BERC-0020-2

MASS SPECTROMETRIC ANALYTICAL SERVICES AND RESEARCH ACTIVITIES TO SUPPORT COAL-LIQUID CHARACTERIZATION RESEARCH

Quarterly Report for the Period
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Stuart E. Scheppele

The Oklahoma State University
Department of Chemistry
Stillwater, Oklahoma 74074

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DISCLAIMER

ABSTRACT

Interfacing of the Perkin Elmer model 3920 gas chromatograph with the CEC 21-110B mass spectrometer has been completed and the GC/MS system is presently being made operational. Detailed descriptions of the heated-probe assembly and the rapid mass-scanning module are given.

The field ionization (FI) source for the CEC 21-110B mass spectrometer is routinely operational. Reproducibility of ion abundances using this source has been investigated using a Synthoil sample and a sample of hydrogenated anthracene oil. For both samples the average percent deviations in the ion abundances are 8.90% and 9.48%, respectively. Application of the technique of FI mass spectrometry to semi-quantitative analysis of coal type mixtures has been explored using known samples. The consequences of sensitivity data on the analytical results have been considered. For known samples relative weight and relative mole sensitivities have been determined with respect to naphthalene. Although inclusion of sensitivity data increases the accuracy of the analysis, reasonable estimates of sample composition can be obtained without their use.

OBJECTIVE AND SCOPE OF WORK

The objective of this program is to obtain qualitative and semi-quantitative information concerning the composition of synthetic fuels and related materials using the technique of mass spectrometry. Information relating to the compound types and/or compounds present in a sample will be obtained from high resolution electron-impact and field-ionization mass spectral, low-resolution field-ionization mass spectral, and combination gas-chromatographic/electron-impact and field-ionization mass spectral data. Field-ionization ion abundances and gas chromatograms will be used to arrive at semi-quantitative estimates of sample composition. Known mixtures of compounds structurally related to those either believed or shown to be present in these samples will be investigated with the view of 1) determining sensitivities towards field ionization and 2) ascertaining for sample quantification the accuracy obtained by various techniques, e.g., low-voltage electron-impact and field-ionization mass spectrometry and various methods of chromatography.

In this research program, attention will, as required, be devoted to the modification of existing and/or the development of new techniques associated with the mass spectral analysis of fossil fuels.

SUMMARY OF PROGRESS TO DATE

Commitments to provide high resolution mass spectral data and assignments of elemental compositions based upon these data are being met. Assembly of proposed equipment, use of the field ionization technique, and determination of analytical data from various techniques are on schedule, if not somewhat ahead.

The principal investigator has devoted ca. 10% of his time to this quarter and will devote 10% of his time to the project in the next quarter.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Gas Chromatography-Mass Spectrometry

Interfacing of a Perkin Elmer model 3920 gas chromatograph with the CEC 21-110B mass spectrometer has been completed and the GC/MS system is presently being made operational. The major difficulties encountered in interfacing the two instruments were the incorporation of the molecular separator into the GC and construction of the heated inlet system. As shown in Figure 1, a single-jet molecular separator obtained from R. H. Allen and Co. was placed in the manifold oven of the GC. The effluent of the chromatographic column is split and passed both to the flame-ionization detector and mass spectrometer. A Nupro high-vacuum--high-temperature valve preceeds the separator. The valve permits removal and replacement of gas chromatographic columns without requiring removal of the heated-inlet system from the mass spectrometer. Since the manifold oven can be heated to ca. 400°, a separate heating system was not required for the jet separator. The 1/4" glass tube exiting the manifold, however, did require external heating. The section of tubing between the manifold oven and the GC chassis was wrapped with nichrome wire and the tubing heated by passing current through the wire. Similarly, the 1/4" to 1/16" reducer and the glass tubing exiting the GC chassis is heated electrically; both sections can be heated to ca. 350°.

The probe used for introduction of the GC effluent to the mass spectrometer is shown in Figure 2. The 1/16" stainless steel capillary tubing is electrically insulated from the 1/4" stainless steel tubing by encassing the former in glass. Silver soldering of the capillary tubing in the 1/4" tube provides electrical connection at the end of the probe. Both the capillary and 1/4" tubes are isolated from the mass spectrometer high voltage by attaching a ceramic probe tip. The capillary tubing is ca. 3.5 feet long and can be maintained at ca. 280° using an AC power supply.

The probe is inserted into the mass spectrometer via the conventional solid-introduction system. The pressure in the ion source is ca. 1.5×10^{-5} mm with a helium flow rate of 25 ml/min.

