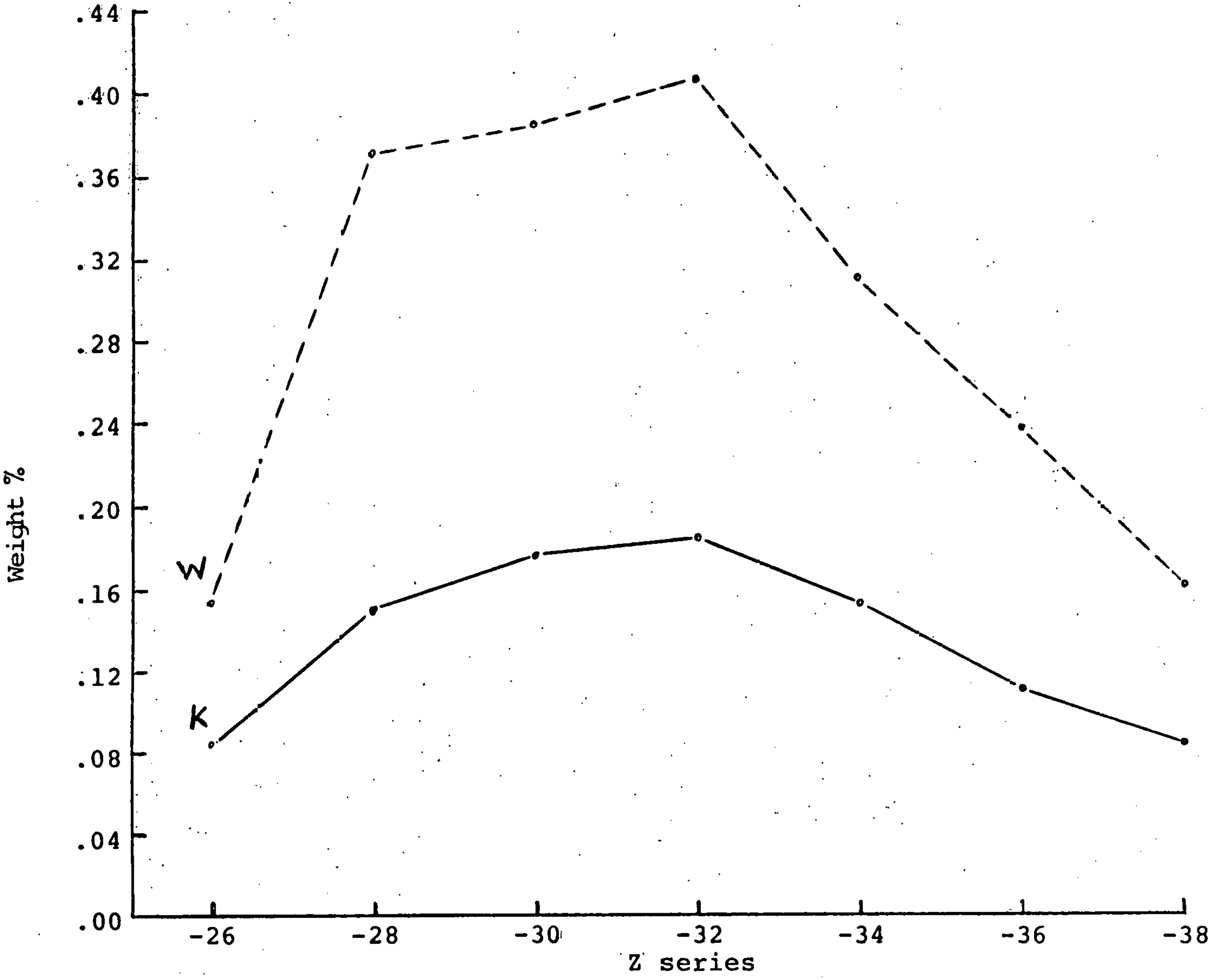


Figure 8. Wt% in SRC vs. Z series for ten and eleven double bond hydrocarbons isolated from Wyodak and Kentucky SRC.

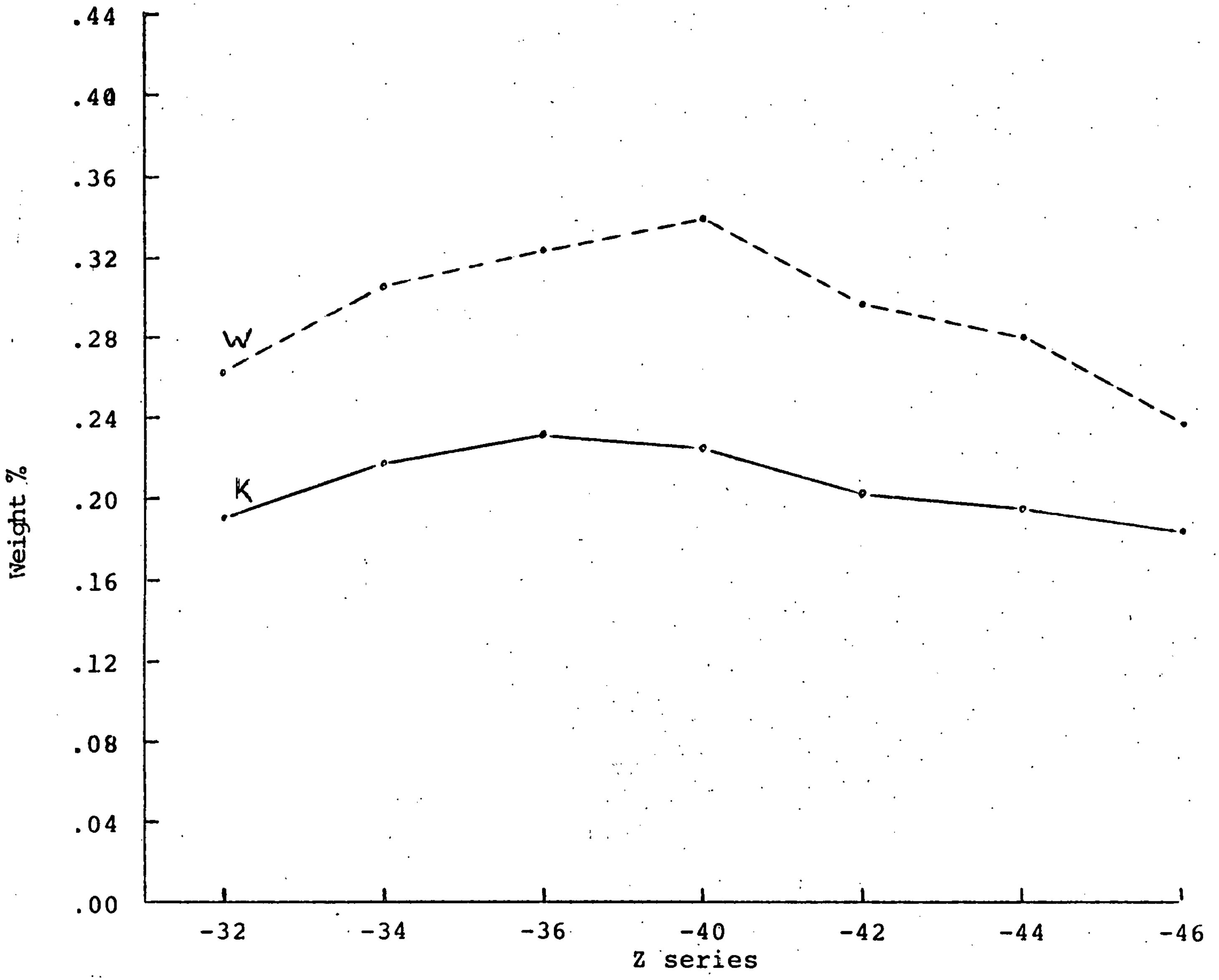
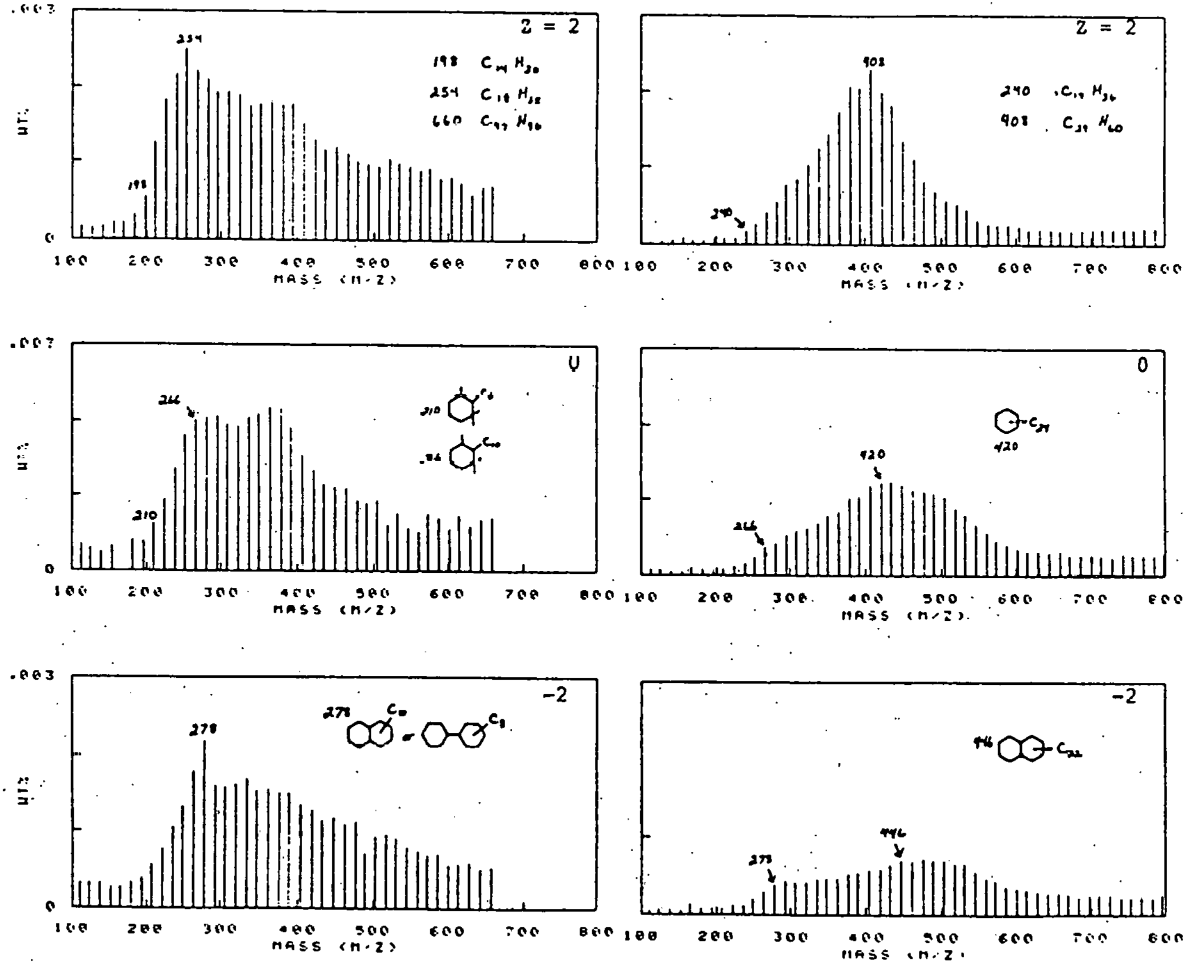


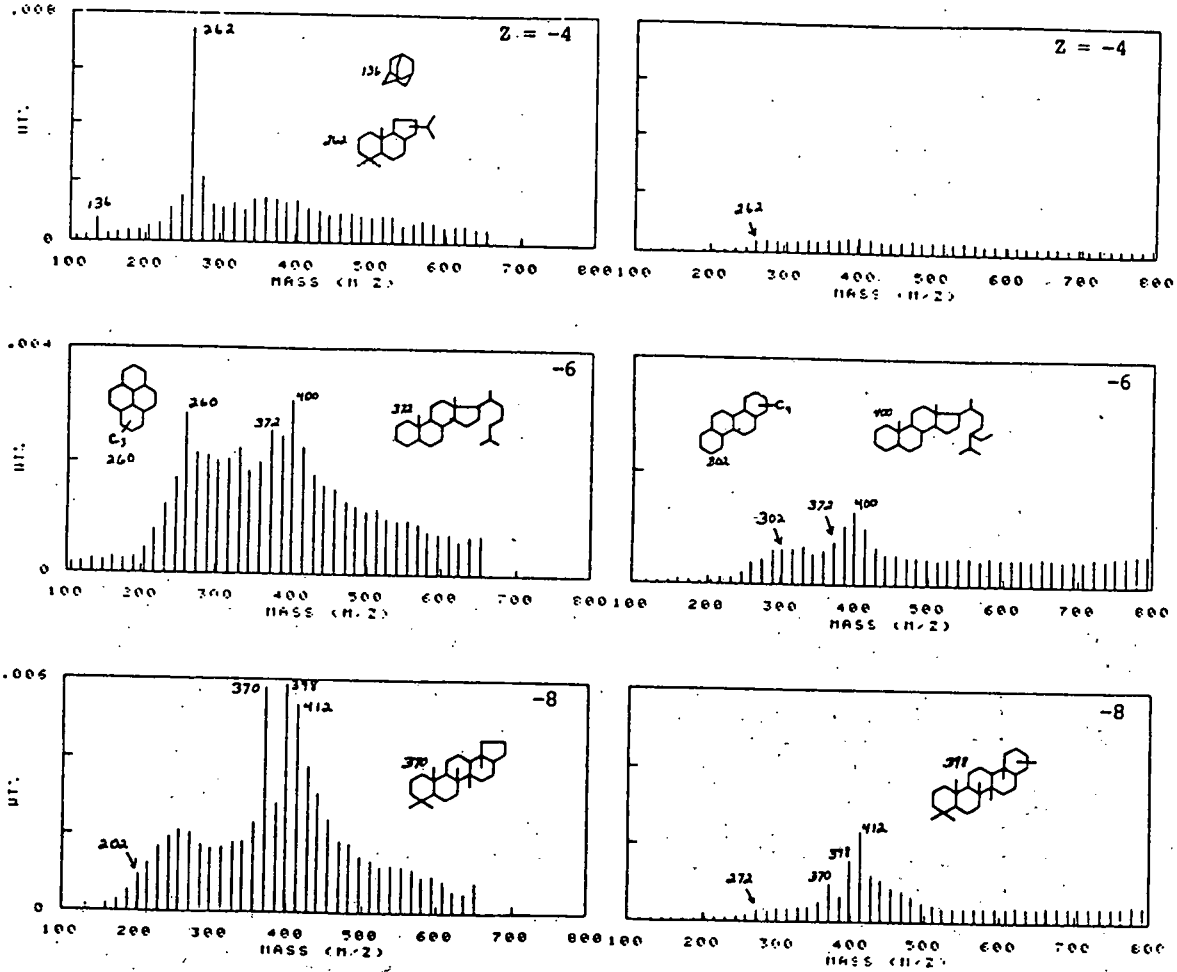
Figure 9. Wt% in SRC vs. Z series for twelve and greater double bond hydrocarbons isolated from Wyodak and Kentucky SRC.



Wyodak

Kentucky

Figure 10. Partial FI mass spectra of the saturates fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

Kentucky

Figure 10. (continued)