Since the magnetic sector on the mass spectrometer does not allow for rapid mass scanning, a fast-scanning module was constructed as shown in Figure 3. The basic electronic design was obtained from Dr. R. D. Grigsby of Texas A & M University. The original design, however, was not compatible with our magnetic sector and required some modifications. In the present configuration, the upper and lower limits to the magnetic field strength and the scan rate can be controlled. The scan rate is variable from ca. 30 to 10 seconds per decade. Due to the response of the magnetic field the latter value constitutes the maximum scan rate for routine operation. However, the rate can be easily increased by decreasing the RC time constant of the capacitor in parallel with operational amplifier (EU-900 NC).

Field Ionization Mass Spectrometry

The field ionization (FI) source for the CEC 21-110B mass spectrometer was constructed and made routinely operational by Mr. G. J. Greenwood (1). Since the FI

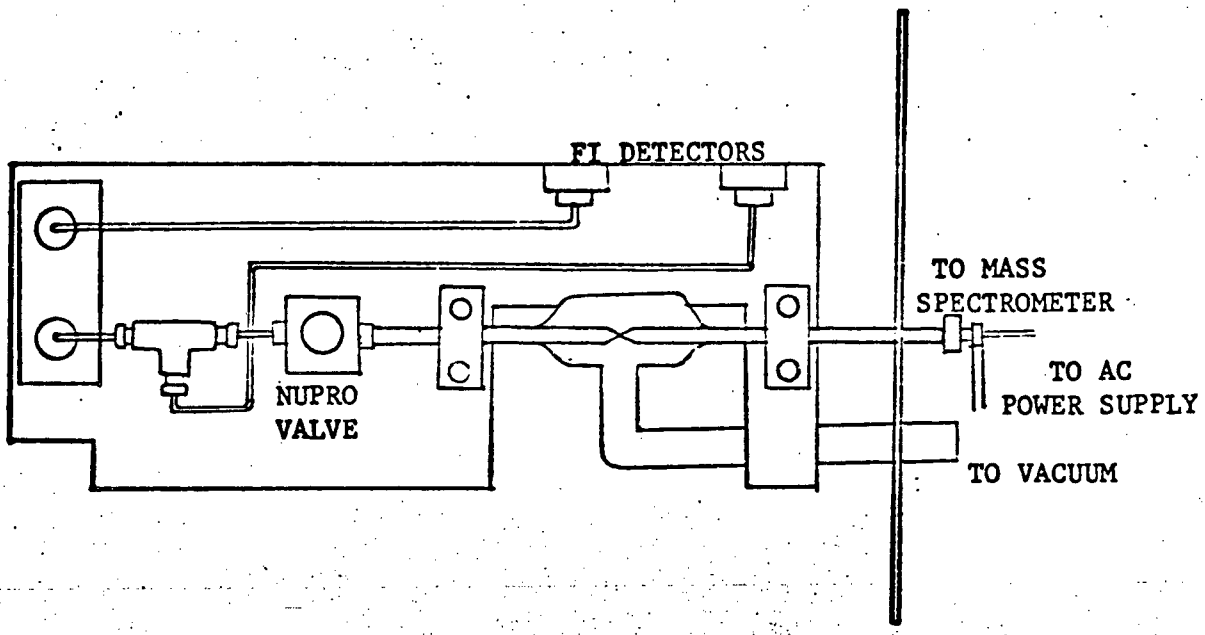


Figure 1. GC Manifold Oven and Molecular Separator Assembly

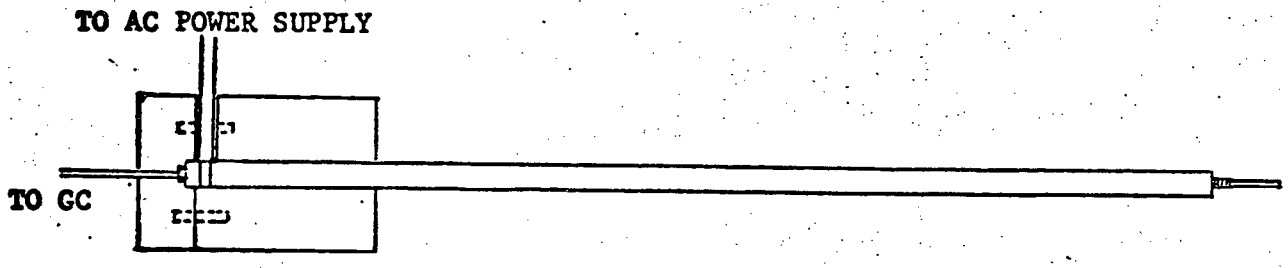


Figure 2. Gas Chromatographic Probe Assembly

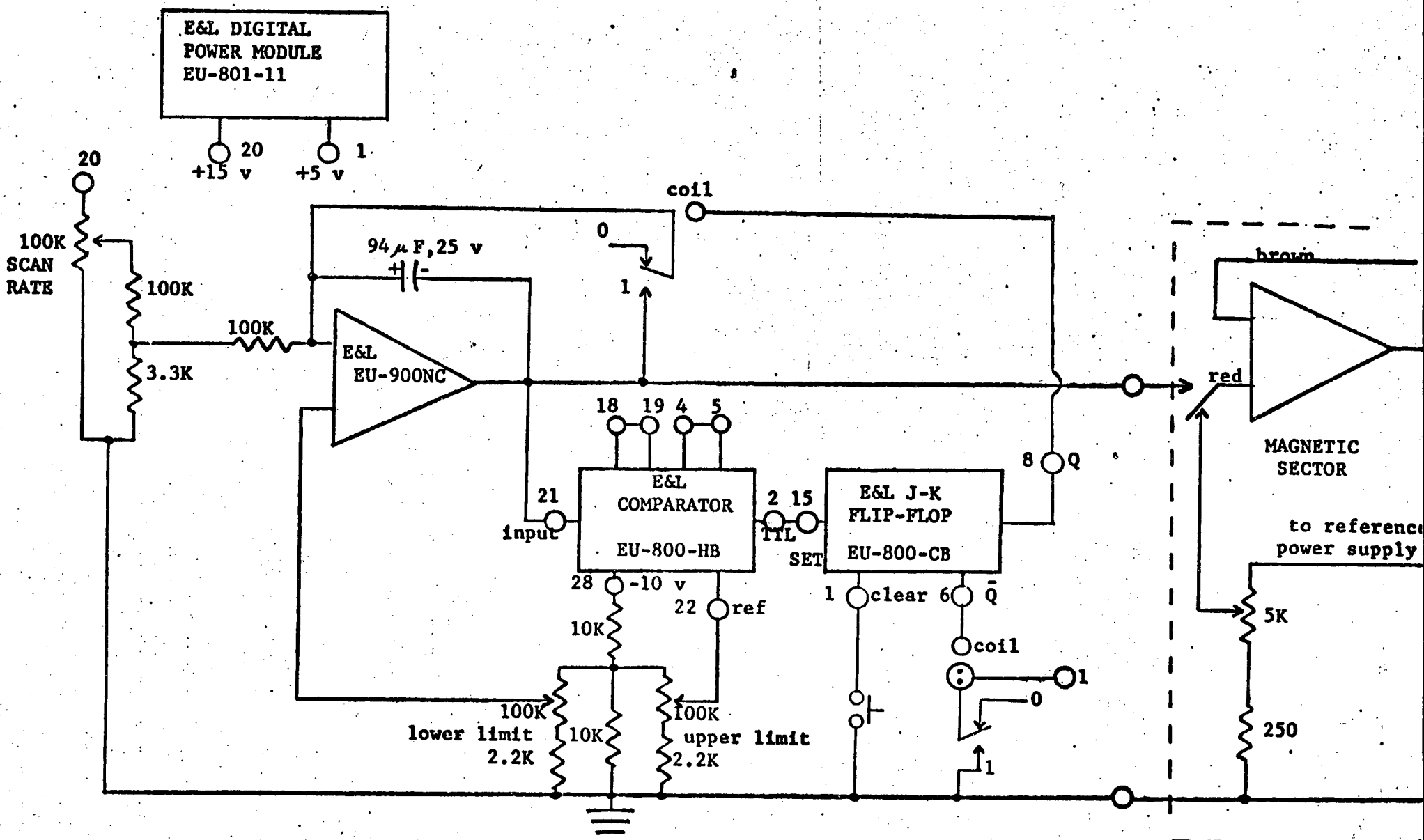


Figure 3. Fast-Scanning Module for CEC 21-110B Mass Spectrometer

system will be used on both ERDA projects, a joint effort was initiated to determine its performance and to investigate its applicability to the semi-quantitative analysis of mixtures. Thus the following discussion and results is a synthesis of the combined efforts of Dr. P. L. Grizzle on this project and Mr. G. J. Greenwood on ERDA project number E(49-18)-2011 (2).

Performance of FI Source

A number of studies were made to check on the reproducibility of the FI spectra from one emitter to another and as a function of time, age of a given emitter, alignment of the emitter with respect to the slit in the field-ionization electrode, and various operating voltages of the mass spectrometer. Tables I and II present typical relative abundance data for a hydrocarbon + ether fraction obtained from separation of a sample of hydrogenated anthracene oil (reactor sample 1, see ref. 3) and the percent total ionization for a fraction obtained from a Synthoil sample by gel permeation chromatography (4), respectively. The reproducibility of the relative ion abundances and the percent total ionization as a function of instrumental parameters is seen to be quite satisfactory. For all ions, the average percent standard deviation is 9.48% from four spectra of reactor sample 1 and 8.90% from three spectra of the Synthoil fraction. It is thus encouraging to note that the reproducibility of the FI relative ion abundances compares well with the reproducibility of the EI relative abundances we have obtained from the CEC 21-110B and CEC 21-103(4) mass spectrometers.