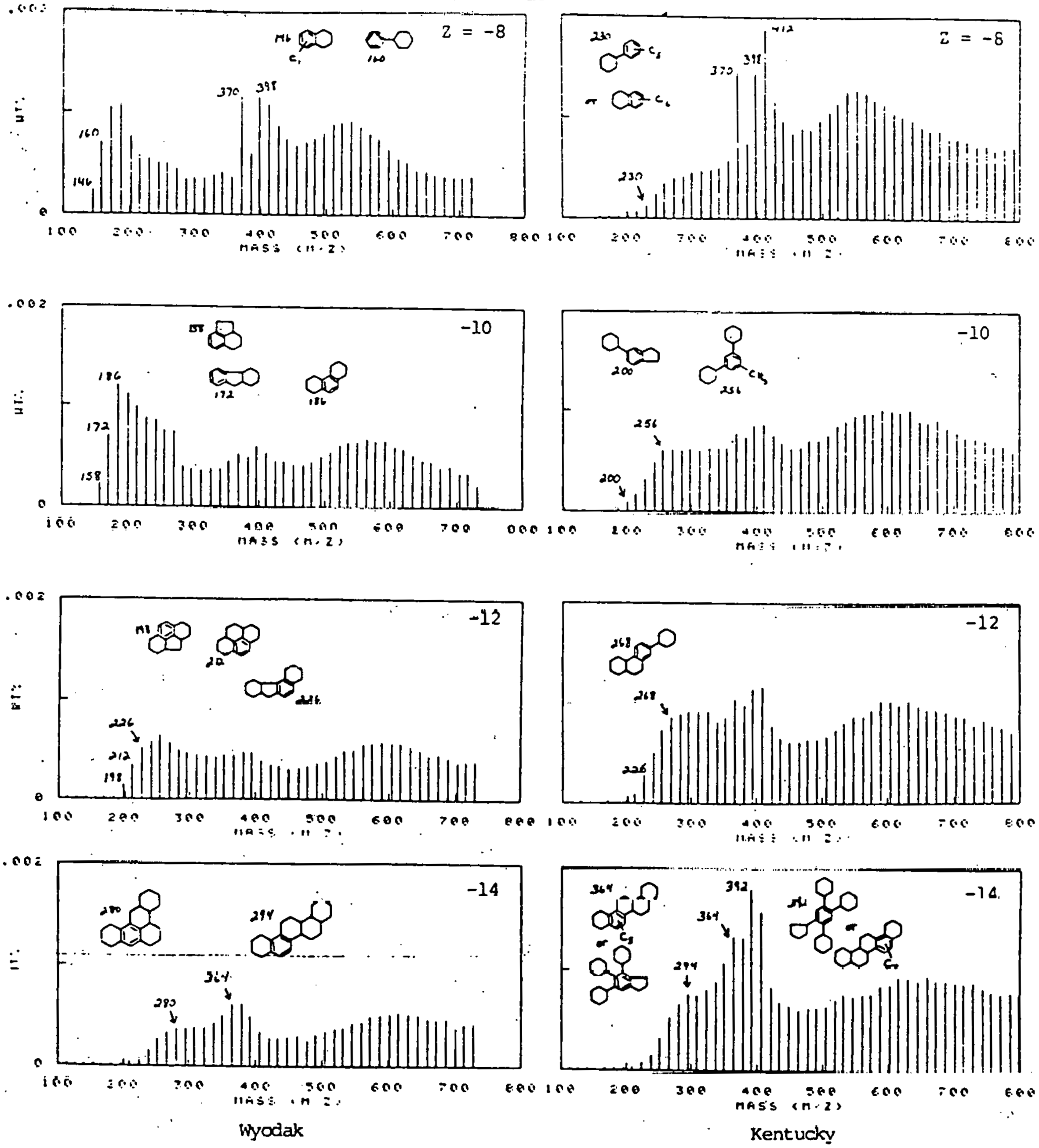
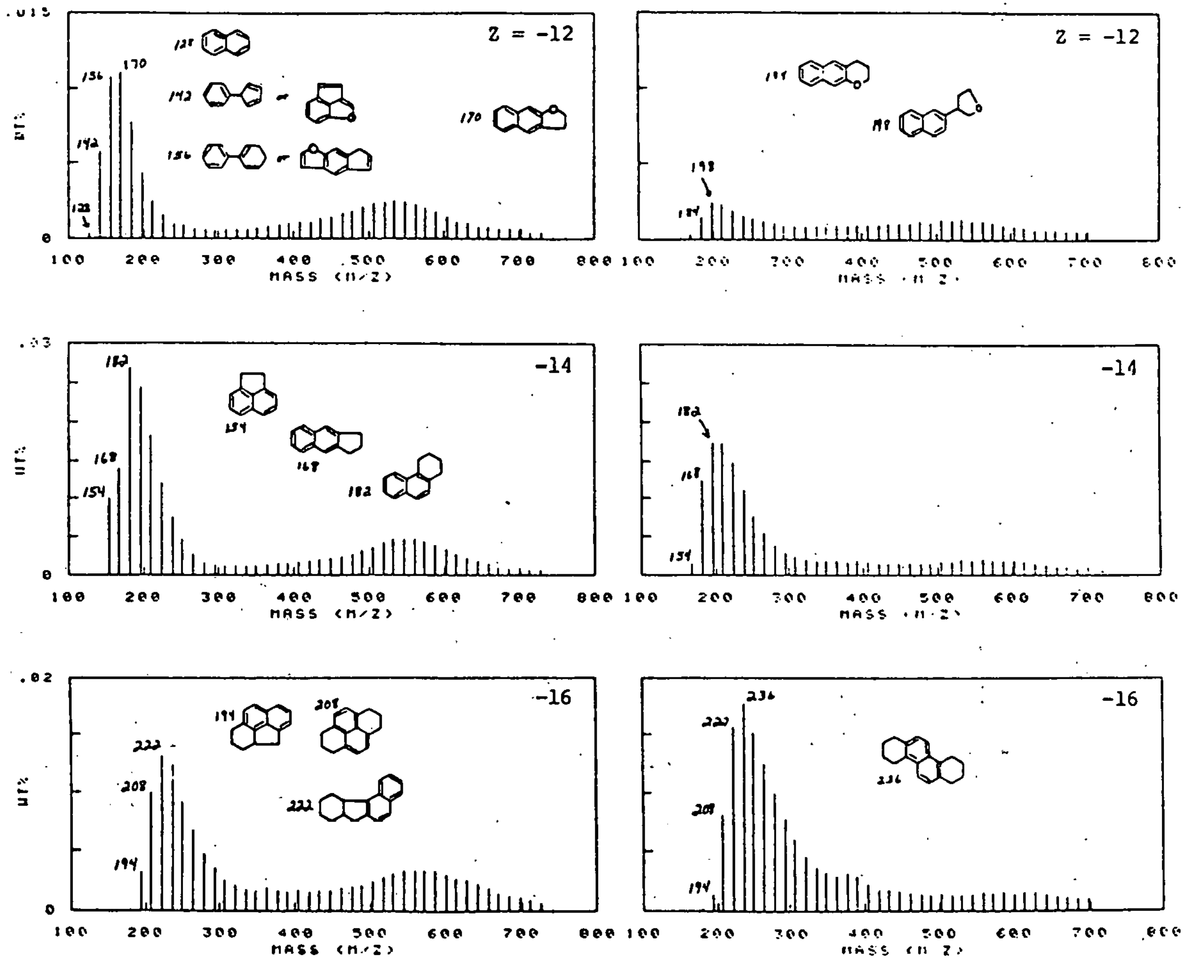
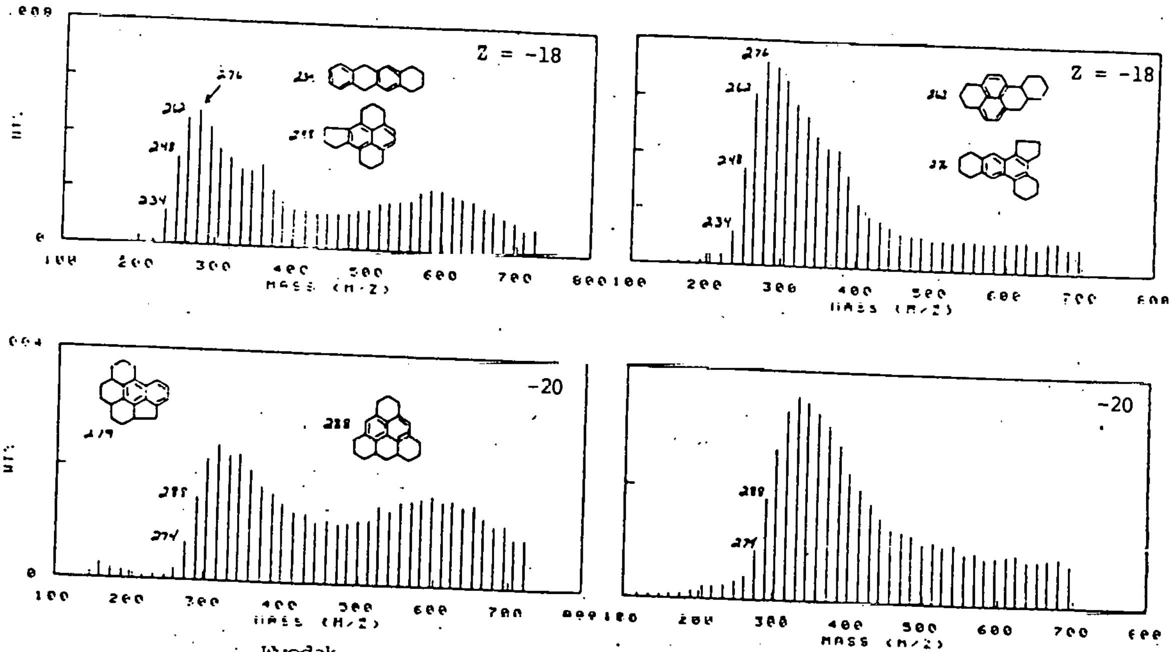


Figure 11. Partial FI mass spectra of the three double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak Kentucky

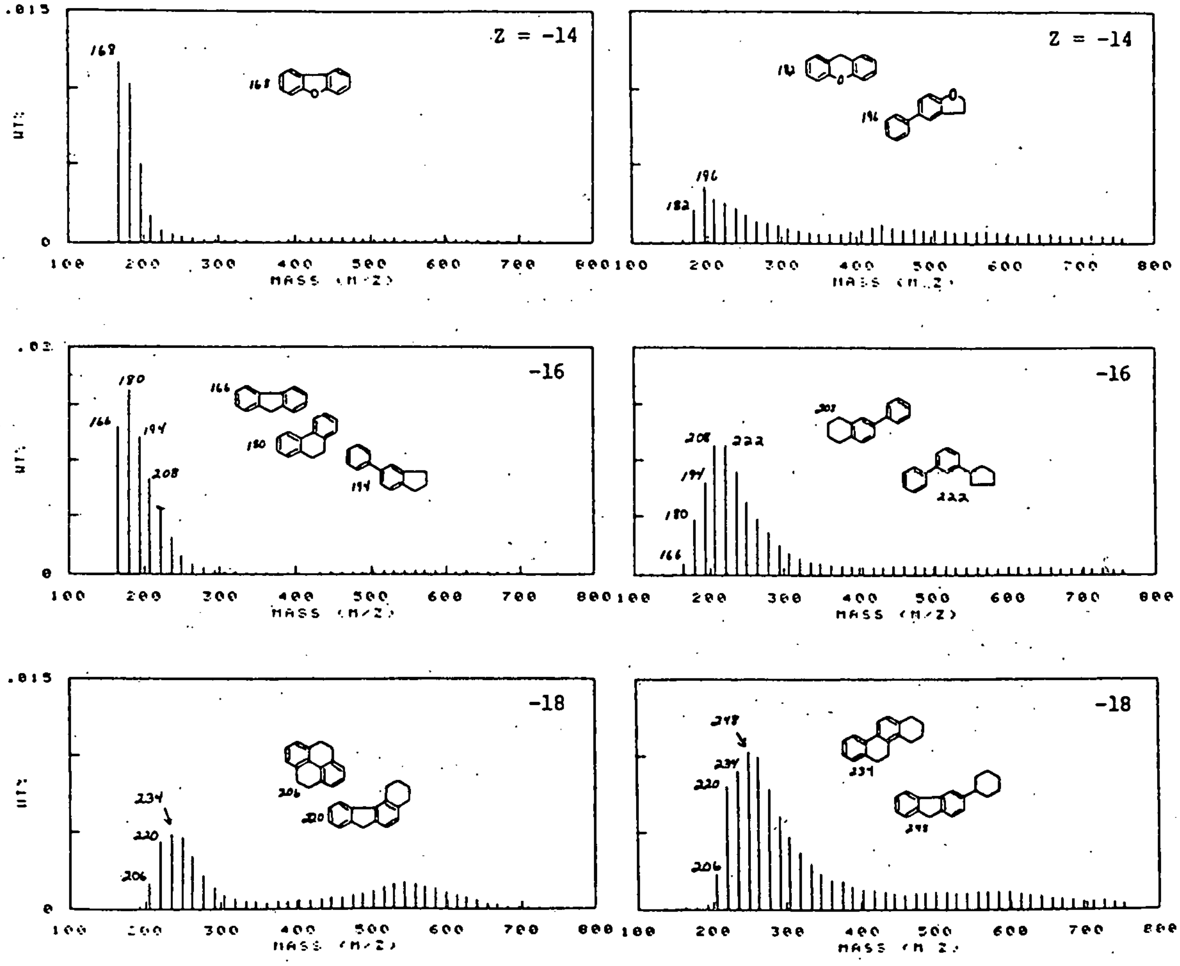
Figure 12. Partial FI mass spectra of the five double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

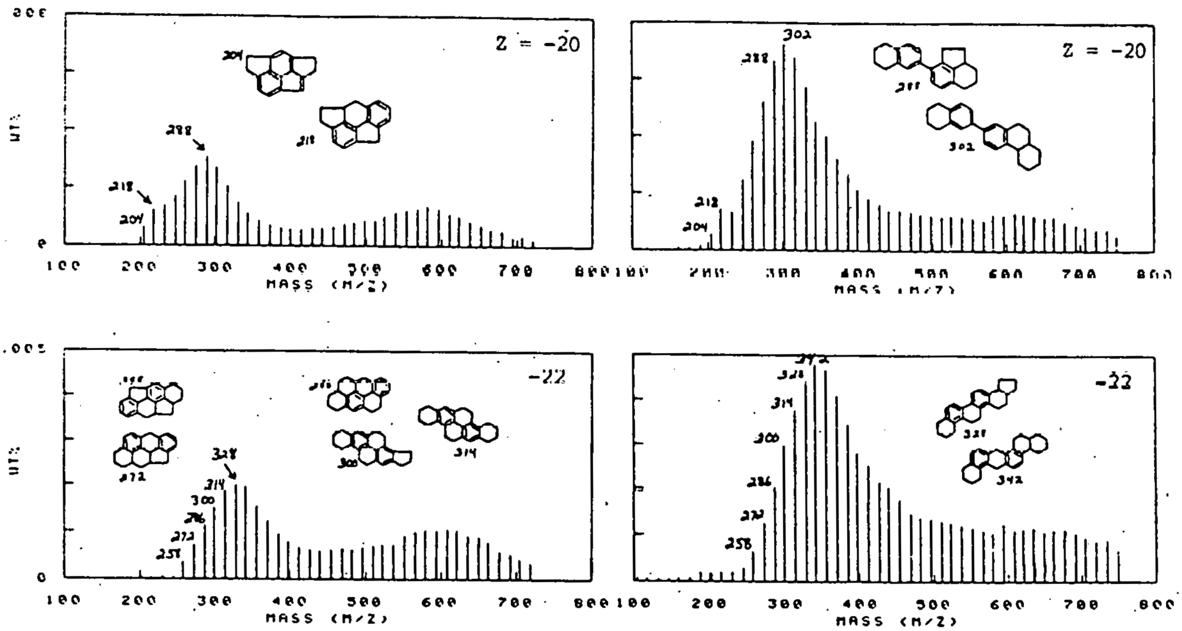
Kentucky

Figure 12. (continued)



Wyodak Kentucky

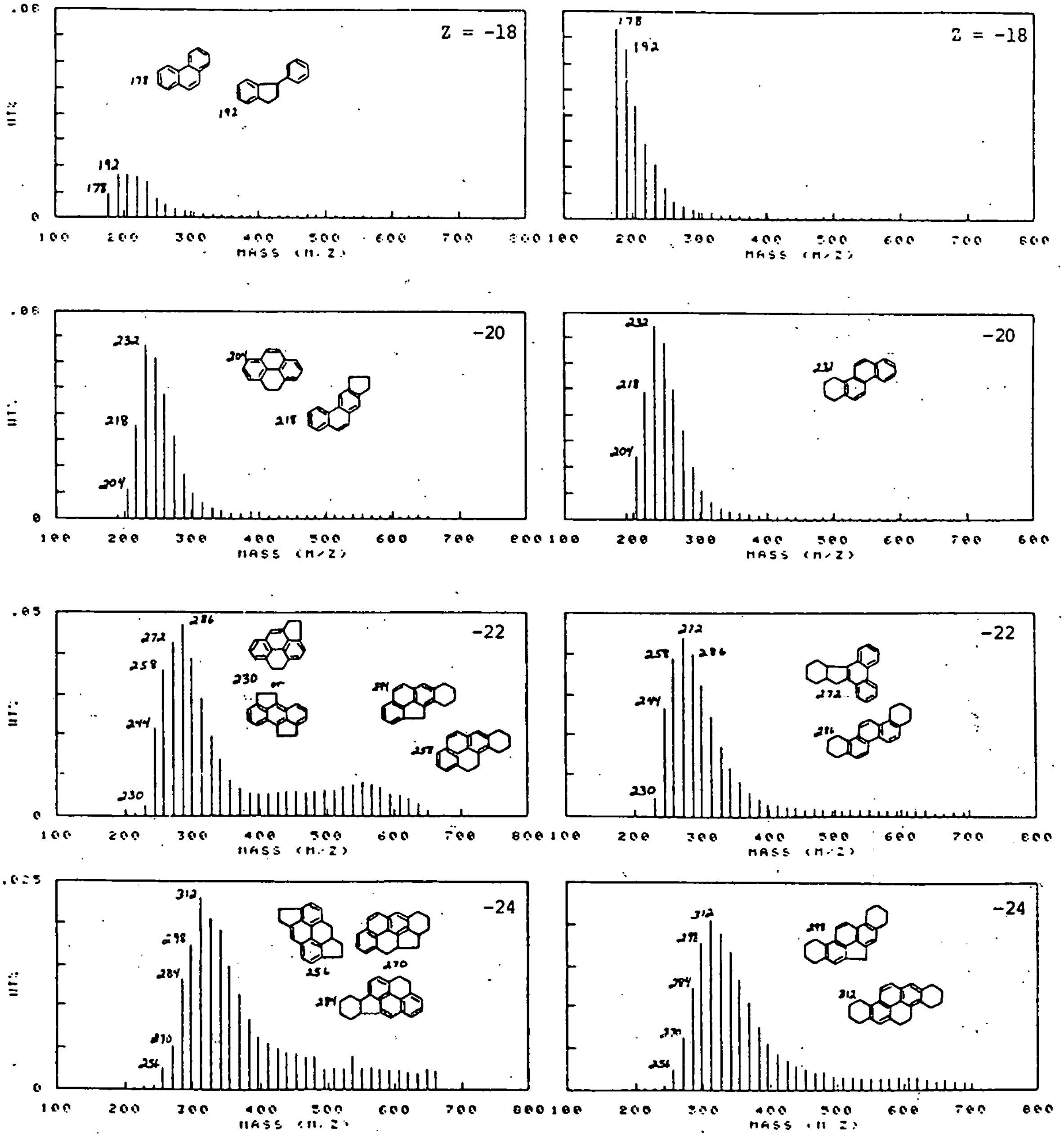
Figure 13. Partial FI mass spectra of the six double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

Kentucky

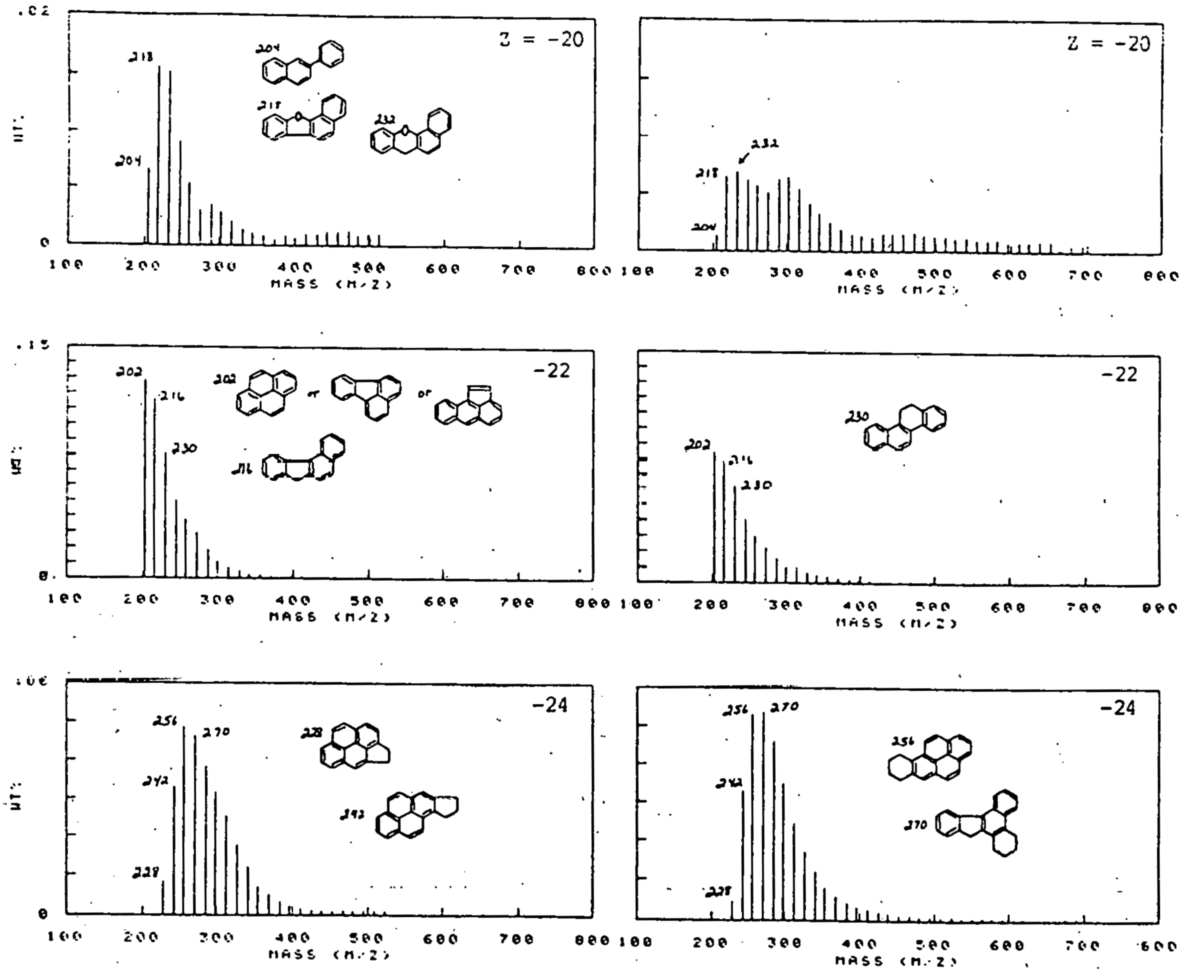
Figure 13. (continued)



Wyodak

Kentucky

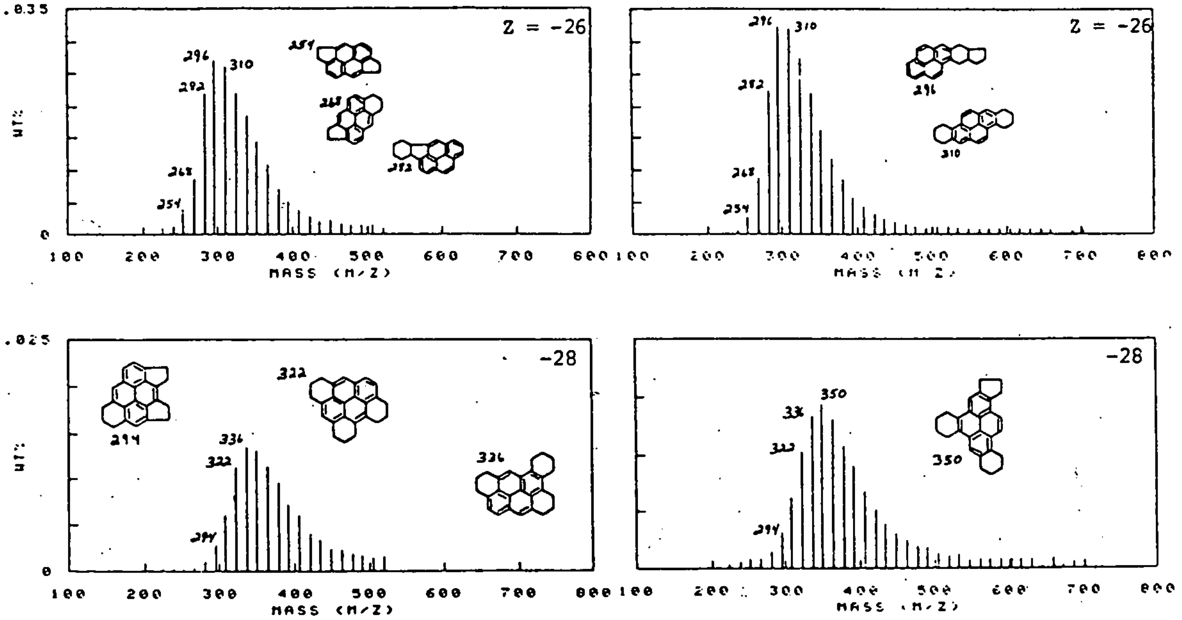
Figure 14.- Partial FI mass spectra of the seven double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

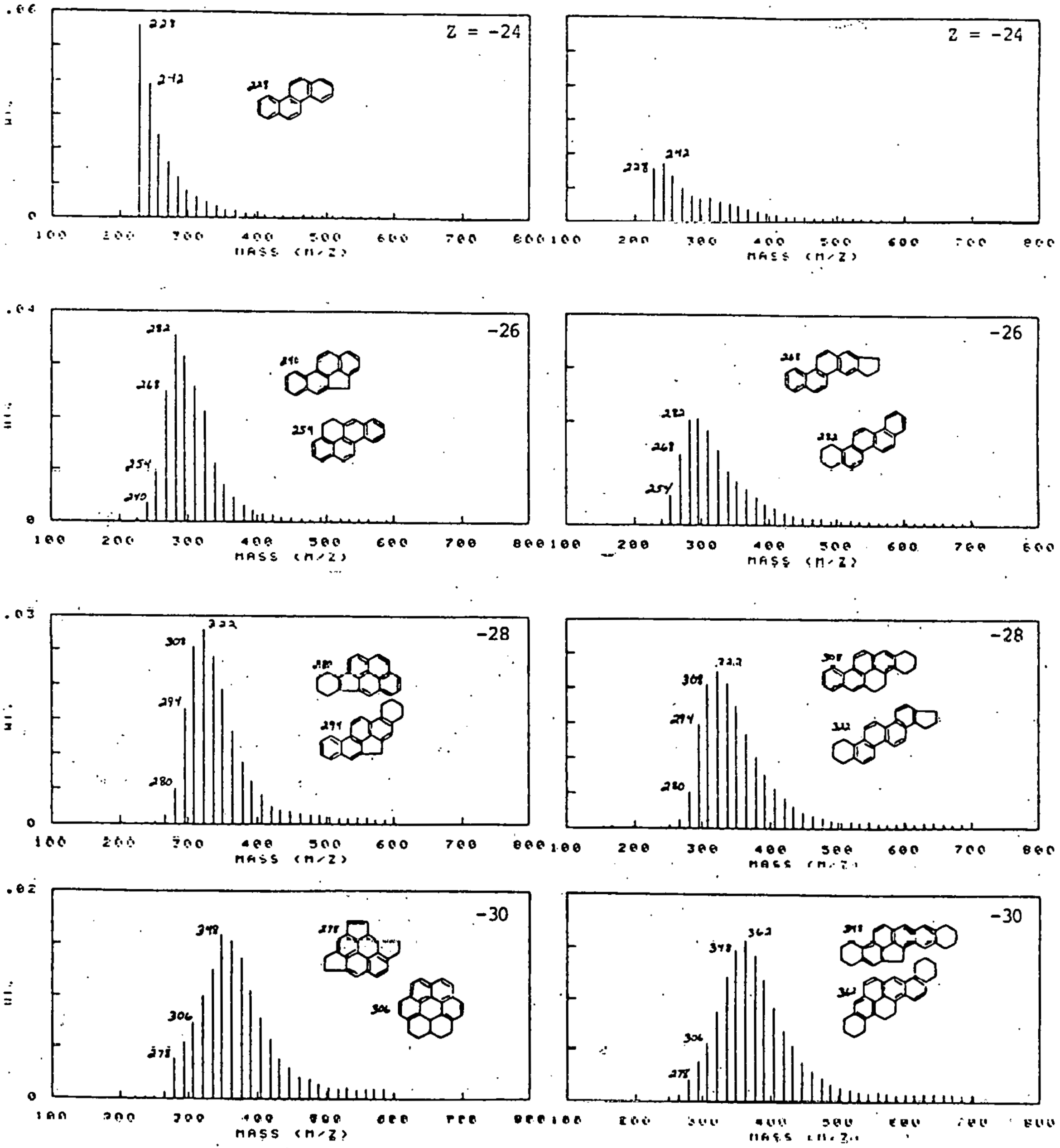
Kentucky

Figure 15. Partial FI mass spectra of the eight double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak Kentucky

Figure 15. (continued)



Wyodak

Kentucky

Figure 16. Partial FI mass spectra of the nine double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.

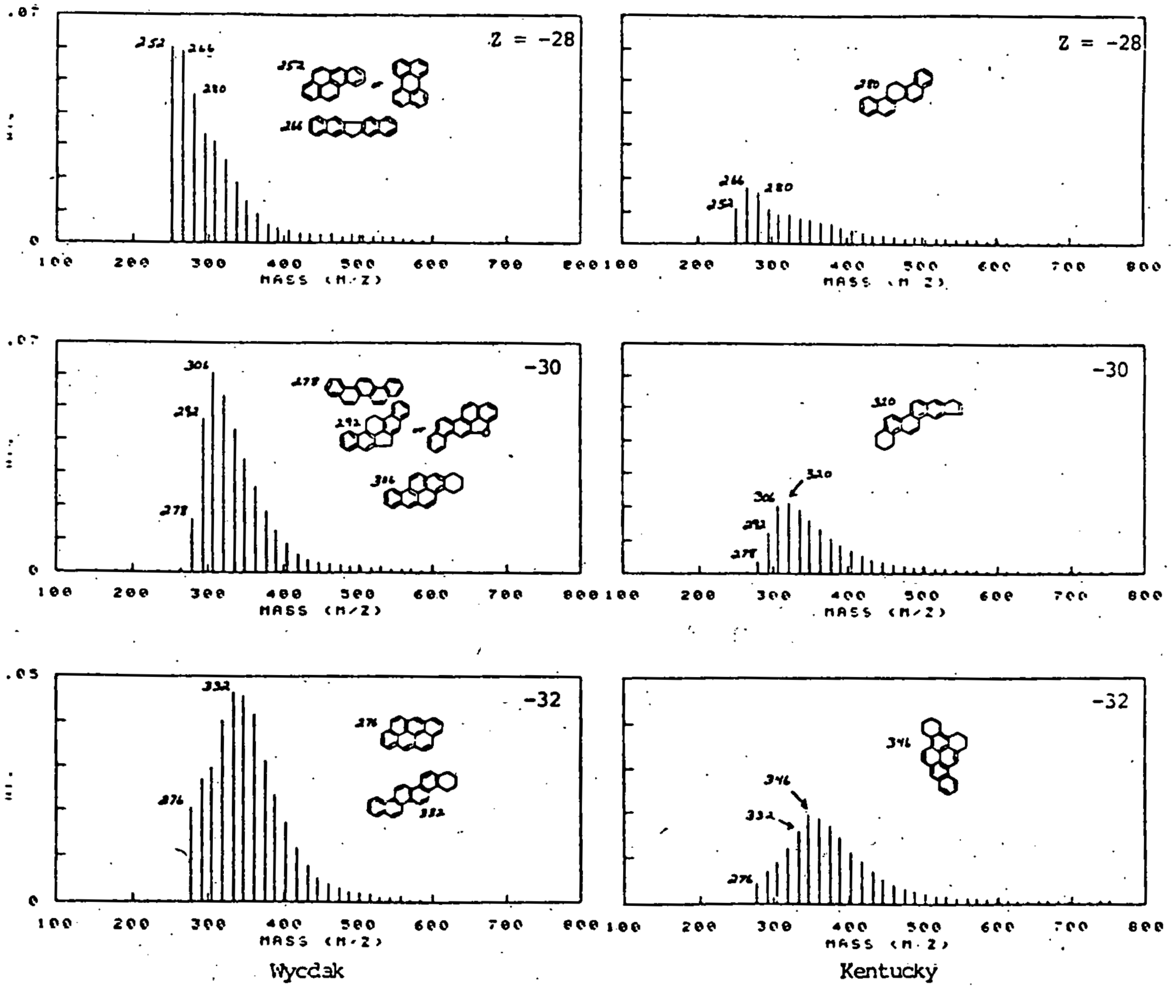
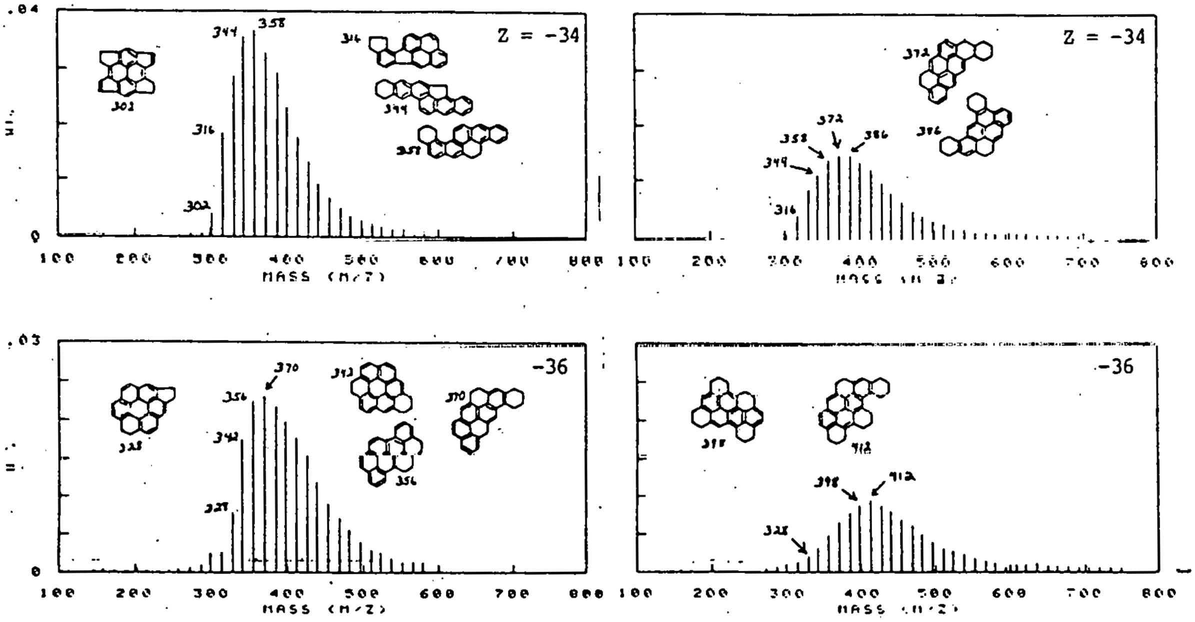


Figure 17. Partial FI mass spectra of the ten and eleven double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

Kentucky

Figure 17. (continued)

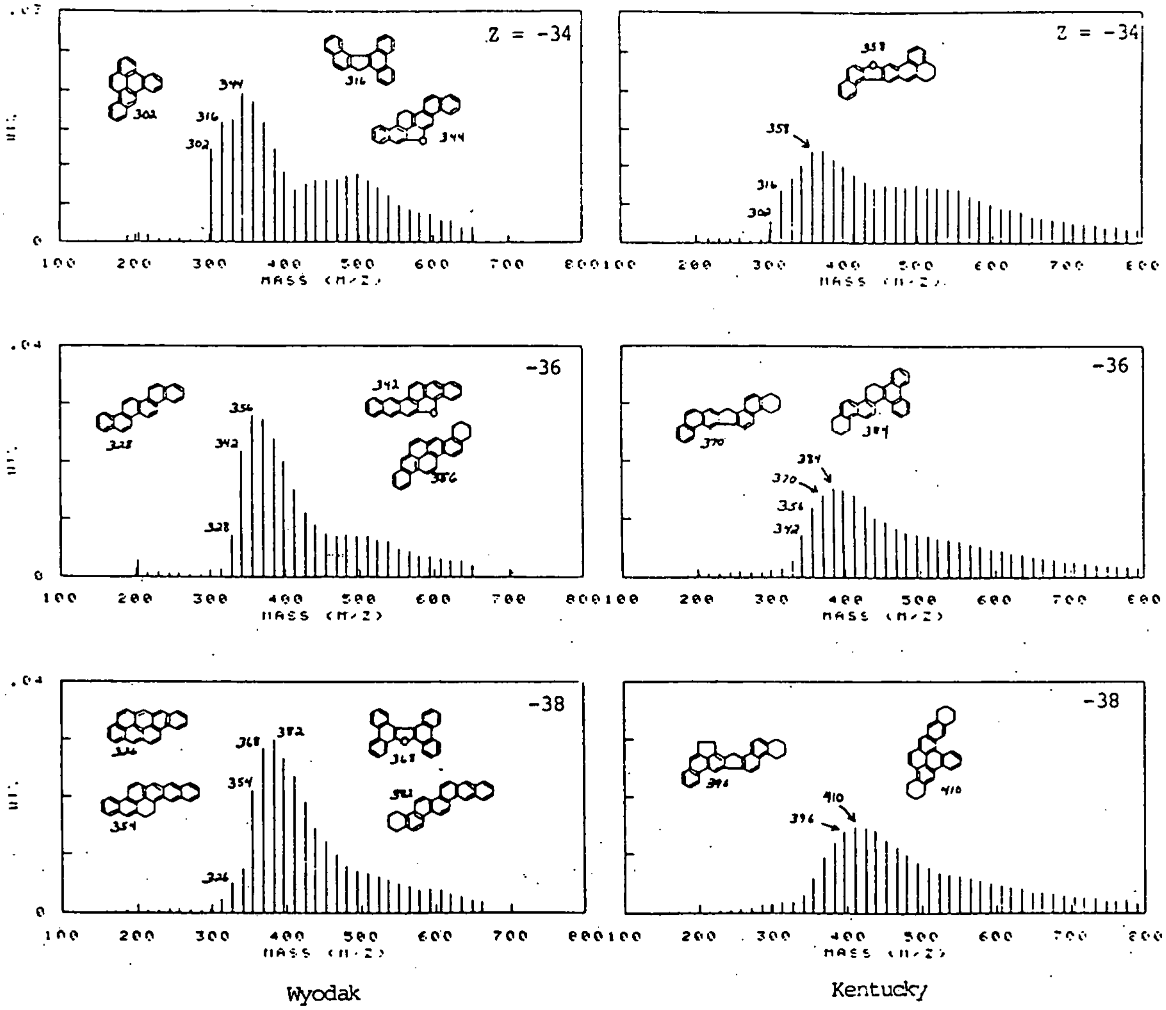
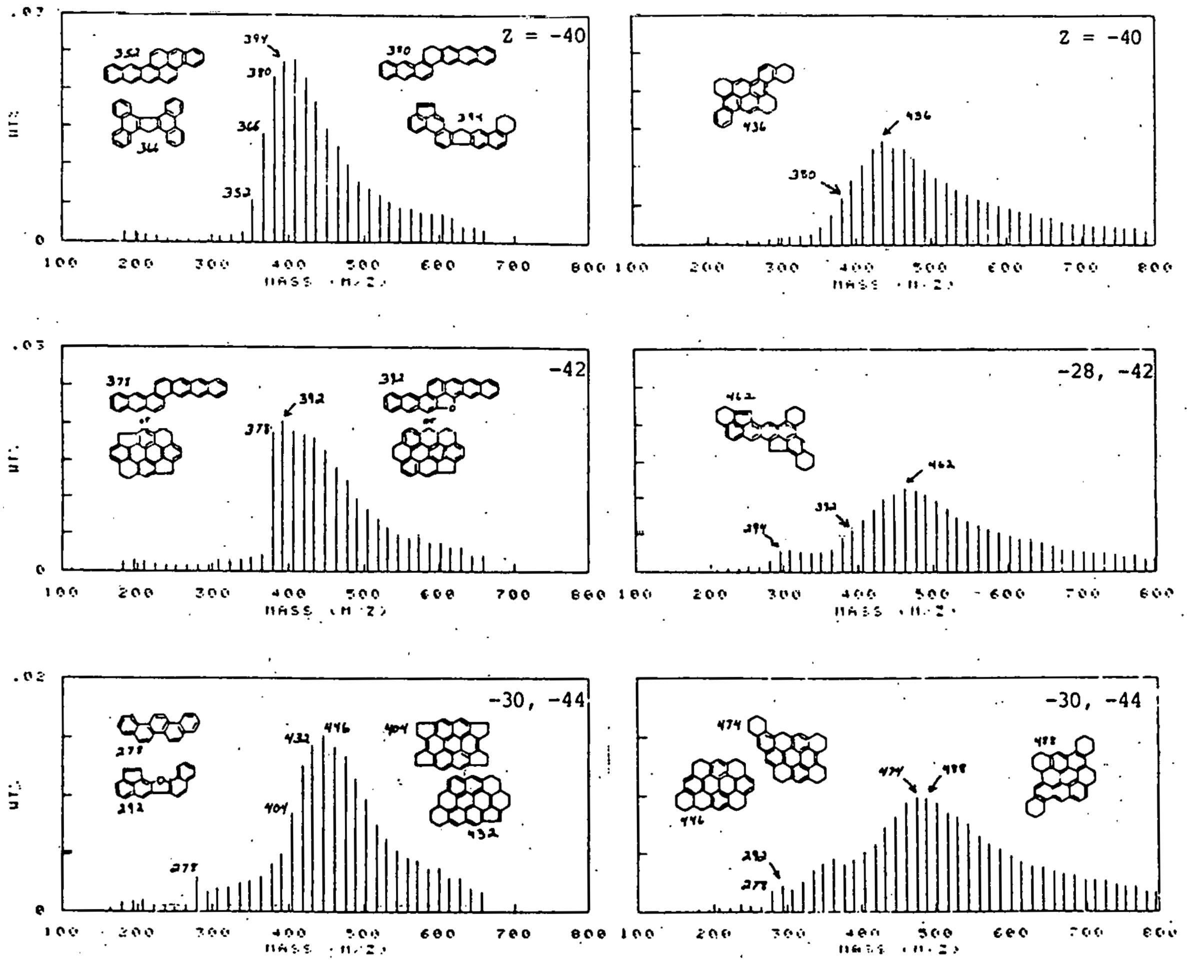


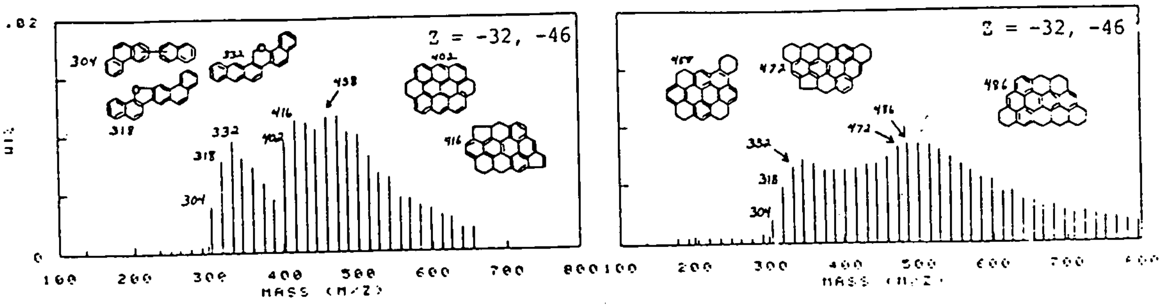
Figure 18. Partial FI mass spectra of the twelve + double bond PAH fraction isolated from Wyodak (F-45) and Kentucky (F-51) SRC.