Use of Field Ionization Mass Spectrometry for Semiquantitative Analysis

Before comparing the results, it is appropriate to briefly consider those factors which relate instrument output to sample composition and their effect on the final analytical data.

The following equations which are derived for a two-component mixture can be generalized to a multi-component mixture. For a mixture of A and B the moles of A, N_A, and of B, N_B, are given by I_A/S_A and I_B/S_B, where I_A and I_B and S_A and S_B are the intensities and sensitivities of A and B, respectively. Equation 1 expresses the mole fraction of component A in terms of these quantities. Thus, by

$$X_A = \frac{I_A}{I_A + \frac{S_A I_B}{S_B}} \qquad (1)$$

defining the mole sensitivity of component B relative to component A as s_B eq 2 is

$$X_A = \frac{I_A}{I_A + s_B I_B} \qquad (2)$$

obtained from eq 1. The value of s_B is given by eq 3. Similarly the relative weight

TABLE I

FI RELATIVE ION ABUNDANCES FOR REACTOR SAMPLE 1

m/e[a]	Relative Ion Abundances for Emitter Number 1	2	2 repositioned		% Std. Dev. in Rel. Abd.
118	9.17	9.60	8.75	8.00	7.68
128	70.83	72.00	70.83	72.00	0.95
132	48.33	48.80	47.50	44.40	4.19
142	33.75	35.20	35.00	34.40	1.89
146	23.33	22.00	19.58	24.00	8.75
154	58.33	54.00	58.33	56.00	3.69
156	27.50	26.40	30.00	24.80	8.04
158	37.08	37.20	40.00	40.80	4.93
166	41.67	42.00	44.58	41.20	3.57
168	55.00	56.00	61.67	56.00	5.32
170	12.08	10.40	14.58	13.60	14.43
172	14.17	12.80	14.58	14.00	5.51
174	10.83	8.00	11.67	10.40	15.40
178	100.00	100.00	100.00	100.00	0.00
180	46.25	52.00	54.17	52.00	6.64
182	62.50	68.00	70.83	72.00	6.20
186	21.67	20.00	20.00	20.00	4.90
190	10.83	11.20	10.83	12.00	4.92
192	26.25	31.20	30.42	33.20	9.66
194	17.50	17.20	18.75	17.60	3.83
196	26.67	25.20	25.83	27.60	3.96
200	7.08	7.20	7.50	9.60	15.08
202	45.00	60.00	46.25	48.00	13.86
204	24.58	22.80	25.00	24.40	3.98
206	39.58	42.00	42.50	43.60	4.05
208	20.42	18.80	20.83	20.00	4.38
210	14.58	8.80	12.50	10.00	22.52
212	15.00	15.60	16.25	17.20	5.88

TABLE I (continued)

m/e[a]	Relative Ion Abundances for Emitter Number 1	2	2 repositioned		% Std. Dev. in Rel. Abd.
216	7.08	9.60	7.08	6.80	17.19
218	11.25	14.00	10.42	10.80	13.98
220	10.42	10.00	10.42	10.00	2.38
222	8.33	8.40	9.58	10.80	12.57
224	2.92	2.40	4.17	3.60	23.66
226	3.33	2.80	2.92	3.60	11.68
228	2.50	3.20	2.92	2.00	19.70
230	6.67	5.20	5.00	4.40	28.12
232	6.25	8.40	7.50	4.80	23.21
234	5.42	5.20	7.83	4.80	8.09
236	2.50	4.40	4.17	3.20	24.71
				Ave.	9.48

(a) Intensities for isotope peaks are not included for sake of brevity.

TABLE II

FI PERCENT TOTAL IONIZATION FOR SYNTHOIL SAMPLE 173-21

m/e	Percent Total Ionization from Scan #1	Scan #2	Scan #3	% Std. Dev. in % Total Ionization
154	0.40	0.68	0.65	26.7
156	1.81	2.00	2.03	6.1
168	4.30	5.10	5.43	11.8
169	0.76	1.10	0.91	18.5
170	8.16	7.62	8.70	6.6
171	1.53	1.32	1.56	8.9
180	0.51	0.71	0.94	29.9
182	10.71	11.62	12.61	8.2
183	1.98	1.84	1.96	3.9
184	6.49	6.07	6.85	6.0
185	0.99	1.00	1.16	9.1
190	0.96	0.74	0.80	13.6
194	3.29	3.55	4.06	10.8
195	0.91	0.77	0.80	8.9
196	18.86	18.78	20.43	4.8
197	3.74	3.74	3.55	3.0
198	1.42	1.55	1.30	8.8
208	6.51	6.32	6.67	2.7
209	1.08	1.23	1.34	10.7
210	9.18	9.20	9.78	3.6
211	2.10	2.39	1.88	12.0
218	0.68	0.58	0.65	8.1
220	1.25	1.55	1.88	20.2
222	5.61	4.97	5.36	6.1
223	1.19	1.29	1.12	7.1
224	2.10	1.61	1.74	14.0
234	1.59	1.23	1.38	12.9
236	1.93	1.45	2.28	22.1
				Ave. 8.90