Wyodak

Kentucky

Figure 18. (continued)



Wyodak

Kentucky

Figure 18. (continued)

d) In Figure 10 in the -4, -6, and -8 Z series, the "biological marker" compounds are much more evident in the Wyodak SRC sample (masses 136, 262; 372, 400; 370, 398, 412).

e) In the -6 and -8 Z series, lower molecular weight material in the Wyodak SRC sample is absent in the Kentucky SRC sample (Figure 10).

Three Double Bonds (Figures 2 and 11)

a) The Kentucky SRC sample contains 1.5 times more three double bond compounds than the Wyodak SRC sample.

b) The Kentucky SRC sample has more material in every Z series compared to the Wyodak SRC samples (Figure 2).

c) In the -8 and -10 Z series, the Wyodak SRC sample has more lower MW material while Kentucky SRC sample has more higher MW material. Initial masses present in Wyodak SRC sample are missing in Kentucky SRC sample (Figure 11).

d) In the -12 and -14 Z series the shapes are very similar, but Kentucky SRC sample is more intense at nearly all masses (Figure 11).

Five Double Bonds (Figures 3 and 12)

a) Overall, the Wyodak SRC sample has 1.1 times more five double bond compounds than the Kentucky SRC sample.

b) The Wyodak SRC sample has more of the -12 and -14 Z series, while Kentucky SRC sample has more of the other series. The -22 and -24 Z series are nearly the same (Figure 3).

c) In the -12 Z series, masses below 184 are missing in Kentucky SRC sample, but are prominent in Wyodak SRC sample (Figure 12).

d) The -14 Z series are similar, but Wyodak SRC sample has more material (Figure 12).

e) In the Kentucky SRC sample, the -16, -18, and -20 Z series dominate, but the appearance of the series are similar with one exception:

  1. A second "hump" around mass 560 is more pronounced in Wyodak SRC sample. This "hump" also appears for the Wyodak SRC sample for the -12 and -14 Z series.

<u>Six Double Bonds</u> (Figures 4 and 13)

a) The Kentucky SRC sample has 1.8 times more six double bond compounds than the Wyodak SRC sample.

b) The Kentucky SRC sample has more material in every Z series (Figure 4).

c) Although Kentucky SRC sample has more material in the -14 and -16 Z series, Wyodak has more material in the initial masses in these series (Figure 13).

d) The -18, -20, and -22 Z series are similar in appearance, with Kentucky SRC sample dominating in each case. The Kentucky series have maxima at one CH_2 unit greater than Wyodak.

<u>Seven Double Bonds</u> (Figures 5 and 14)

a) The Kentucky SRC sample has 1.1 times more seven double bond compounds than the Wyodak SRC sample.

b) The Kentucky SRC sample has more of the -18 Z series and more of the -20 Z series. The Wyodak SRC sample has more of the -22, -24 and -26 Z series. The amounts of the -16 and -28 Z series are essentially the same in both samples (Figure 5 and Table 1).

c) The -18 Z series is very different, with Wyodak SRC sample having relatively small amounts of phenanthrenes and anthracenes (Figure 14).

d) The appearance of the -20, -22 and -24 Z series in the Wyodak and Kentucky SRC samples are similar, differing mainly in intensity.

Eight Double Bonds (Figures 6 and 15)

a) The amounts of eight double bond compounds in the Wyodak and Kentucky SRC samples are about the same.

b) The Wyodak SRC sample has much more of the -22 Z series. Kentucky has slightly more of the -24, -26, -30 and -32 Z series. Both samples have the same amount of the -20 Z series (Figure 6 and Table 1).

c) Although both samples have the same amount of the -20 Z series, the distribution is quite different. The Wyodak SRC sample dominates at the lower masses (Figure 15).

d) In the -22 Z series, it appears to be a matter of intensity, as both series are similar in shape except the Wyodak SRC sample contains more material (Figure 15).

e) The -24, -26, and -28 Z series also appear to differ mainly in intensity.

Nine Double Bonds (Figure 7 and 16)

a) Both Wyodak and Kentucky SRC samples contain the same amount of double bond compounds.

b) The Wyodak SRC sample contains much more of the -24 and -26 Z series, and more of the -28 and -30 Z series. The Kentucky SRC sample contains more of the -22, -32 and -34 Z series (Figure 7).

c) The difference in the -24 Z series, which contains chrysene types, is mainly in relative amounts. The Kentucky SRC sample has much less chrysene and/or tetracene compared to Wyodak SRC sample (Figure 16).

d) The appearance of the -26 and -28 series is very similar with the Wyodak SRC sample containing more material. The -30 Z series are similar in shape and amounts for both samples (Figure 16).

Ten and Eleven Double Bonds (Figures 8 and 17)

a) The Wyodak SRC sample has 2.3 times as much ten and eleven double bond compounds as the Kentucky SRC sample.

b) The Wyodak SRC sample has much more of all Z series (Figure 8 and Figure 17).

c) In the -28, -30 and -32 Z series, the Kentucky SRC sample maxima are at one CH_2 unit higher than Wyodak SRC sample.

d) In the -34 Z series mass 302 is almost missing in the Kentucky SRC sample. Again, the Kentucky SRC maximum is at higher masses.

e) The -36 Z series are similar except for intensity and maximum.

Twelve and Greater Double Bonds (Figues 9 and 18)

a) The Wyodak SRC sample has 1.3 times as much twelve and greater double bond compounds as the Kentucky SRC sample.

b) The Wyodak SRC sample has more of every Z series (Figure 9).

c) In the Kentucky SRC sample, the maxima in all series are at higher masses than Wyodak SRC sample (Figure 18).

d) The shapes of the -34, -36, and -38 Z series in both samples are similar except for intensities. This is true also of the -30, -44 and the -32, -46 series.

e) The appearance of the -42 Z series is quite different in both samples. The Kentucky SRC sample has small amounts of the -28 homologous series present. This series is absent in Wyodak SRC samples.

Using the data in Table 1 and Figures 10-18 the total amount of aromatics, hydroaromatics, and saturates can be estimated. Table 2 gives the results obtained. Based on work done in the previous DOE contract (DE-AC22-79ET14874) the Kentucky (F-51) sample is a better liquefaction medium than the Wyodak

(F-45) sample when blended with other coal derived components (2). It is interesting that the aromatic, hydroaromatic, and saturate content of the F-51 sample is less than the F-45 sample. To make any definitive conclusion on these results and their relationship to coal liquefaction, the composition of other coal liquid samples would have to be obtained experimentally. These coal liquid samples would have to be run under well defined coal liquefaction conditions. Also, it is important to realize that the results in Table 2 account for relatively small portions of the entire SRC samples.

Table 2. Estimated Wt% of Aromatics, Hydroaromatics, and Saturates in Wodak and Kentucky SRC Samples

Sample	Aromatics	Hydroaromatics	Saturates
Wyodak	3.16	5.47	0.35
Kentucky	1.94	5.11	0.13

With the large amount of data obtained from the Wyodak and Kentucky hydrocarbon samples, it is difficult to make easy compositional comparisons among the samples. Because of this difficulty, it was decided to develop a computer program that would plot the data in a three dimensional fashion. Figures 19-21 show the results obtained. These Figures are a great help in summarizing the hydrocarbon data. The numbers above "K" and "W" refer to a particular Z series. Mass is defined by the axis labeled "Mass". The heights of the lines perpendicular to the mass axes are in terms of wt%. With Figures 19-21, it is relatively easy to make rapid comparison among the various hydrocarbon fractions. Also, one gets a general overview of the hydrocarbon content in the Wyodak and Kentucky samples. This is virtually impossible when evaluating each FIMS spectrum in detail. Thus, we have the capability of

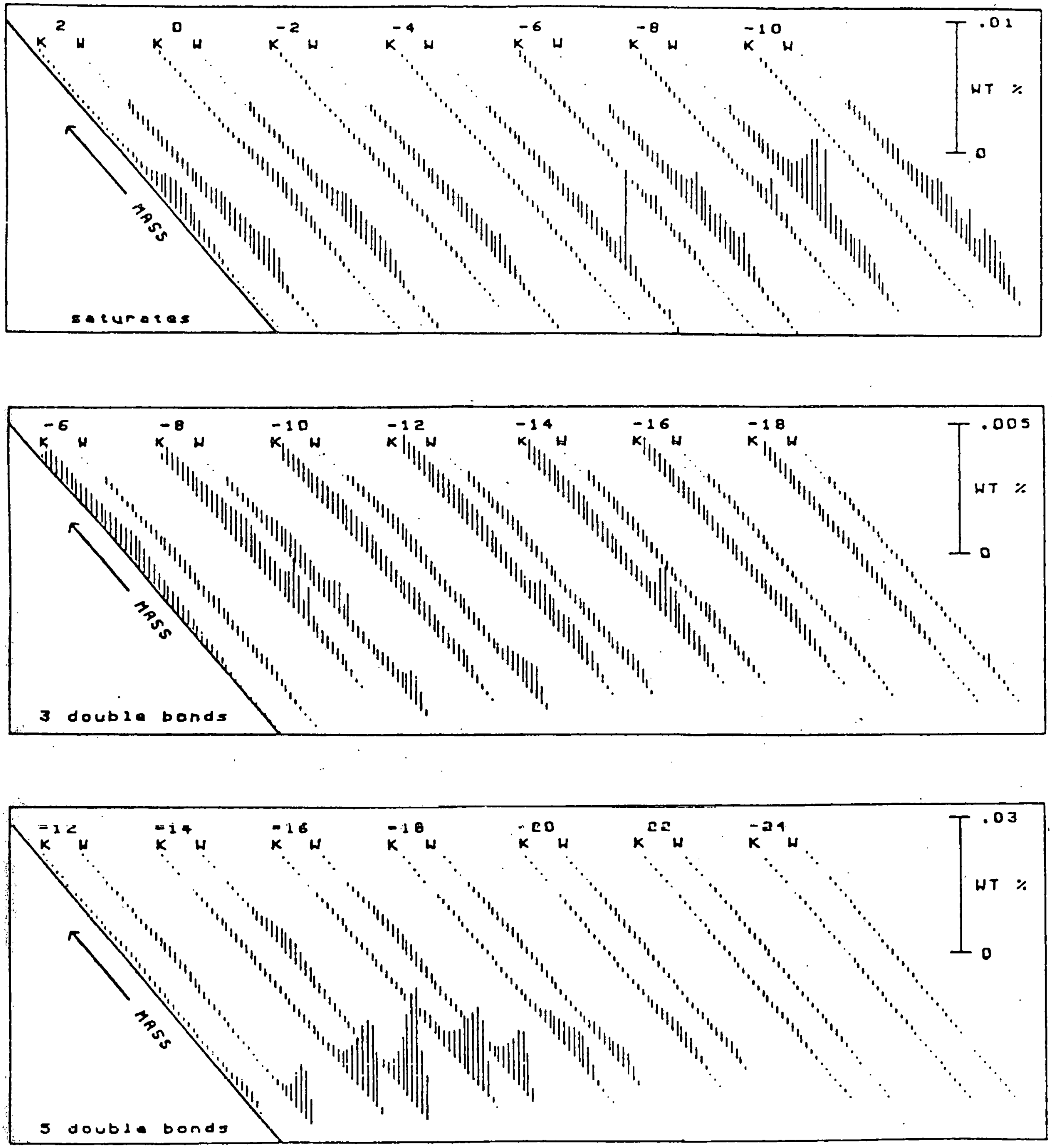


Figure 19. Comparison of nominal mass Z series in saturates, three double bond and five double bond hydrocarbons isolated from Kentucky (K) and Wyodak (W) SRC.

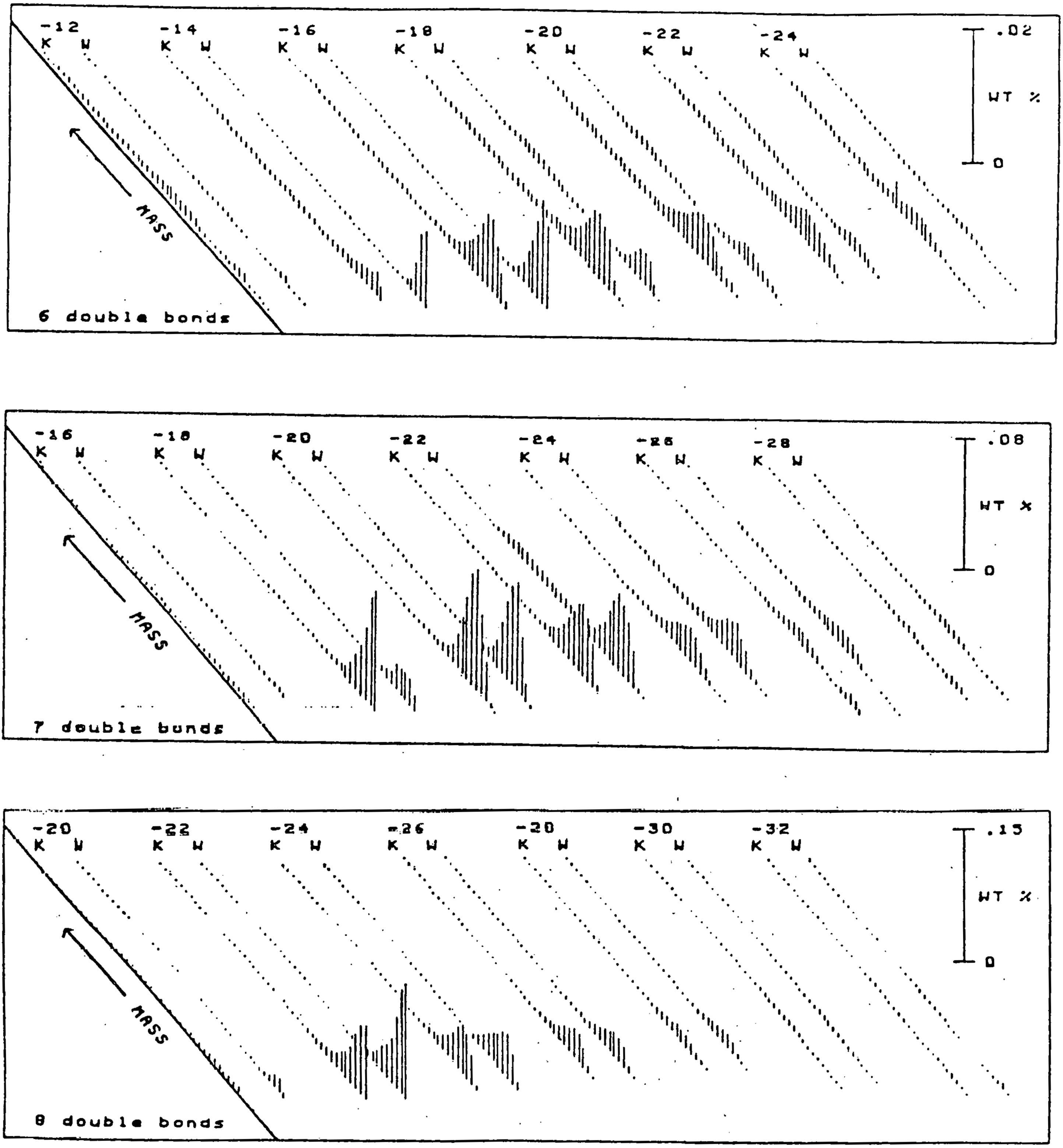


Figure 20. Comparison of nominal mass Z series in six double bond, seven double bond and eight double bond hydrocarbons isolated from Kentucky (K) and Wyodak (W) SRC.

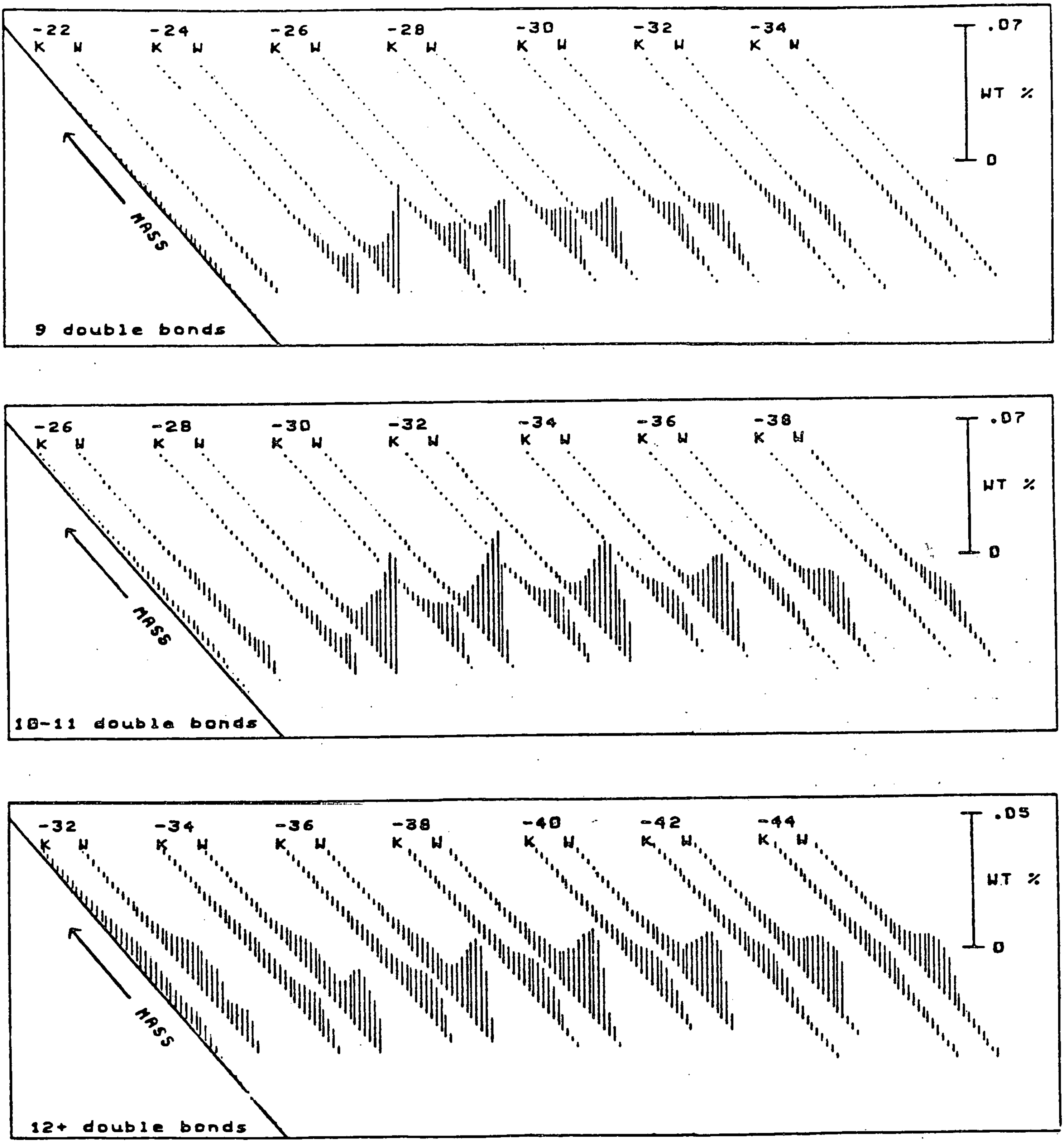


Figure 21. Comparison of nominal mass Z series in nine double bond, ten and eleven double bond, and $\geq$ twelve double bond hydrocarbons isolated from Kentucky (K) and Wyodak (W) SRC.

obtaining detailed compositional hydrocarbon data or obtaining a general profile of the hydrocarbon content in coal liquid samples.