$$s_B = \left(\frac{I_B}{I_A}\right)\left(\frac{X_A}{1 - X_A}\right) \qquad (3)$$

sensitivity of component B is given by eq 4 in which w_A is the weight fraction of A

$$s'_B = \left(\frac{I_B}{I_A}\right)\left(\frac{w_A}{1 - w_A}\right) \qquad (4)$$

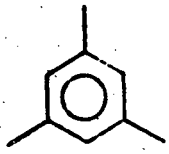
defined by $g_A/(g_A + g_B)$. The weight percents are thus obtainable from eq 5.

$$\%wt_i = \left[\frac{I_i/S_i s'_i}{\sum_{i=1}^{n} (I_i/s'_i)}\right] 100 \qquad (5)$$

In the present instance sensitivities for compounds in known mixtures were obtained relative to naphthalene. Thus, in addition to any contributions from instrument factors, the accuracy of an analysis is determined by the availability of sensitivity data or parenthetically the validity of assuming that $S_j/S_1 = 1$ for the j^{th} component and the contribution to the intensity at the m/e value of the j^{th} molecular ion from fragmentations of ions at higher mass.

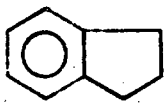
Results Obtained from Analysis of Known Samples

Five hydrocarbon mixtures were prepared using weighed quantities of the following compounds. Except for samples 7, 10, 19, and 20 which were obtained from



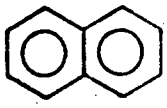
1

Mesitylene



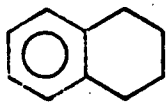
2

Indane



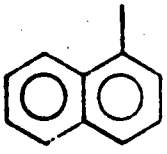
3

Naphthalene



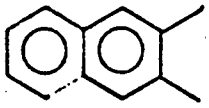
4

Tetralin



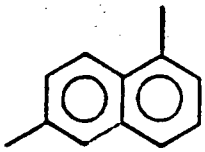
5

1-Methylnaphthalene



6

2,3-dimethyl-naphthalene



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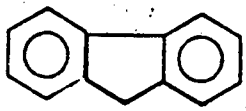
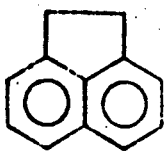
1,6-dimethyl-naphthalene



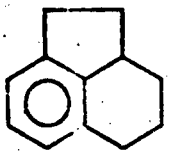
8

fluorene



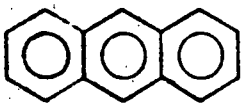
9

acenaphthene



10

tetrahydroacenaphthene



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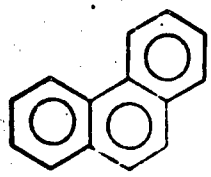
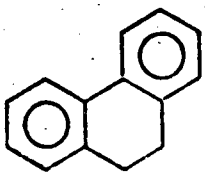
anthracene



12

phenanthrene



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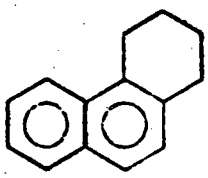
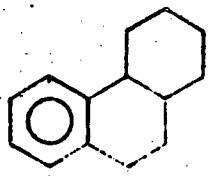
dihydrophenanthrene



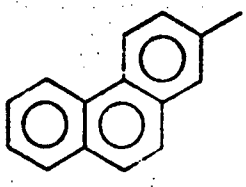
14

tetrahydrophenanthrene



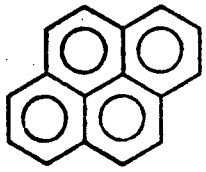
15

octahydrophenanthrene



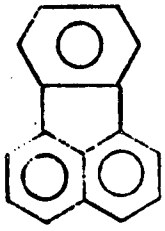
16

2-methylphenanthrene



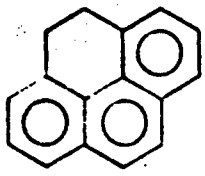
17

pyrene



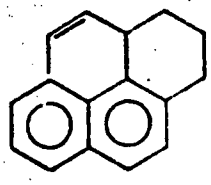
18

fluoranthene



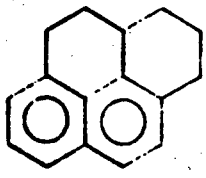
19a

dihydropyrene



19b

tetrahydropyrene



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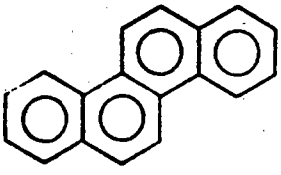
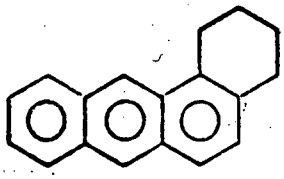
hexhydropyrene



21

chrysene



22

tetrahydrobenzanthrene

the Bartlesville Energy Research Center (5), the samples were obtained from either Professor E. J. Eisenbraun (5) or commercial sources. The mixtures were subjected to GC and FI analysis; for mixture 5, which was chronologically the first one, low-voltage data (6) were also obtained.

For mixture 1 through 4 the weights (moles) and FI relative ion abundances were used to obtain weight (mole) sensitivities for each compound relative to the sensitivity for naphthalene. The results are shown in Tables III through VI. The minimum purity of samples obtained from OSU is indicated to be 97% or greater. Sample 19 was found to contain two components 19a and 19b. Assuming equal flame ionization detector sensitivities the sample is composed of 57.9% of 19a and 42.1% of 19b. Therefore, these weight percents and the total weight of sample 19 taken were used in calculating the sensitivities for 19a and 19b. GC analysis indicated that sample 5 was composed of 8.3, 6.8, and 77.6% of 13, 14, and 15, respectively; three additional components which account for 7.3% of the sample were observed but have not yet been identified. The FI spectrum exhibited three ions whose m/e values were not consistent with those for any of the compounds. Thus as a first approximation these peaks were assigned to the unidentified components present in 15. Compound 13 is seen to be common to mixtures 1, 2, and 3; compounds 7 and 10 are common in mixtures 1 and 2. Considering that the samples are not analytically pure, it is gratifying to note that the relative sensitivities for these compounds in the various mixtures agree within the limits of precision calculated from the standard deviations in the ion abundances.

To investigate the neglect of sensitivities on the weight percents obtained by both GC and FI, the analysis of mixtures 1 through 4 are so constructed in Tables VII through X. Finally mixture 5 was analyzed using GC and both low-voltage and field-ionization mass spectrometry. For the latter data sets the weight-percent composition was calculated including and excluding sensitivities. The results are presented in Table XI. If only a reasonable level of accuracy is required the data in Tables VII through XI show that GC peak areas and FI relative ion abundances can be used without sensitivity corrections. The following comments are, however, pertinent. The accuracy of the FI analysis is generally improved by including the sensitivities. Before any real generalizations can be made concerning the neglect of sensitivities on the compositional data, these studies must be expanded to include a wider range in molecular weights and compound types. In Table XI the compositional data obtained from low-voltage mass spectrometry is seen to be somewhat improved by including sensitivities. In conclusion, for the range of compound types and molecular weights covered in this investigation, the results suggest that all methods yield a reasonable first approximation to the sample composition.

Routine Sample Analysis

During the last quarter, eighteen Synthoil coal-liquid samples have been processed for the Energy Research Center at Bartlesville. For each sample, high (70 eV) and low (8 eV) energy low-resolution mass spectra were obtained and high-resolution (70 eV) spectra were recorded on photographic plates. Empirical formulas for approximately 2000 total ions were obtained from the photographic plates by computer processing of the line positions for each ion measured with respect to lines corresponding to ions from perfluorokerosene.

In addition, analysis of Synthoil samples using field ionization mass spectrometry has been started. Efforts are being made to utilize FI mass spectrometry

TABLE III

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 1

Compound Number	Compound Name	Relative Sensitivities by Weight[a]	Relative Sensitivities by Moles[a]
3	Naphthalene	1.00	1.00
5	1-Methylnaphthalene	0.95 ± 0.09	1.06 ± 0.07
7	1,6-Dimethylnaphthalene	1.00 ± 0.11	1.22 ± 0.10
10	Tetrahydroacenaphthene	0.80 ± 0.09	0.99 ± 0.07
12	Phenanthrene	0.94 ± 0.02	1.24 ± 0.09
13	Dihydrophenanthrene	0.88 ± 0.08	1.28 ± 0.06
18	Fluoranthene	0.69 ± 0.03	1.08 ± 0.10
22	Dihydrobenzanthrene	0.60 ± 0.03	1.08 ± 0.10

[a]Average of three determinations; deviations are standard deviations.