B. Solubility Tests and Preliminary Open-Column Chromatography Results for Preasphaltenes-1 and Preasphaltenes-2.

The pyridine soluble-chloroform insoluble material, defined as preasphaltenes-2, was tested for solubility in various binary and ternary solvents. The main reason for the solubility test was to find solvents that could be used in the open-column adsorption chromatography of preasphaltenes-2. As discussed in the last quarterly report, preasphaltenes-1(chloroform soluble) were soluble in several binary solvents. Table 3 gives the results obtained for the solubility of preasphaltenes-2 from F-45 and F-51. The results in Table 3 are somewhat encouraging because binary solvents and a ternary solvent can be used to dissolve preasphaltenes-2. Some of these solvents will be used to fractionate the preasphaltenes-2 with silica gel as a stationary phase.

Work was begun in determining the chromatographic migration characteristics of several model compounds in open-column silica gel chromatography. The model compounds were chosen because of their multiple functionality and the possibility they would appear in the preasphaltene fractions. The model compounds are: 5-hydroxyquinoline; 2-hydroxycarbazole; 1,7-dihydroxynaphthalene; 2,4-quinolinediol; phenazine; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; 1,4,9,10-tetrahydroxyanthracene; 2,3-dihydroxypyridine; 1,8-dihydroxyanthraquinone; 1,3-dihydroxynaphthalene; and 4,5,7-trihydroxyflavanone.

Table 3. Solubility of Preasphaltenes-2 from F-45 and F-51 in Various Solvents

Solvent		Solubility[1]
pyridine:n-heptane	1:9(v/v)	I
	5:5(v/v)	PS
	7:3(v/v)	PS
	9:1(v/v)	PS
pyridine:chloroform	5:5(v/v)	PS
	7:3(v/v)	MS
	9:1(v/v)	MS
pyridine:chloroform:tetrahydrofuran	6:3:1(v/v/v)	PS
	6:2:2(v/v/v)	PS
	6:1:3(v/v/v)	PS
	6:0:4(v/v/v)	PS
	7:1:2(v/v/v)	MS

[1] I = isoluble, PS = partially soluble, MS = mostly soluble (some fine solid material settled after sitting overnight)

C. Other Experiments with Preasphaltenes

As mentioned in the previous quarterly report, infrared and proton NMR spectra were obtained from the preasphaltenes-1 and preasphaltenes-2 from F-45 and F-51. The samples were dissolved in deuterated pyridine and the proton NMR spectra we were obtained with a JEOL FX 270 MX NMR spectrometer. All the NMR spectra appeared the same and no distinquishing features were noted.

Infrared spectra of the P-1 and P-2 fractions from F-51 and F-45 were obtained from KBr pellets of the samples. The infrared spectra were very similar; however, some important information and differences were noted in the spectra. These are listed below:

a) The hydroxyl group absorption band was obvious in all the spectra.
b) No aldehyde, ketone, carboxyl, or ester functionality was indicated.
c) The P-2 fractions were distinctly more aromatic than the P-1 fractions.
d) The P-2 material in F-45 appears to be somewhat more aromatic than the P-2 material in F-51.
e) The P-1 material in F-51 appears to be somewhat more aromatic than the P-1 material in F-45.

The last three conclusions are supported by the data in Table 4. Also included in Table 4 is data on the aliphatic bands. The data in Table 4 was obtained by cutting out the appropriate bands from the infrared spectrum and weighing the corresponding paper from the spectrum. Obviously, this approach only gives an approximate measure of the aliphatic and aromatic content in the fractions. Figure 22 shows the partial infrared spectrum of P-2 fraction from F-51. The other infrared spectra were similar.

Table 4. Approximate Amounts of Aliphatic and Aromatic Material in the Preasphaltenes of F-45 and F-51.

	Wt of Spectrum Tracing, mg		
Fraction	aliphatic	aromatic	Aliphatic/Aromatic Ratio
F-51,P-2	39.9	118	0.34
F-45,P-2	23.8	86.4	0.28
F-51,P-1	39.8	88.7	0.45
F-45,P-1	70.8	141	0.50

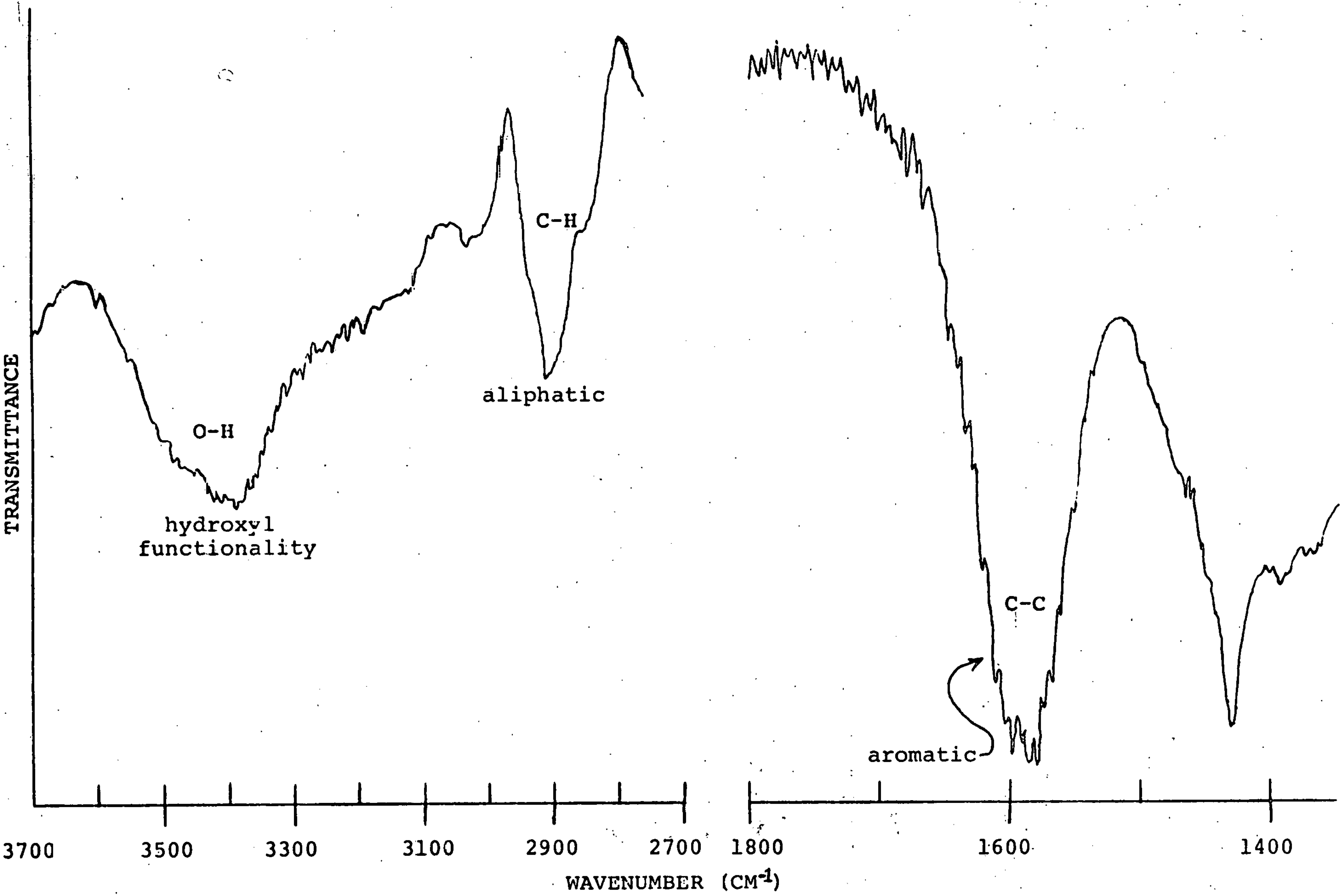


Figure 22. Partial infrared spectrum of pyridine soluble-chloroform insoluble preasphaltenes isolated from Kentucky (F-51) SRC. Spectrum obtained from KBr pellet.

D. Replacement of Fluoropak with Chromasorb T in the Fluoropak-Basic Alumina Procedure

Chromasorb T was investigated as a substitute for Fluoropak in the Fluoropak-basic alumina procedure because Fluoropak is no longer available. Chromasorb T is manufactured by Johns-Mannsville, Inc. and was purchased from Supelco, Inc. Both Chromasorb T and Fluoropak are made of Teflon 6, but the Chromasorb T is a finer mesh size (30/60) compared to Fluoropak (20/40).

Table 5 shows the results for duplicate runs using Chromasorb T and Fluoropak. The procedure employed has been described in the literature (3,4). Comparison of the Chromasorb T results with the Fluoropak results shows reasonably good agreement. Based on the results in Table 5 Chromasorb T is an adequate substitute for Fluoropak. However, additional experiments will be run in the future in which these two materials (Chromasorb T and Fluoropak) are compared. It is important to mention that sample homogeneity is an important factor, and some of the discrepancy of the data in Table 5 could be due to this factor.

Table 5. Comparison of Results Obtained with Chromasorb T and Fluoropak Using F-45

Column Packing	Oils[1]	Asph.[2]	Preasph.[3]	Oils HC	Oils N	Oils OH	Asph. HC+N	Asph. OH	Preasph. chloroform soluble	Preasph. pyridine[4] soluble
Chromasorb T	19.2	37.4	43.4	9.0	4.8	5.4	12.6	24.8	11.9	31.5
Chromasorb T	19.1	36.7	44.2	8.7	4.8	5.7	12.6	24.1	11.7	32.5
Average	19.1	37.1	43.8	8.8	4.8	5.6	12.6	24.4	11.8	32.0
Fluoropak	17.2	36.8	46.0	8.4	4.0	4.8	13.5	23.3	12.5	33.5
Fluoropak	16.6	35.6	47.6	7.9	3.6	5.1	13.1	22.7	12.7	34.9
Average	16.9	36.2	46.8	8.2	3.8	5.0	13.3	23.0	12.6	34.2

Asph = asphaltenes, Preasph = preasphaltenes, HC= hydrocarbons, N = nitrogen compounds

OH = hydroxyl aromatics

[1] Oils = HC(Oils) + N(Oils) + OH(Oils)

[2] Asph = N(Asph) + OH(Asph)

[3] Preasph = chloroform soluble + pyridine soluble(pyridine soluble obtained by difference)

[4] Obtained by difference

E. High Performance Liquid Chromatography

1. Hydroxyl Aromatics

As discussed in the last quarterly report, the chromatographic characteristics of thirty-six hydroxyl aromatic standards were investigated by normal-phase chromatography. The same standards have been investigated by reversed-phase chromatography using a C-18 column. Table 6 gives the mobile phases investigated. It was found that linear relationships were obtained between log (capacity factor) versus volume percent of the strong solvent in the mobile phase, and log(capacity factor) versus solubility parameter of the mobile phase. The linear relationships have been used in optimizing the mobile phases for the "best" resolution of hydroxyl aromatics. Two optimization methods are being employed, namely, a solubility parameter method (5) and a window diagram method (6). The results from the opimization methods are very encouraging. It appears that the "best" mobile phase for the separation of hydroxyl aromatics using reversed-phase chromatography can be predicted a priori. In addition, the limitations of the chromatographic systems are defined by the optimization methods. The same optimization methods will be applied to normal-phase chromatographic systems. Detailed results for the reversed-phase and normal-phase chromatoraphic systems will be given in future reports.

2. Nitrogen Heterocycles and Aromatic Amines

The chromatographic characteristics of thirty-five nitrogen heterocycle and aromatic amine standards were investigated on several normal-phase chromatography systems. Table 7 lists the compounds studied and Table 8 gives the chromatographic systems investigated. The results from these experiments are still being interpreted. More details on the results will be given in later reports.

Table 6. Reversed-Phase High Performance Liquid Chromatography Mobile Phases Investigated for Hydroxyl Aromatics with a C-18 Column

1. Ternary mobile phases investigated for three monohydroxyl compounds

methanol:acetonitrile:water(v/v/v)	methanol:tetrahydrofuran:water(v/v/v)
50:10:40	50:10:40
35:20:45	35:20:45
20:30:50	20:30:50
5:40:55	5:40:55

2. Ternary mobile phases investigated for three dihydroxyl compounds

methanol:acetonitrile:water(v/v/v)	methanol:tetrahydrofuran:water(v/v/v)
10:10:80	10:10:80
15:15:70	15:15:70
20:20:60	20:20:60
25:25:50	25:25:50

3. Ternary mobile phase investigated for twenty-one monohydroxyl compounds

methanol:tetrahydrofuran:water(v/v/v)
30.0:21.5:48.5

4. Ternary mobile phase investigated for fourteen dihydroxyl compounds

methanol:tetrahydrofuran:water(v/v/v)
9:20:71

Table 7. Standard Nitrogen Heterocycles and Aromatic Amines in High Performance Liquid Chromatography Experiments.

1. 2,7-Diaminofluorene
2. 13H-Dibenzo[a,i]carbazole
3. 5-Aminoindole
4. 5-Aminoisoquinoline
5. 5,6-Dimethylbenzimidazole
6. 5,6-Benzoquinoline
7. Benzo[c]cinnoline
8. 2,6-Dimethylquinoline
9. 2,2'-Biquinoline
10. 6,13-Dihydrodibenzo[b,i]phenazine
11. 5-Aminoquinoline
12. 3-Amino-9-ethylcarbazole
13. 3-Aminofluoranthene
14. 7-Azaindole
15. Carbazole
16. 1-Azapyrene
17. 1-Aminoanthracene
18. 5-Aminoindazole
19. Iminostilbene
20. 4-Phenylpyridine
21. 4-Azafluorene
22. Acridine
23. 7,8-Benzoquinoline
24. 4,5-Diphenylimidazole
25. Indole
26. 4-Azabenzimidazole
27. 1,2-Bis(4-pyridyl)ethane
28. 5-Aminoindan
29. 6-Aminoindazole
30. Iminodibenzyl
31. 7-Methylindole
32. 2-Phenylbenzimidazole
33. 2-Phenylindole
34. 1,2,3,4-Tetrahydrocarbazole
35. 2,3,4,5-Tetraphenylpyrrole

Table 8. Normal-Phase Chromatographic Systems Investigated for Nitrogen Heterocycles and Aromatic Amines

Stationary Phase	n-Heptane:2-Propanol(v/v)Mobile Phases
μ-Bondapak NH_2	60:40
μ-Bondapak NH_2	75:25
μ-Bondapak NH_2	85:15
μ-Bondapak CN	70:30
μ-Bondapak CN	75:25
μ-Bondapak CN	80:20
μ-Bondapak CN	85:15
μ-Porasil	85:15
μ-Porasil	95:5
μ-Porasil	99:1

3. Compound Class Separation of Polycyclic Aromatic Hydrocarbons, Nitrogen Heterocycles, and Hydroxyl Aromatics

Compound class separation of polycyclic aromatic hydrocarbons, nitrogen heterocycles, and hydroxyl aromatics in heavy coal liquid samples has not been accomplished yet by high performance liquid chromatogrpahy. In this work, both mobile phase optimization and prediction of retention are particularly important because of the possible overlap of compounds in the various compound classes. Several mobile phases and high-performance chromatographic columns are being investigated to determine the best chromatographic systems to separate compound classes. Table 9 lists the stationary phases and mobile phases studied. Experiments with other columns and mobile phases are still being carried out and definitive results and conclusions will be reported in later reports.

F. Manuscripts

1. A manuscript entitled "Composition of Distillate Recycle Solvents Derived from Direct Coal Liquefaction in the SRC-1 Process" will be submitted to Fuel for review in the near future. The manuscript is attached to this report as Appendix A. The results described in this manuscript were obtained under the previous DOE contract (No.DE-AC22-79ET14874).

2. A manuscript is being written in which the hydrocarbon composition of moderately and severely hydrogenated F-45 is compared. The data were obtained during the previous DOE contract period.

3. A manuscript is being written in which the hydrocarbon composition of F-45 and F-51 are compared. Some of the data were obtained during the previous DOE contract period.

Table 9. Stationary Phases and Mobile Phases for Compound Class Separation

1. μ-Bondapak NH_2 (normal-phase)

   n-heptane, chloroform, n-heptane:chloroform 25:1(v/v), n-heptane:chloroform 15:1(v/v), n-heptane:chloroform 10:1(v/v), n-heptane:chloroform 5:1(v/v), n-heptane:2-propanol 25:1(v/v), n-heptane:2-propanol 100:1(v/v), n-heptane:methylene dichloride 25:1(v/v), n-heptane:methylene dichloride 10:1(v/v), n-heptane:ethyl acetate 10:1(v/v)

2. μ-Porasil (normal-phase)

   n-heptane, 2-propanol:n-heptane 1:100 (v/v)

3. Basic Alumnum Oxide (normal-phase)

   n-heptane, dioxane:n-heptane 21:79(v/v), n-heptane:dioxane 100:1(v/v), n-heptane:chloroform 95:5(v/v)

4. μ-Bondapak C_{18} (reversed-phase)

   methanol:water 60:40(v/v)

5. μ-Bondapak CN (normal-phase)

   n-heptane, chloroform

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Appendix A

Compositions of Distillate Recycle Solvents Derived from Direct Coal Liquefaction in the SRC-1 Process

Mieczyslaw M. Boduszynski,[1] Robert J. Hurtubise, and Todd W. Allen
Chemistry Department
The University of Wyoming
Laramie, WY 82071

Howard F. Silver
Chemical Engineering Department
The University of Wyoming
Laramie, WY 82071

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[1] Present address: Chevron Research Company
Richmond, CA 96802

Brief

Liquid chromatography and field ionization mass spectrometry were used for analysis of coal-derived 260-427°C distillate recycle solvents from direct coal liquefaction processes.

Abstract

The qualitative and quantitative compositions of 260-427°C distillate recycle solvents derived from direct liquefaction of subbituminous Wyodak coal and bituminous Kentucky 9/14 coal in the SRC-1 process are discussed.

A liquid chromatography method which involves a column switching technique was used to provide solubility characteristics and compound-class compositions. The compound-class fractions of hydrocarbons, nitrogen compounds, and hydroxyl aromatics were separated from hexane soluble "oils" and toluene soluble-hexane insoluble "asphaltenes". The hydrocarbons were further separated into saturates and mono-through tetracyclic aromatics using high performance liquid chromatography (HPLC).

Field ionization mass spectrometry (FIMS) was used to analyze the compound-class fractions. The apparent concentrations for various homologous series (Z series) of compound-class fractions from the two coal-derived distillate recycle solvents are compared.

Many attempts have been made in the past to correlate the effectiveness of coal liquefaction recycle solvents with their chemical and physical properties (1-15). It is known that a good recycle solvent must be compatible with the products of the thermal dissolution of coal and it must also provide a readily available source of hydrogen. The liquefaction solvent may function as a direct source of hydrogen (hydrogen donor), indirect source of hydrogen (hydrogen shuttler), or as a hydrogen abstractor. In a commercial process, the solvent is derived from coal and must be suitable for recycle operation.

In order to fully understand the chemistry of coal liquefaction and the performance of coal-derived recycle solvents a thorough knowledge of their chemical composition is necessary. In recent years, considerable progress has been made in developing methods for separation and characterization of coal derived liquids (16-28).

The objective of this work was to provide details of the composition of two 260-427°C distillate recycle solvents derived from a direct liquefaction of a subbituminous Wyodak coal and a bituminous Kentucky 9/14 coal in the SRC-1 process. These two solvents were selected because of their different coal liquefaction performance; the Kentucky 9/14 coal derived distillate being the more effective coal liquefaction solvent.

EXPERIMENTAL

Distillate recycle solvent samples.

Wyodak coal derived distillate recycle solvent was produced from a subbituminous coal from the Canyon Anderson seams in the Amax Coal Co., Bell Ayr Mine in Wyoming. The recycle solvent sample was supplied by Catalytic, Inc. from the Southern Company Services, Inc., SRC pilot plant located at Wilsonville, AL. This sample was redistilled using ASTM D-86/1160 procedures to remove a low-boiling fraction.

Kentucky 9/14 coal derived distillate recycle solvent was produced from a bituminous Kentucky 9/14 coal. The sample, supplied by the Pittsburgh and Midway Coal Mining Co., SRC pilot plant near Tacoma, WA, was analyzed as received.

Some analytical data on the two distillate recycle solvents have been reported elsewhere (29).

Separation into solvent-derived and compound-class fractions.

A coal derived distillate recycle solvent sample was coated on an inert fluorocarbon support material. An Altex glass chromatographic column was then packed with the sample-coated support material, and the column was connected to two basic alumina columns. Solvent-derived fractions of "oils" (hexane soluble) and "asphaltenes" (toluene soluble-hexane insoluble) were directly introduced into a respective basic alumina column for further separation into three compound-class fractions - hydrocarbons, nitrogen compounds, and hydroxyl aromatics. A toluene insoluble-pyridine soluble fraction of "preasphaltenes" was eluted with pyridine directly from the inert support material in the first column. The detailed procedure was described elsewhere (24, 25).

HPLC separation of hydrocarbons

The liquid chromatograph used was a Waters Model ALC/GPC 244 equipped with a Model U6K injector, a Model 6000A pump, a Model ALC 201 differential refractometer and a Model 440 UV absorbance detector, a strip chart recorder, and a Bascom-Turner Model 8120 computerized recorder.

The hydrocarbon fractions isolated from hexane soluble oils of each distillate recycle solvent were further separated into saturates and the following "double bond" (d.b.) aromatic hydrocarbon fractions: 3 d.b., 5 d.b., 6 d.b., 7 d.b., 8 d.b., and 9 + d.b. A 10 μm particle size μ-Bondapak NH_2 semipreparative column from Waters with n-heptane as a mobile phase were used to separate the hydrocarbon fractions. The details of the HPLC procedure were described previously (27), and yields of the fractions were determined gravimetrically.

Field Ionization Mass Spectrometry.

FIMS was used to analyze the compound-class fractions separated from Wyodak and Kentucky 9/14 coal-derived distillate recycle solvents. Field ionization (FI) mass spectra were obtained from samples submitted to SRI International in Menlo Park, CA. The spectra were obtained by repeated multiscanning. The conversion from ion counts to corrected relative intensity was automatically performed by the computer. The relative intensities were normalized for each spectrum to a total of 10,000 and may easily be converted to mole percent of material (30).

FIMS produces unfragmented molecular ions and their isotope signals. Computer programs were devised which allow for correction of peak intensities for material abundance of carbon-13 and subsequent conversion to weight percent of the sample. An HP-87 computer with an HP Model 82901M flexible disk drive and an HP Model 82905B printer were used to evaluate the FIMS data obtained from SRI.

Infrared Spectrometry.

A Perkin-Elmer Model 621 grating infrared spectrophotometer was used for the analysis of functionalities present in the fractions. The infrared spectra were recorded in methylene chloride using 0.5 mm NaCl cells.

RESULTS AND DISCUSSION

Compound-Class Composition.

A separation method originally developed for solvent refined coal (24, 25) was applied in this work to separate the distillate recycle solvents into solvent-derived and compound-class fractions. The separation scheme is shown in Figure 1. The average results from triplicate separations are given in Table 1. Precautions were taken to prevent loss of volatile components during removal of solvents from chromatographic fractions. Data in Table 1 show that hexane soluble oils are the predominant solvent-derived fractions in both Wyodak and Kentucky coal-derived distillate recycle solvents, accounting for 94.5 and 91.8 wt%, respectively. Toluene soluble-hexane insoluble asphaltenes are represented by 4.3 wt% (Wyodak) and 5.9 wt% (Kentucky) while pyridine soluble-toluene insoluble preasphaltenes account for 0.6 and 2.3 wt%, respectively. Results in Table 1 also show that hydrocarbons are the major compound-class components in both Wyodak and Kentucky coal-derived recycle solvents, accounting for 63.1 and 61.7 wt%, respectively. The hydrocarbons are present almost entirely in hexane soluble oils. Hydroxyl aromatics are the next largest compound-class fraction, accounting for 26.8 wt% (Wyodak) and 23.6 wt% (Kentucky). Nitrogen compounds in Wyodak and Kentucky coal-derived recycle solvents are represented by 8.9 and 12.4 wt%, respectively. The hydroxyl aromatics and nitrogen compounds are distributed among both oils and asphaltenes.

In terms of solubility characteristics the Wyodak coal derived solvent contains more oils and less asphaltenes and preasphaltenes than the Kentucky 9/14 coal derived solvent. In terms of compound-class composition the Wyodak coal derived solvent contains more hydrocarbons and hydroxyl aromatics but less nitrogen compounds than the Kentucky 9/14 coal derived solvent.

HPLC/FIMS Analysis of Hydrocarbons.

The hydrocarbons separated from hexane soluble oils in Wyodak and Kentucky coal-derived distillate recycle solvents were analyzed using a previously described HPLC/FIMS method (27, 28). Hydrocarbons in toluene soluble-hexane insoluble asphaltenes were present in too small amounts to justify further characterization of these fractions. The HPLC technique provides separation according to the number of double bonds in aromatic ring systems while FIMS separates according to molecular mass and Z number corresponding to the general formula, C_nH_{2n+Z}. For example, C_4-pyrene and hexahydrobenzpyrene both would be represented by the C_nH_{2n-22} formula and a single peak in FI mass spectrum at M/Z 258. However, the first one has 8 double bonds in the ring system while the other one has only 7 double bonds. With an HPLC separation step prior to to the FIMS analysis, the two compounds would be present in different fractions and thus could be identified. The interpretation of the FI mass spectra is based on an assignment of the initial structure to the lowest molecular weight homologue in the spectrum. The peaks following the lowest molecular weight homologue, at every 14 units ($-CH_2-$), correspond to alkyl-substituted homologues.

Alkanes. Data in Table 2 show that saturates (SAT) account for 5.7 and 4.4 wt% of distillate recycle solvents derived from Wyodak (W) and Kentucky (K) coal, respectively. The FI mass spectra of the SAT W and SAT K fractions are shown in Figure 2. The apparent concentrations for various Z series in FI mass spectra of these fractions are given in Table 3. The data show that saturates consist of various homologous series ranging from acyclic alkanes ($Z = +2$) through pentacyclic ($Z = -8$), and possibly hexacyclic ($Z = -10$) alkanes. The latter, however, may interfere in the FI mass spectrum of monoaromatics which would contain tetrahydroacenaphthenes, hexahydrofluorenes, and octahydrophenanthrenes/anthracenes. Some degree of chromatographic overlap between pentacyclic alkanes and monoaromatics was likely to occur, as was discussed elsewhere (27, 28). Acyclic alkanes (C_nH_{2n+2}) in both distillate recycle solvents range from about C_{15} through C_{32}, with the C_{25} (M/Z 352) being most abundant in the SAT W fraction and the C_{19} (M/Z 268) in the SAT K fraction (Figure 2). Overall concentration of monocyclic through hexacyclic alkanes in the SAT W and SAT K fractions are fairly similar (Table 3). However, there are considerable differences between molecular weight distributions of various homologous series in both samples. Cycloalkanes in the SAT W fraction cover a wider molecular weight range and show lower concentrations of the low molecular weight species than those in the SAT K fraction (Figure 2).

Monoaromatics. Data in Table 2 show that monoaromatics (3 d.b. fraction) account for 3.2 wt% Wyodak (W) and 6.2 wt% Kentucky (K) in the distillate recycle solvents. Figure 2 shows the FI mass spectra of the 3 d.b.W and 3 d.b.K fractions. (Note the differences in intensity scale.) The apparent concentrations for various Z series in the FI mass spectra of the 3 d.b. fractions are given in Table 4. Alkylbenzenes, C_nH_{2n-6}, are represented by 0.3 wt% in both the 3 d.b.W and 3 d.b.K samples. Homologous series C_nH_{2n-8} and C_nH_{2n-10} dominate in monoaromatics from both coal-derived solvents. The C_nH_{2n-8} series with initial peaks at M/Z 146, 160, 174 etc., can be assigned to alkylindanes, alkyltetralins, and cyclohexylbenzenes. This homologous series accounts for 1.1 and 2.2 wt% of 3 d.b.W and 3 d.b.K samples, respectively. The C_nH_{2n-10} series, with initial peaks at M/Z 158, 172, 186 etc., (Figure 2) can be assigned to tetrahydroacenaphthenes, hexahydrofluorenes, and octahydrophenanthrenes/anthracenes. A better liquefaction solvent, derived from Kentucky

9/14 coal, has a higher concentration of these compound-types (2.5 wt% in 3 d.b.K) than the Wyodak coal-derived solvent (1.0 wt% in 3 d.b.W).

Dicyclic aromatics. Data in Table 2 show that dicyclic aromatics were separated into 5 d.b. and 6 d.b. fractions. The FI mass spectra of the dicyclic aromatic hydrocarbon fractions are shown in Figure 2. The 5 d.b. aromatics dominate in both Wyodak (19.8 wt%) and Kentucky (24.4 wt%) coal-derived solvents. Two major homologous series, C_nH_{2n-12} and C_nH_{2n-14}, are present in 5 d.b.W and 5 d.b.K fractions. The apparent concentrations of the homologous series are given in Table 5. The C_nH_{2n-12} series, with initial peaks at M/Z 128, 142, 156 etc., (Figure 2) can be assigned to naphthalenes. The C_4-naphthalene (M/Z 170) being the most abundant. The C_nH_{2n-14} series can be assigned to acenaphthenes (M/Z 154, 168, etc.) and tetrahydrophenanthrenes/anthracenes (M/Z 182, 196, etc.). These homologous series account for 9.2 and 11.0 wt% of 5 d.b.W and 5 d.b.K, respectively. The C_nH_{2n-16} series can be assigned to tetrahydrocyclopentanophenanthrenes, hexahydropyrenes, hexahydrobenzfluorenes, and octahydrobenzophenanthrenes/anthracenes.

The 6 d.b. dicyclic aromatics account for 9.4 and 6.2 wt% of Wyodak and Kentucky coal-derived solvents, respectively (Table 2). The apparent concentrations for various Z series in FI mass spectra of 6 d.b. fractions (Figure 2) are given in Table 6. The C_nH_{2n-16} series dominates. The initial peak at M/Z 166 can be assigned to fluorene and a following peak at M/Z 180 can be assigned to C_1-fluorene and/or dihydrophenanthrene/anthracene. Other ring-types, such as phenylindans (M/Z 194) and phenyltetralins (M/Z 208) may overlap with alkylfluorenes. The C_nH_{2n-14} series overlaps with the $C_nH_{2n-16}O$ series and accounts for 3.6 wt% of the 6 d.b.W fraction and only 1.2 wt% of the 6 d.b.K fraction. A very low intensity of the peak at M/Z 154 (biphenyl) as compared with the intensity of the peak at M/Z 168 (dibenzofuran and/or C_1-biphenyl) implies that dibenzofurans dominate in this series.

The C_nH_{2n-18} series, with initial peaks at M/Z 206, 220, 234, etc., (Figure 2) can be assigned to tetrahydropyrenes, tetrahydrobenzfluorenes, and hexahydrobenzophenanthrenes/anthracenes, respectively. Cyclohexylfluorenes (M/Z 248) and cyclohexyldihydrophenanthrenes/anthracenes (M/Z 262) may also be present. Data in Table 6 show that the C_nH_{2n-18} series is represented by 0.8 wt% of the 6 d.b.K fraction and 0.6 wt% of the 6 d.b.W fraction.

Tricyclic aromatics. The tricyclic aromatic hydrocarbons (7 d.b. fraction) account for 13.5 and 11.2 wt% of Wyodak and Kentucky coal-derived recycle solvents, respectively (Table 2). The FI mass spectra of the 7 d.b.W and 7 d.b.K fractions are shown in Figure 2. Please note the differences in intensity scale. The apparent concentrations of the homologous series in the FI mass spectra of these fractions are given in Table 7. The C_nH_{2n-18} series dominates in both 7 d.b.W (9.4 wt%) and 7 d.b.K (5.4 wt%) fractions. Interestingly, phenanthrene and/or anthracene alone (peak at M/Z 178) accounts for 6.3 wt% of 7 d.b.W and only about 2.6 wt% of 7 d.b.K. However, the concentrations of alkyl-substituted phenanthrenes/anthracenes in both 7 d.b.W and 7 d.b.K are very similar and rapidly decrease with the increase of aliphatic carbon number: C_1 about 1.7 wt%, C_2 about 0.6 wt%, C_3 about 0.3 wt%, and C_4 about 0.2% wt%.

The C_nH_{2n-20} series includes unsubstituted and alkyl-substituted dihydropyrenes, dihydrobenzfluorenes, and tetrahydrobenzophenanthrenes/anthracenes as major components. Small amounts of cyclopentanophenanthrenes are also present. The concentration of the C_nH_{2n-20} series is slightly higher in 7 d.b.K (2.5 wt%) than in 7 d.b.W fraction (2.2 wt%). The C_nH_{2n-22} series accounts for 0.7 wt% in the 7 d.b.W fraction and 1.2 wt% in the 7 d.b.K fraction, and includes hexahydrobenzpyrenes, hexahydrodibenzfluorenes, and octahydrodibenzophenanthrenes/anthracenes. Small amount (0.6 wt% in Table 7) of unsubstituted through C_4-alkyl substituted dibenzothiphenes (M/Z 184, 198, 212, etc.) were also found.

Tetracyclic aromatics. The HPLC method enables separation of tetracyclic aromatics into 8 d.b. and 9 d.b. fractions. Because the concentration of 9 d.b. tetracyclic aromatics and greater polycyclic aromatic hydrocarbons was less than 2 wt% in both distillate recycle solvents (Table 2), only the 8 d.b.W and 8 d.b.K fractions were analyzed by FIMS. These two fractions account for 4.2 and 2.4 wt%, respectively. The FI mass spectra are shown in Figure 2. The apparent concentrations of the homologous series in the 8 d.b.W and 8 d.b.K are given in Table 8.

The C_nH_{2n-22} series accounts for 2.6 wt% in the 8 d.b.W fraction and 1.4 wt% in the 8 d.b.K fraction. The initial peak at M/Z 202 in this homologous series can be assigned to pyrene and/or fluoranthene. Similarly as in the case of tricyclic aromatics, the concentration of unsubstituted pyrene/fluoranthene (M/Z 202) is higher in the 8 d.b.W (about 1.4 wt%) than in 8 d.b.K (about 0.5 wt%). Alkyl substituted pyrenes/fluoranthenes may overlap with benzfluorenes (M/Z 216) and dihydrobenzophenanthrenes/anthracenes (M/Z 230). The C_nH_{2n-24} series is represented by 0.5 wt% of the 8 d.b.W and 0.4 wt% of the 8 d.b.K fraction. This homologous series includes tetrahydrobenzpyrenes (M/Z 256) and tetrahydrodibenzfluorenes (M/Z 270). An overlap with benzophenanthrenes/anthracenes (M/Z 228, 242, 256, etc.) is also possible.

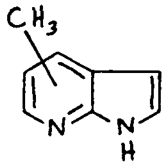
FIMS Analysis of Nitrogen Compounds.

Nitrogen compound fractions separated from hexane soluble oils (02W and 02K) and from toluene soluble-hexane insoluble asphaltenes (A2W and A2K) in each coal derived distillate recycle solvent (see Figure 1 and Table 1) were further analyzed by FIMS. The FI mass spectra of the 02W, 02K, A2W and A2K fractions are shown in Figure 3. The apparent concentrations of various homologous series in the FI mass spectra of the 02W and 02K fractions are given in Table 9. Nitrogen compounds belonging to homologous series from $C_nH_{2n-5}N$ (alkylpyridines and/or cyclohexylpyrroles) through C_nH_{2n-27} (dibenzcarbazoles) were found in oils of both distillate recycle solvents. This is consistent with the earlier results published by Schiller (17). Indoles ($C_nH_{2n-9}N$), carbazoles ($C_nH_{2n-15}N$), and benzcarbazoles ($C_nH_{2n-21}N$) are the major nitrogen compound types. The $C_nH_{2n-15}N$ series dominates in both the 02W (1.3 wt%) and 02K (1.6 wt%) fractions. The initial peak at M/Z 167 can be assigned to carbazole which alone accounts for almost 0.2 wt% in 02W and 0.3 wt% in 02K. The peaks at M/Z 181, 195, 209 and so on, correspond to C_1-, C_2-, C_3-alkylcarbazoles, respectively. Alkylcarbazoles up to about C_8 are present. The FI mass spectra alone, however, do not allow one to distinguish between various compound types within a given homologous series. For example, a peak at M/Z 181 can be assigned to methylcarbazole, dihydrobenzquinoline, and/or aminofluorene. All three compound types belong to the $C_nH_{2n-15}N$ series. The infrared spectra of the 02W and 02K fractions, which showed a strong absorption band at 3460 cm^{-1}, provided further support that carbazoles dominate in this homologous series. However, the infrared spectrum does not allow one to identify pyridine-type N as the characteristic absorption band around 1600 cm^{-1} interferes with the one for aromatic C-C. No absorption bands characteristic of $-NH_2$ were observed. The $C_nH_{2n-17}N$ series, represented by acridines/phenanthridines and tetrahydrobenzcarbazoles, accounts for 0.7 and 1.0 wt% in the 02W and 02K fractions, respectively.

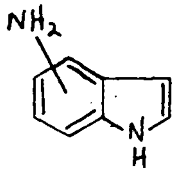
Quinolines and/or phenylpyrroles, $C_nH_{2n-11}N$, account for 0.4 and 0.5 wt% in the 02W and 02K fractions, respectively. The results in Table 9 also show that there is an overlap between some of the homologous series in the FI mass spectra. For example , a peak at M/Z 229 can be assigned to C_8-indole ($C_nH_{2n-9}N$) and/or to dibenzquinoline ($C_nH_{2n-23}N$). A bimodal distribution of peaks in this series implies that both homologous series are present. Similar interferences were found in the case of other homologous series (see Table 9). The nitrogen compound types identified in the FI mass spectra of the 02W and 02K fractions account for 4.8 and 6.6 wt%, respectively.

Non-nitrogen compounds found in these fractions are mostly represented by various alkyl substituted hydroxyl aromatics which interfere with nitrogen compounds during the chromatographic separation. This is also supported by infrared spectra of the 02W and 02K fractions which showed small absorption bands at about 3585 cm^{-1} characterisitc of free phenolic OH. Data in Table 9 show that hydroxyl aromatics which eluted together with nitrogen compounds are mainly represented by hydroxyl monocyclic aromatics. Steric hindrance of the hydroxyl group is a most likely reason for the earlier elution of these compounds.

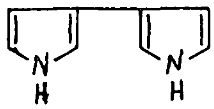
Small amounts of aromatic ketone-types which probably result from oxidation of aromatic hydrocarbons may also be present in the 02W and 02K fractions. The infrared spectra showed characteristic absorption bands at about 1700 cm^{-1}. The quantitative interpretation of FI mass spectra of A2W and A2K fractions (nitrogen compounds in asphaltenes) in Figure 3 was not attempted because of the complexity of these spectra. However, two prominent even-numbered nominal mass homologous series can be distinguished in both spectra. These imply the presence of diaza compounds. The first, with initial peaks at M/Z 132, 146, 160 etc., can most likely be assigned to diaza compound types described by the general formula $C_nH_{2n-8}N_2$. Four different diaza compound-types can be assigned to a peak at M/Z 132:



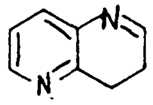
I



II

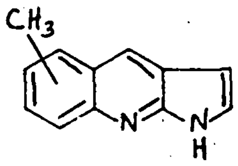


III



IV

Compound-types I and IV seem to be the most likely ones. The concentrations of the $C_nH_{2n-8}N_2$ series in A2W and A2K fractions are about the same. The second series with initial peaks at M/Z 182, 196, 210, etc., can be assigned to the $C_nH_{2n-14}N_2$ diaza compounds. The peak at M/Z 182 can be represented by the following diaza compound-types:



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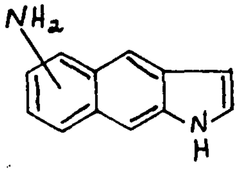

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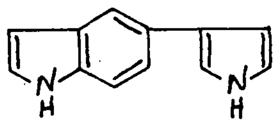
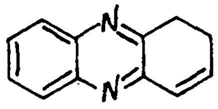


III



IV

Again compound-types I and IV seem to be the most likely ones. The concentration of the $C_nH_{2n-14}N_2$ series is considerably higher in the A2W than the A2K fraction.