TABLE IV

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 2

Compound Number	Compound Name	Relative Sensitivities by Weight[a]	Relative Sensitivities by Moles[a]
3	Naphthalene	1.00	1.00
7	1,6-Dimethylnaphthalene	1.03 ± 0.09	1.26 ± 0.04
10	Tetrahydroacenaphthene	0.81 ± 0.08	1.00 ± 0.06
11	Anthracene	1.03 ± 0.04	1.39 ± 0.01
13	Dihydrophenanthrene	0.83 ± 0.08	1.17 ± 0.06
17	Pyrene	0.80 ± 0.03	1.25 ± 0.08
19a	Dihydropyrene	0.90 ± 0.01	1.43 ± 0.09
19b	Tetrahydropyrene	0.83 ± 0.02	1.32 ± 0.08
20	Hexahydropyrene	0.69 ± 0.01	1.14 ± 0.04

[a]Average of three determinations; deviations are standard deviations.

TABLE V

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 3

Compound Number	Compound Name	Relative Sensitivities by Weight[a]	Relative Sensitivities by Moles[a]
2	Indane	0.90 ± 0.04	0.83 ± 0.02
3	Naphthalene	1.00	1.00
4	Tetralin	0.82 ± 0.06	0.85 ± 0.03
13	Dihydrophenanthrene	0.72 ± 0.12	1.02 ± 0.10
14	Tetrahydrophenanthrene	0.74 ± 0.04	1.05 ± 0.05
15	Octahydrophenanthrene	0.64 ± 0.03	0.93 ± 0.03

[a]Average of three determinations; deviations are standard deviations.

TABLE VI

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 4

Compound Number	Compound Name	Relative Sensitivites by Weight[a]	Relative Sensitivites by Moles[a]
1	Mesitylene	0.99 ± 0.02	0.92 ± 0.02
3	Naphthalene	1.00	1.00
8	Fluorene	0.87 ± 0.04	1.15 ± 0.06
9	Acenaphthene	0.99 ± 0.14	1.19 ± 0.17
16	Methylphenanthrene	0.83 ± 0.13	1.25 ± 0.19
21	Chrysene	0.31 ± 0.01	0.55 ± 0.01

[a]Average of three determinations; deviations are standard deviations.

TABLE VII

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 1
EXCLUDING SENSITIVITY CORRECTIONS

Compound Number	Compound Name	Weight Percents Obtained From Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
3	Naphthalene	10.61	11.26	9.58
5	1-Methylnaphthalene	18.64	18.79	17.86
7	1,6-Dimethylnaphthalene	16.81	16.40	18.57
10	Tetrahydroacenaphthene	18.49	18.33	16.44
12	Phenanthrene	3.44	3.71	4.00
13	Dihydrophenanthrene	15.10	14.84	16.84
18	Fluoranthene	6.88	6.76	6.81
22	Dihydrobenzanthrene	10.3	9.40	9.90

[a]All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b]Peak areas determined by using peak height and width at half height.

TABLE VIII

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 2
EXCLUDING SENSITIVITY CORRECTIONS

Compound Number	Compound Name	Weight Percents Obtained From Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
3	Naphthalene	8.86	8.66	8.05
7	1,6-Dimethylnaphthalene	21.37	20.79	25.72
10	Tetrahydroacenaphthene	22.49	21.76	19.39
11	Anthracene	9.39	14.86	12.21
13	Dihydrophenanthrene	19.69	17.58	20.95
17	Pyrene	7.12	6.72	8.13
19a	Dihydropyrene	5.36	2.54	2.44
19b	Tetrahydropyrene		1.85	3.11
20	Hexahydropyrene	5.77	5.24	5.89

[a]All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b]Peak areas determined by using peak height and width at half height.

TABLE IX

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 3
EXCLUDING SENSITIVITY CORRECTIONS

Compound Number	Compound Name	Weight Percents Obtained From Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
2	Indane	15.75	15.45	13.86
3	Naphthalene	8.72	10.47	9.23
4	Tetralin	19.61	21.56	17.60
13	Dihydrophenanthrene	25.30	25.39	27.27
14	Tetrahydrophenanthrene	15.31	12.69	17.60
15	Octahydrophenanthrene	15.31	14.28	15.02

[a]All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b]Peak areas determined by using peak height and width at half height.

TABLE X

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 4
EXCLUDING SENSITIVITY CORRECTIONS

Compound Number	Compound Name	Weight Percents Obtained From Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
1	Mesitylene	34.32	34.13	31.18
3	Naphthalene	19.33	19.62	18.99
8	Fluorene	17.54	18.07	19.80
9	Acenaphthene	15.44	15.50	18.00
16	Methylphenanthrene	5.92	6.14	3.38
21	Chrysene	7.46	6.54	8.62

[a] All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b] Peak areas determined by using peak height and width at half height.