The same odd-numbered nominal mass homologous series that were found in the 02W and 02K fractions (nitrogen compounds in oils see Table 9) were also found in the A2W and A2K fractions (nitrogen compounds in asphaltenes). The major differences were concentrations of components within overlapping homologous series. A more aromatic (lower Z number) series prevailed in the A2W and A2K fractions. The FI mass spectrum of the A2W fraction in Figure 3 shows a prominent odd-numbered nominal mass series with initial peaks at M/Z 339, 353, 367, etc., which is not present in the A2K fraction.

FIMS Analysis of Hydroxyl Aromatics.

Figure 4 shows FI mass spectra of hydroxyl aromatic 03W, 03K, and A3W, A3K fractions which were separated from oils and asphaltenes in Wyodak and Kentucky

9/14 coal derived distillate recycle solvents. The structural assignments for hydroxyl aromatics were based on initial peaks in the FI mass spectra and a very strong infrared absorption band at 3585 cm^{-1} that is characteristic of free phenolic-OH group. In addition, infrared spectra of these fractions showed a very broad band around 3200 cm^{-1} which is due to hydrogen bonding. The apparent concentrations of various homologous series in FI mass spectra of the 03W and 03K fractions from $C_nH_{2n-6}O$ through $C_nH_{2n-24}O$ are given in Table 10. Interestingly, a better liquefaction solvent which was derived from Kentucky 9/14 coal has a much higher concentration of the $C_nH_{2n-8}O$ series than Wyodak coal derived solvent; 2.1 and 0.9 wt% in 03 fraction, respectively. The initial peak at M/Z 134 in this series can be assigned to indanol and a following peak at M/Z 148 to C_1-indanol and/or tetrahydronaphthol. The $\geq C_6$ indanols and $\geq C_5$ tetrahydronaphthols (M/Z 218, 232, 246, etc.) overlap in the FI mass spectra with the $C_nH_{2n-22}O$ series (hydroxypyrenes and hydroxybenzfluorenes). The $C_nH_{2n-6}O$ series, including C_2 through C_8 alkylphenols, accounts for 0.6 wt% in 03W and 0.9 wt% in 03K fraction. The $\geq C_9$ alkylphenols overlap with the $C_nH_{2n-20}O$ series. The latter can be assigned to phenylnaphthols, hydroxydihydropyrenes, and hydroxytetrahydrobenzphenanthrenes/anthracenes. The $C_nH_{2n-10}O$ series with initial peaks at M/Z 174, 188, 202, etc., can be assigned to hydroxytetrahydroacenaphthenes, hydroxyhexahydrofluorenes, and hydroxyoctahydrophenanthrenes/anthracenes, respectively. Components of this homologous series overlap with the $C_nH_{2n-24}O$ series. The homologous series $C_nH_{2n-14}O$, $C_nH_{2n-16}O$, and $C_nH_{2n-18}O$, show very broad monomodal molecular weight distributions indicating considerable alkyl substitution of hydroxyaromatic ring systems. The $C_nH_{2n-14}O$ series with initial peak at M/Z 170 can be assigned to phenylphenols and/or hydroxyacenaphthenes having alkyl substituents up to about C_{20}. The $C_nH_{2n-16}O$ series includes fluorenols (M/Z 182) and hydroxydihydrophenanthrenes/anthracenes (M/Z 196). Again, alkyl substituents up to about C_{20} are present. The $C_nH_{2n-18}O$ series with the initial peak at M/Z 194 can be assigned to hydroxyphenanthrenes/anthracenes. This homologous series may also include such compound types as hydroxytetrahydropyrenes (M/Z 222), hydroxytetrahydrobenzfluorenes (M/Z 236), and hydroxyhexahydrobenzphenanthrenes/anthracenes (M/Z 250). The hydroxyl aromatics identified in the FI mass spectra of O3W and O3K fractions account for 15.6 and 14.7 wt%, respectively.

Figure 4 also shows FI mass spectra of hydroxyl aromatic A3W and A3K fractions which were separated from hexane insoluble-toluene soluble asphaltenes (see Figure 1 and Table 1). The complexity of these spectra does not allow a detailed interpretation and quantification of the results. However, two prominent mass series can be distinguished. Both can most likely be assigned to dihydroxyl aromatics. The first, $C_nH_{2n-14}O_2$, is represented by biphenols. The initial peak at M/Z 186 is assigned to unsubstituted biphenols. Alkyl substituted biphenols (peaks at M/Z 200, 214, 228, 242, 256, 270, and so on) prevails with the C_2-biphenol (M/Z 214) being the most prominent one. The distribution of biphenols in the A3W and A3K fractions is very similar. The second series, $C_nH_{2n-16}O_2$, is represented by dihydroxyl fluorenes. The initial peak at M/Z 198 is assigned to unsubstituted dihydroxylfluorenes. The C_2-dihydroxylfluorenes (M/Z 226) prevail in the A3W and A3K fraction. However, the concentration of the $C_nH_{2n-16}O_2$ series in the A3W fraction is higher than in the A3K fraction (see Figure 4).

A detailed comparison between the FI mass spectra of hydroxyl aromatics in oils and in asphaltenes (Figure 6) showed that the same homologous series are present in both solvent-derived fractions. For example, the $C_nH_{2n-8}O$ and $C_nH_{2n-22}O$ homologous series are present in both oils and asphaltenes. Asphaltenes, however, contain significantly greater amounts of components in the $C_nH_{2n-22}O$ series. This trend was also observed for other homologous series.

SUMMARY AND CONCLUSIONS

Results of this work demonstrate the necessity for a high degree of sample separation followed by a detailed characterization of the fractions in order to provide adequate compositional information. The yields of solvent-derived and compound-class fractions alone do not explain the differences in liquefaction behavior between the two coal-derived distillate recycle solvents. The use of HPLC and FIMS for analysis of hydrocarbon fractions was essential to reveal the important compositional differences between the two solvents. The better, Kentucky 9/14 coal-derived distillate was shown to have a high concentration of various hydroaromatic types (good hydrogen donors) and a low concentration of unsubstituted phenanthrenes/anthracenes and pyrenes/fluoranthenes: Hydrocarbon data in Tables 4 through 8 were combined to find the ratio of aromatic types to hydroaromatic types, resulting in approximate values of 0.9 and 0.5 for the Wyodak and Kentucky distillates, respectively. The FIMS analyses of nitrogen compound fractions separated from Wyodak and Kentucky coal derived distillate recycle solvents show considerable similarities between the two samples. Indoles, carbazoles, and benzcarbazoles dominate in both solvents. The FIMS analyses of hydroxyl aromatics revealed that the better Kentucky 9/14 coal derived recycle solvent contains higher concentrations of various hydroxyhydroaromatics: Data in Tables 9 and 10 were combined to find the ratio of hydroxyaromatic types to hydroxyhydroaromatic types, resulting in approximate values of 0.9 and 0.7 for the Wyodak and Kentucky distillates, respectively. The FIMS analyses of nitrogen compounds and hydroxyl aromatics also show that further separation into various compound types would be needed in order to facilitate the interpretation of the FI mass spectra.

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Table 1. Results of separation of coal-derived distillate recycle solvents into solvent-derived and compound-class fractions.

Fraction[1]	Wt% in distillate recycle solvent derived from	
	Wyodak coal	Kentucky 9/14 coal
Hydrocarbons, Fr. 01	62.9	61.5
Nitrogen compounds, Fr. 02	8.3	11.4
Hydroxyl aromatics, Fr. 03	23.3	18.9
Hexane soluble oils	94.5	91.8
Hydrocarbons, Fr. A1	0.2	0.2
Nitrogen compounds, Fr. A2	0.6	1.0
Hydroxyl aromatics, Fr. A3	3.5	4.7
Toluene soluble-hexane insoluble asphaltenes	4.3	5.9
Pyridine soluble-toluene insoluble preasphaltenes	0.6	2.3

[1] see Figure 1.

Table 2. Results of separation of hydrocarbons on semipreparative μ-Bondapak NH_2 column.

Compound-Type	Fraction	Wt% in distillate recycle solvent derived from	
		Wyodak coal	Kentucky 9/14 coal
Saturates	SAT	5.7	4.4
Monoaromatics	3 d.b.	3.2	6.2
Dicyclic aromatics	5 d.b.	19.8	24.4
	6 d.b.	9.4	6.2
Tricyclic aromatics	7 d.b.	13.5	11.2
Tetracyclic aromatics	8 d.b.	4.2	2.4
	9+ d.b.	1.5	1.8
TOTAL:		57.3[1]	56.6[2]

[1] 91.1% recovery

[2] 91.9% recovery

Table 3. Apparent concentrations for various Z series in FI mass spectra of SAT W and SAT K fractions.

Z in C_nH_{2n+Z}	Compound Types	Wt% (in distillate) SAT W	SAT K
+2	Acyclic alkanes	1.0	0.9
0	Monocyclic alkanes	1.0	0.7
−2	Dicyclic alkanes eg. hexahydroindanes, decalins, bicyclohexanes	0.8	0.5
−4	Tricyclic alkanes eg. perhydrofluorenes, perhydrophenanthrenes/anthracenes, tricyclic terpanes	0.8	0.6
−6	Tetracyclic alkanes eg. perhydropyrenes/fluoranthenes, perhydrobenzfluorenes, perhydrobenzphenanthrenes/anthracenes, steranes	0.8	0.7
−8	Pentacyclic alkanes eg. perhydrobenzpyrenes, perhydroperylenes, perhydrodibenzphenanthrenes/anthracenes, hopanes	0.6	0.5
−10	Hexacyclic alkanes (possible overlap with tetrahydroacenaphthenes, hexahydrofluorenes, and octahydrophenanthrenes/anthracenes	0.4	0.3
	TOTAL:	5.4	4.2

Table 4. Apparent concentrations for various Z series in FI mass spectra of 3 d.b.W and 3 d.b.K fractions.

Z in C_nH_{2n+Z}	Compound Type	Wt% (in distillate) 3 d.b.W	 3 d.b.K
-6	Alkylbenzenes	0.3	0.3
-8	Indanes, tetralins, cyclohexylbenzenes	1.1	2.2
-10	Tetrahydroacenaphthenes, hexahydrofluorenes, octahydrophenanthrenes/anthracenes	1.0	2.5
-12	Decahydropyrenes/fluoranthenes dodecahydrobenzofluorenes, dodecahydrobenzophenanthrenes/anthracenes, octahydrocyclopentanophenanthrenes	0.4	0.7
-14	Tetradecahydrodibenzphenalenes, hexadecahydropicenes, and overlap with acenaphthenes, tetrahydrophenanthrenes/anthracenes	0.2	0.3
	TOTAL	3.0	6.0

Table 5. Apparent concentrations for various Z series in FI mass spectra of 5 d.b.W and 5 d.b.K fractions

Z in C_nH_{2n+Z}	Compound Type	Wt% (in distillate) 5 d.b.W	Wt% (in distillate) 5 d.b.K
-12	Naphthalenes	6.3	7.4
-14	Acenaphthenes, tetrahydrophenanthrenes/anthracenes	9.2	11.0
-16	Tetrahydrocyclopentanophenanthrenes, hexahydropyrenes/fluoranthenes, hexahydrobenzofluorenes, octahydrobenzophenanthrenes/anthracenes	2.5	3.7
-18	Hexahydrocyclopentanopyrenes, decahydrobenzopyrenes, and overlap with hexahydrobenzophenanthrenes/anthracenes	0.6	0.8
	TOTAL	18.6	22.9

Table 6. Apparent concentrations for various Z series in FI mass spectra of 6 d.b.W and 6 d.b.K fractions.

Z in C_nH_{2n+Z}	Compound Type	Wt% (in distillate) 6 d.b.W	Wt% (in distillate) 6 d.b.K
-14	Biphenyls and dibenzofurans ($C_nH_{2n-16}O$)	3.6	1.2
-16	Fluorenes, dihydrophenanthrenes/anthracenes	4.4	3.0
-18	Tetrahydropyrenes, tetrahydrobenzfluorenes, hexahydrobenzophenanthrenes/anthracenes (possible small overlap with phenanthrenes/anthracenes)	0.6	0.8
-20	Most likely overlap with tricyclic aromatics	0.4	0.5
	TOTAL	9.0	5.5

Table 7. Apparent concentrations for various Z series in FI mass spectra for 7 d.b.W and 7 d.b.K fractions.

Z		Wt% (in distillate)	
in C_nH_{2n+Z}	Compound Type	7 d.b.W	7 d.b.K
-18	Phenanthrenes/anthracenes	9.4	5.4
-20	Dihydropyrenes, dihydrobenzfluorenes, tetrahydrobenzophenanthrenes/anthracenes, cyclopentanophenanthrenes	2.2	2.5
-22	Dihydrocyclopentanoaceanthrylenes, tetrahydrocyclopentanochrysenes, hexahydrobenzpyrenes, hexahydrodibenzfluorenes, octahydrodibenzophenanthrenes/anthracenes	0.7	1.2
-24	Dihydrodicyclopentanopyrenes, hexahydrocyclopentanobenzpyrenes, octahydrocyclopentanopicenes, decahydrodibenzpyrenes	0.3	0.5
-16S	Dibenzothiophenes ($C_nH_{2n-16}S$)	0.6	0.6
	TOTAL	13.2	10.2

Table 8. Apparent concentrations for various Z series in FI mass spectra for 8 d.b.W and 8 d.b.K fractions.

Z in C_nH_{2n+Z}	Compound Type	Wt% (in distillate) 8 d.b.W	Wt% (in distillate) 8 d.b.K
-22	Pyrenes, fluoranthenes, benzfluorenes	2.6	1.4
-24	Cyclopentanopyrenes, tetrahydrobenzpyrenes, tetrahydrodibenzfluorenes	0.5	0.4
-26	Dicyclopentanopyrenes, octahydrodibenzpyrenes	0.4	0.2
-28	Tetrahydrodicyclopentanoperylenes, decahydrobenzanthanthrenes, octahydrocyclopentanodibenzpyrenes	0.2	0.1
	TOTAL	3.7	2.1

Table 9. Apparent concentrations of various Z series in FI mass spectra of nitrogen compound fractions 02W and 02K.

Z Series	M/Z range	$C_nH_{2n+Z}N$ Compound Types	Wt% (in distillate)	
			02W	02K
-5	121 - 191	Alkylpyridines, cyclohexylpyrroles	0.1	0.1
	205 - 443	above overlap with $C_nH_{2n-19}N$ eg. phenylquinolines, diphenylpyrroles	0.4	0.6
-7	133 - 189	Tetrahydroquinolines, dihydroindoles	0.1	0.2
	203 - 441	above overlap with $C_nH_{2n-21}N$ eg. azapyrenes, benzcarbazoles	0.5	0.8
-9	117 - 215	Indoles	0.3	0.2
	229 - 453	above overlap with $C_nH_{2n-23}N$ eg. dibenzquinolines	0.3	0.5
-11	129 - 241	Quinolines, phenylpyrroles	0.4	0.5
	255 - 451	above overlap with $C_nH_{2n-25}N$ eg. phenylbenzquinolines, biphenylindoles	0.2	0.3
-13	169 - 253	Benzylpyridines, dihydrobenzindoles	0.3	0.5
	267 - 449	above overlap with $C_nH_{2n-27}N$ eg. dibenzcarbazoles	0.2	0.3
-15	167 - 433	Carbazoles, dihydrobenzquinolines	1.3	1.6
-17	179 - 445	Acridines/phenanthridines, tetrahydrobenzcarbazoles	0.7	1.0
		TOTAL Nitrogen Compound Types	4.8	6.6
Z Series	M/Z range	Interfering $C_nH_{2n+Z}O$ Compound Types		
-6 (-20)	122 - 444	Alkylphenols	0.5	0.4
-8 (-22)	148 - 442	Tetrahydronaphthols, cyclohexylphenols	0.5	0.5
-10(-24)	174 - 440	Hydroxytetrahydroacenaphthenes, hydroxyoctahydrophenanthrenes/anthracenes	0.4	0.4
-12	186 - 438	Alkylnaphthols, > C_3	0.3	0.3
-14	184 - 436	Benzylphenols	0.4	0.4
-16	182 - 434	Fluorenols	0.4	0.5
		TOTAL Hydroxyl Aromatic Types	2.5	2.5

Table 10. Apparent concentrations of various Z series in FI mass spectra of hydroxyl aromatic fractions 03W and 03K.

Z Series	M/Z range	$C_nH_{2n+Z}O$ Compound Types	Wt% (in distillate) 03W	03K
-6	122 - 206	Alkylphenols C_2 through C_8	0.6	0.9
	220 - 500	above overlap with $C_nH_{2n-20}O$ eg. phenylnaphthols, hydroxydihydropyrenes	2.2	1.5
-8	134 - 204	Indanols, tetrahydronaphthols, cyclohexylphenols	0.9	2.1
	218 - 498	above overlap with $C_nH_{2n-22}O$ eg. hydroxypyrenes	2.2	1.7
-10	174 - 244	Hydroxytetrahydroacenaphthenes, hydroxyoctahydrophenanthrenes/anthracenes, hydroxyhexahydrofluorenes	0.3	0.5
	258 - 496	above overlap with $C_nH_{2n-24}O$ eg. hydroxybenzphenanthrenes/anthracenes	1.5	1.2
-12	144 - 494	Naphthols, hydroxydihydroacenaphthenes, hydroxyhexahydrophenanthrenes/anthracenes	1.8	1.5
-14	170 - 492	Phenylphenols, hydroxyacenaphthenes, hydroxytetrahydrophenanthrenes/anthracenes	2.2	2.2
-16	182 - 490	Fluorenols, hydroxydihydrophenanthrenes/anthracenes	2.2	2.0
-18	194 - 488	Hydroxyphenanthrenes/anthracenes	1.7	1.3
		TOTAL hydroxyl aromatic types	15.6	14.9

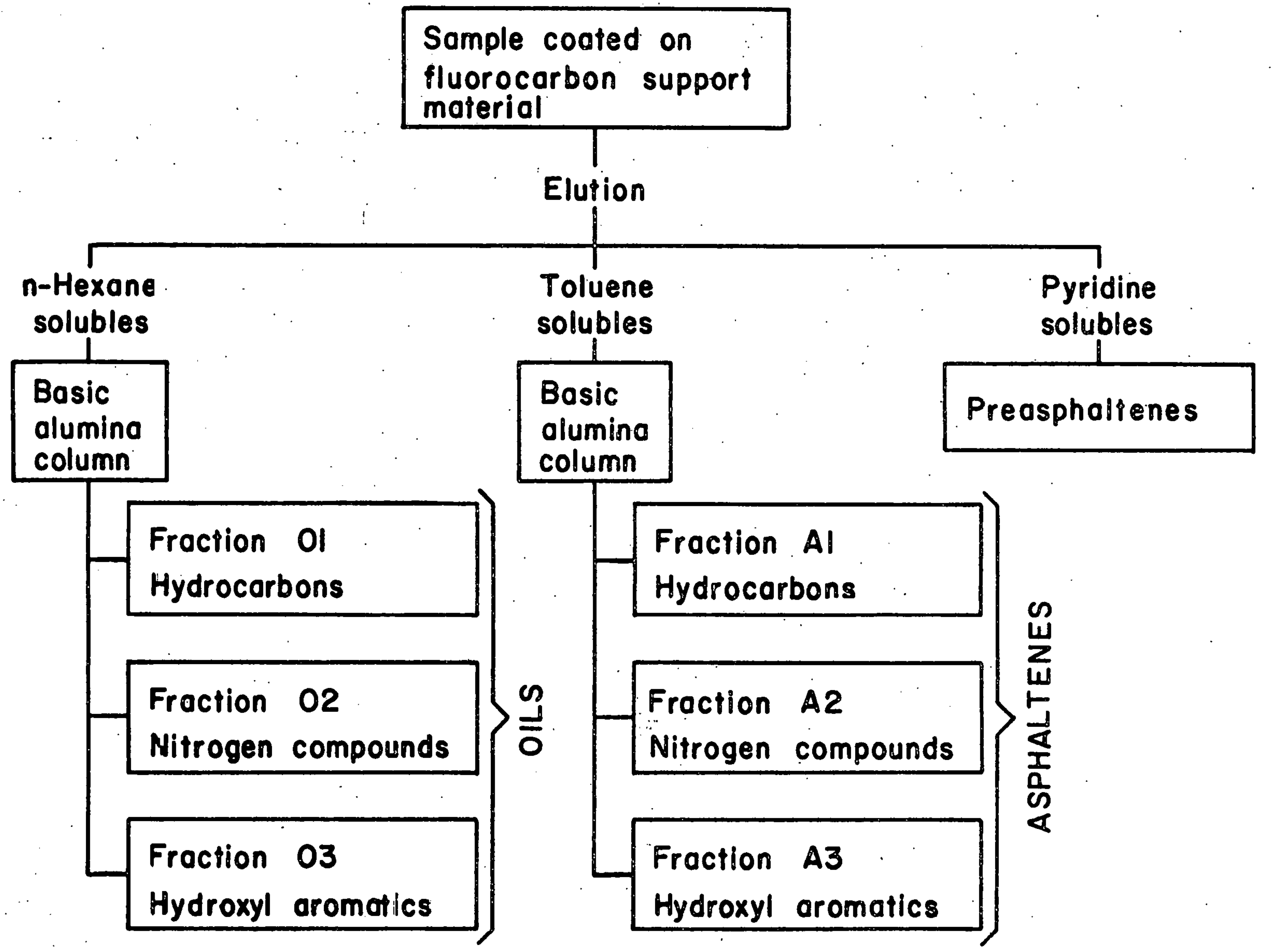
FIGURE CAPTIONS.

Figure 1. Separation scheme for coal derived liquids.

Figure 2. FI mass spectra of saturate (SAT) and monocyclic (3 d.b.) through tetracyclic (8 d.b.) aromatic hydrocarbon fractions in Wyodak (W) and Kentucky (K) coal derived distillate recycle solvents.

Figure 3. FI mass spectra of nitrogen compound fractions in hexane soluble oils (02) and toluene soluble-hexane insoluble asphaltenes (A2) from Wyodak (W) and Kentucky (K) coal derived distillate recycle solvents.

Figure 4. FI mass spectra of hydroxyl aromatic fractions in hexane soluble oils (03) and toluene soluble-hexane insoluble asphaltenes (A3) from Wyodak (W) and Kentucky (K) coal derived distillate recycle solvents.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Basic alumina column
Basic alumina column
Preasphaltenes
Fraction O1 Hydrocarbons
Fraction O2 Nitrogen compounds
Fraction O3 Hydroxyl aromatics
OILS
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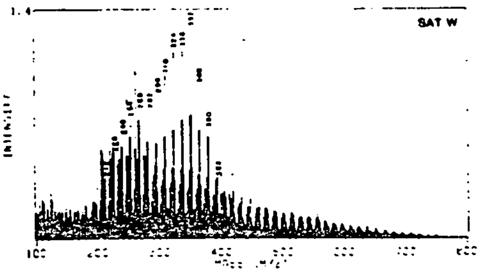
Fraction A2 Nitrogen compounds
Fraction A3 Hydroxyl aromatics
ASPHALTENES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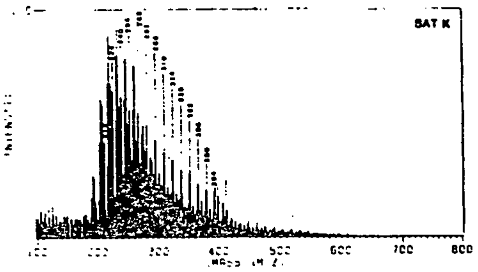
MASS (M/Z)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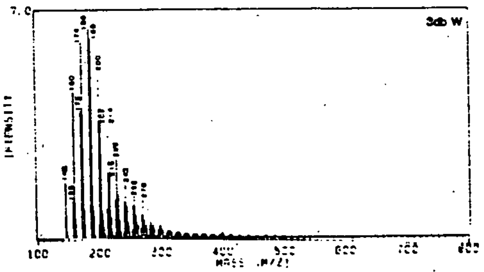
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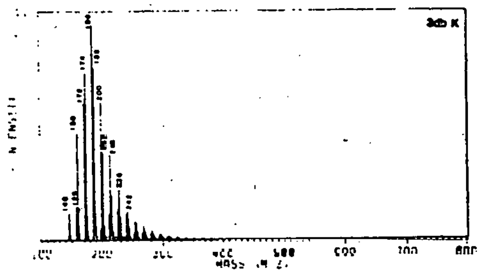
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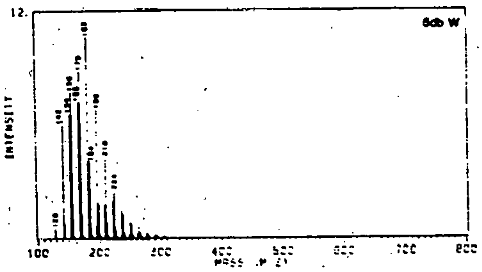
MASS (M/Z)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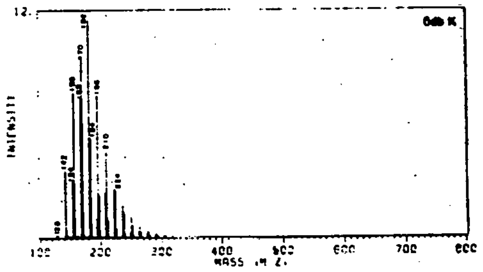
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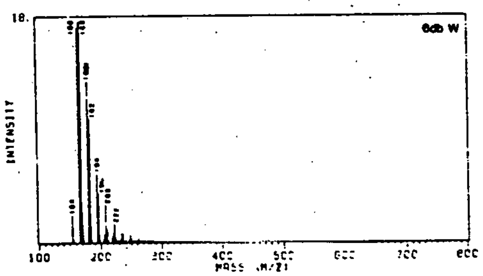
MASS (M/Z)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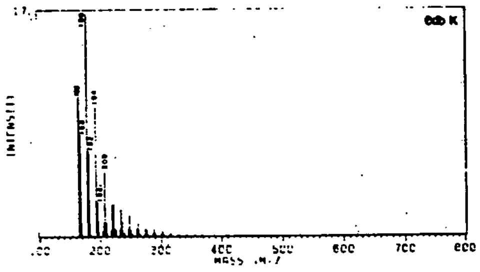
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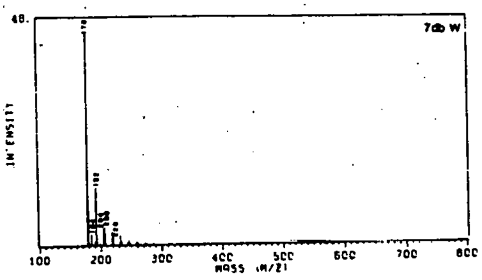
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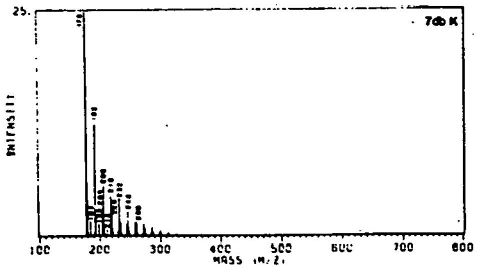
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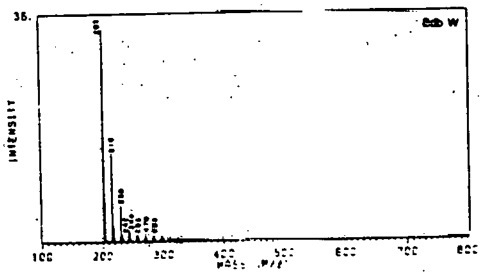
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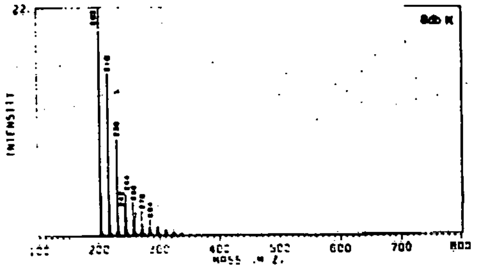
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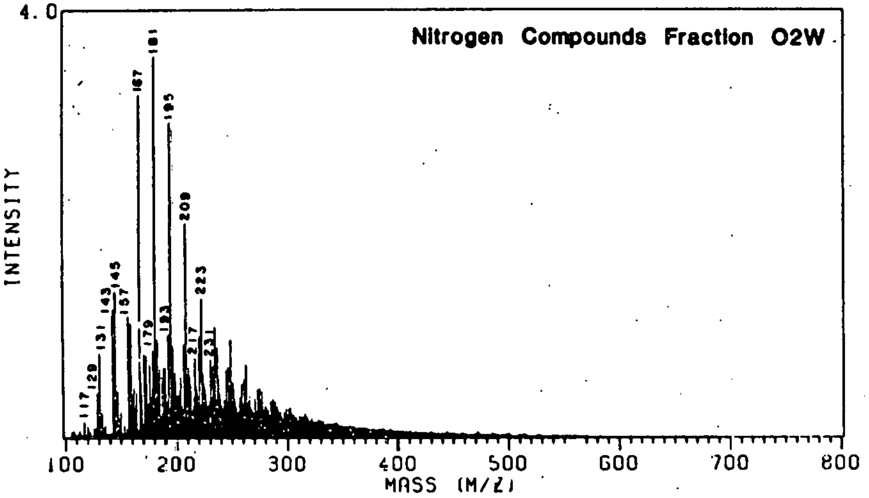
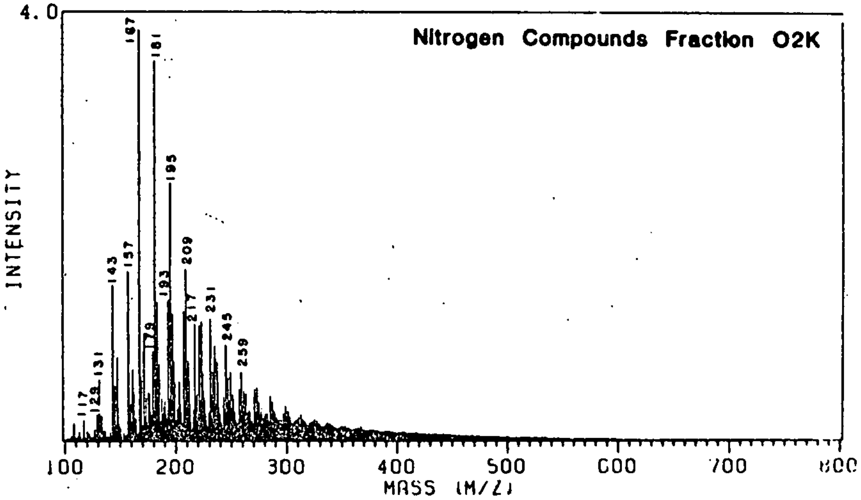
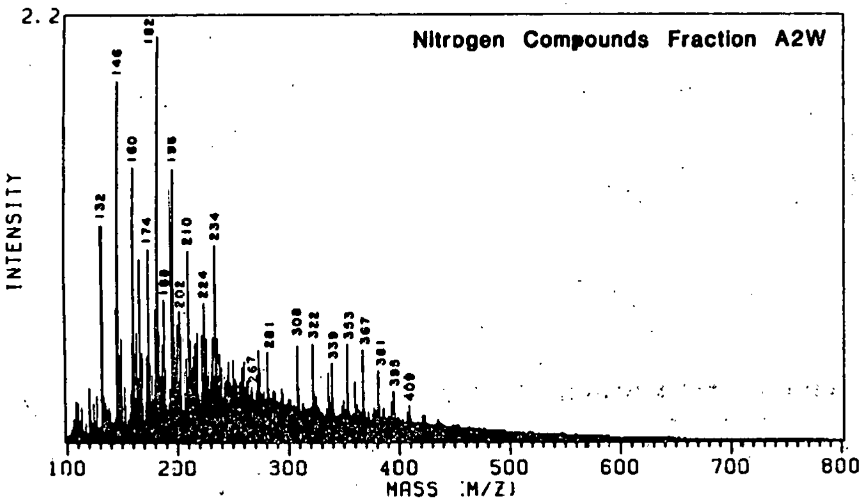
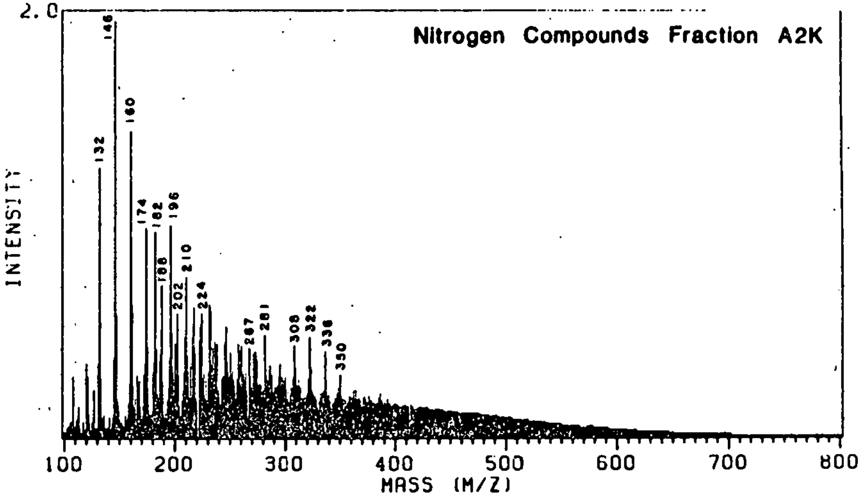
MASS (M/Z)









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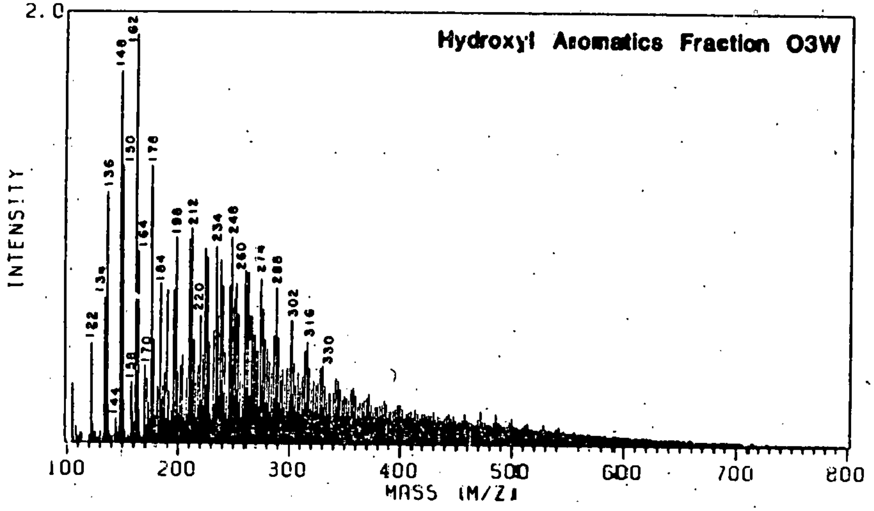

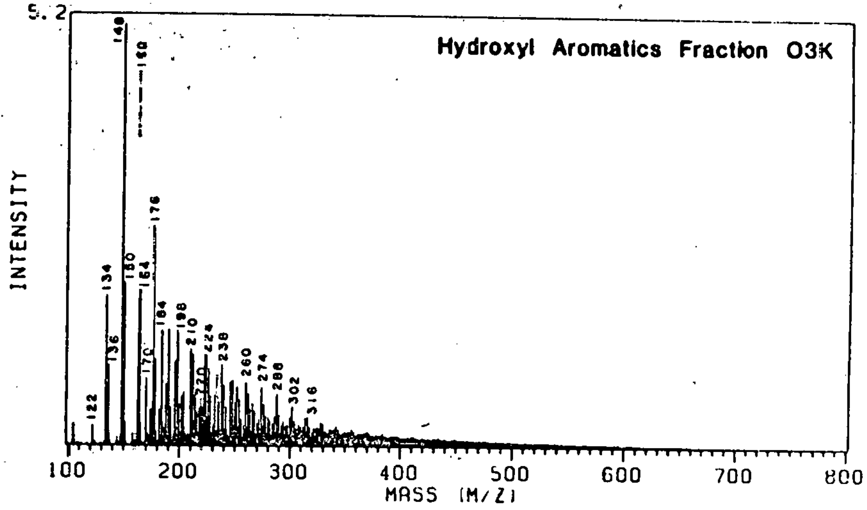

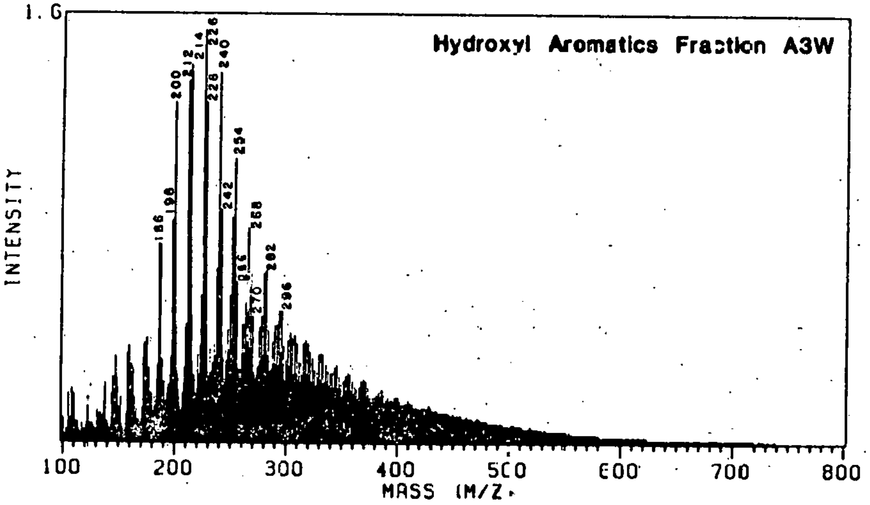

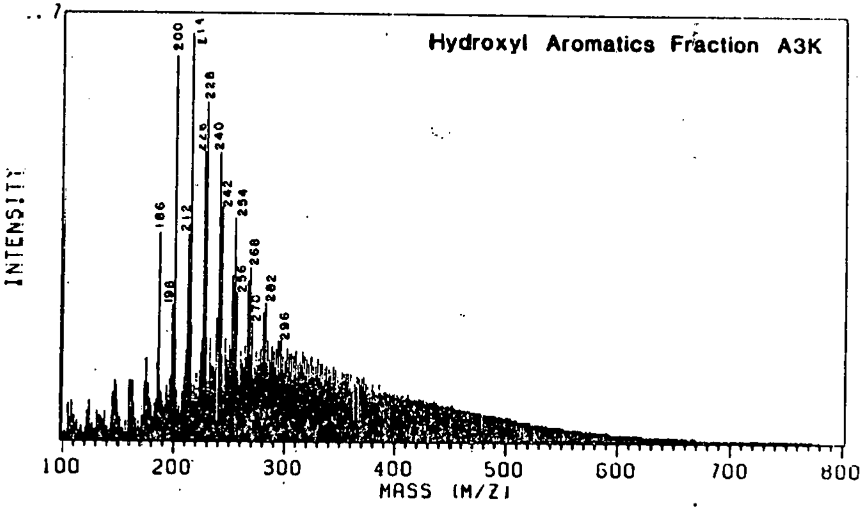

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