TABLE XI

WEIGHT PERCENT OF VARIOUS COMPONENTS IN MIXTURE 5

Compound Number	Compound Name	Grams	GLC Peak Areas	Low Voltage Mass Spectrometry		Field Ionization Mass Spectrometry	
				without sensitivity corrections	with sensitivity corrections	without sensitivity corrections	with sensitivity corrections
3	Naphthalene	5.20	5.26	3.45	5.41	4.47	4.76
5	1-Methylnaphthalene	22.57	23.07	17.29	19.74	20.05	20.25
6	2,3-Dimethylnaphthalene	3.68	3.92	3.86	3.93	5.22	4.56
8	Fluorene	4.72	4.85	4.36	5.57	4.63	4.36
13	Dihydrophenanthrene	5.25	4.12	8.40	6.66	5.76	4.45
14	Tetrahydrophenanthrene	27.44	28.45	28.15	28.05	28.76	30.24
11,12	Anthracene, Phenanthrene	21.35[a]	21.16	21.66	22.01	22.32	22.58
16	2-Methylphenanthrene	1.59	1.65	2.13	1.66	1.64	1.40
17	Pyrene	2.23	2.20	8.05[b]	5.06	6.23	5.60
18	Fluoranthene	3.96	3.57				
21	Chrysene	2.01	1.75	2.63	1.90	1.93	1.80

[a]Total consists of 63.2 and 36.8 percent by weight phenanthrene and anthracene, respectively.

[b]Compounds 10 and 11 have the same exact mass.

in both semi-quantitative and qualitative analysis. Since FI spectra are characterized by the absence of peaks corresponding to fragment ions, the FI spectra can be used as a guide to determine those ions for which high-resolution electron-impact spectral data should be obtained. The advantage of this approach is demonstrated by the following. The low-voltage mass spectra of Synthoil sample 173-18 indicated the necessity of obtaining high-resolution data for 58 nominal mass values. In contrast, the FI spectra of sample 173-18 exhibited only 21 nominal mass values, excluding isotope peaks. For these 21 nominal mass values (22 ions) the data is presented in Table XII. We plan to use the technique of field ionization to obtain high-resolution mass spectral data. Suitable compounds for calibration of the mass scale on the photographic plate must be obtained.

The Bartlesville Energy Research Center has utilized low-voltage ion abundances to characterize complex mixtures according to Z number. This approach has been applied to Synthoil samples 172-15 and 173-18 using FI ion abundances. The results are shown in Figures 4 and 5. In this approach each curve constitutes a family of hydrocarbons in the same Z series. Evaluation of the area under each curve produces an estimate of the composition of the coal-liquid in terms of compound types. Comparison of the ion abundances, assuming equal sensitivities, directly yields semi-quantitative estimates of sample compositions. It should be noted that comparison of these data with those obtained for the same samples on the CEC 21-103 at Bartlesville constitutes another check on the reliability of the FI data. When analysis of all samples by Z class using FI have been completed, the results will be compared in detail to those obtained by low-voltage electron impact mass spectrometry.

TABLE XII

ELEMENTAL COMPOSITION DATA FOR NOMINAL MASS VALUES IN FI SPECTRA OF SYNTHOIL SAMPLE 173-18

m/e	Composition	Exact Mass		$\Delta M \times 10^3$
		EXP	CALC	
182	$C_{14}H_{14}$	182.112	182.110	2
184	$C_{14}H_{16}$	184.124	184.125	1
194	$C_{15}H_{14}$	194.108	194.110	2
196	$C_{15}H_{16}$	196.124	196.125	1
198	$C_{15}H_{18}$	198.141	198.141	0
206	$C_{16}H_{14}$	206.111	206.110	1
208	$C_{16}H_{16}$	208.124	208.125	1
210	$C_{16}H_{18}$	210.141	210.141	0
212	$C_{16}H_{20}$	212.159	212.157	2
220	$C_{17}H_{16}$	220.125	220.125	0
222	$C_{17}H_{18}$	222.142	222.141	1
224	$C_{17}H_{20}$	224.159	224.157	2
234	$C_{18}H_{18}$	234.142	234.141	1
236	$C_{18}H_{20}$	236.154	236.157	3
238	$C_{17}H_{18}O$	238.139	238.136	3
	$C_{18}H_{22}$	238.174	238.172	2
246	$C_{19}H_{18}$	246.142	246.141	1
248	$C_{19}H_{20}$	248.157	248.157	0
250	$C_{19}H_{22}$	250.173	250.172	1
252	$C_{19}H_{24}$	252.189	252.188	1
262	$C_{20}H_{22}$	262.176	262.172	4
264	$C_{20}H_{24}$	264.184	264.188	4

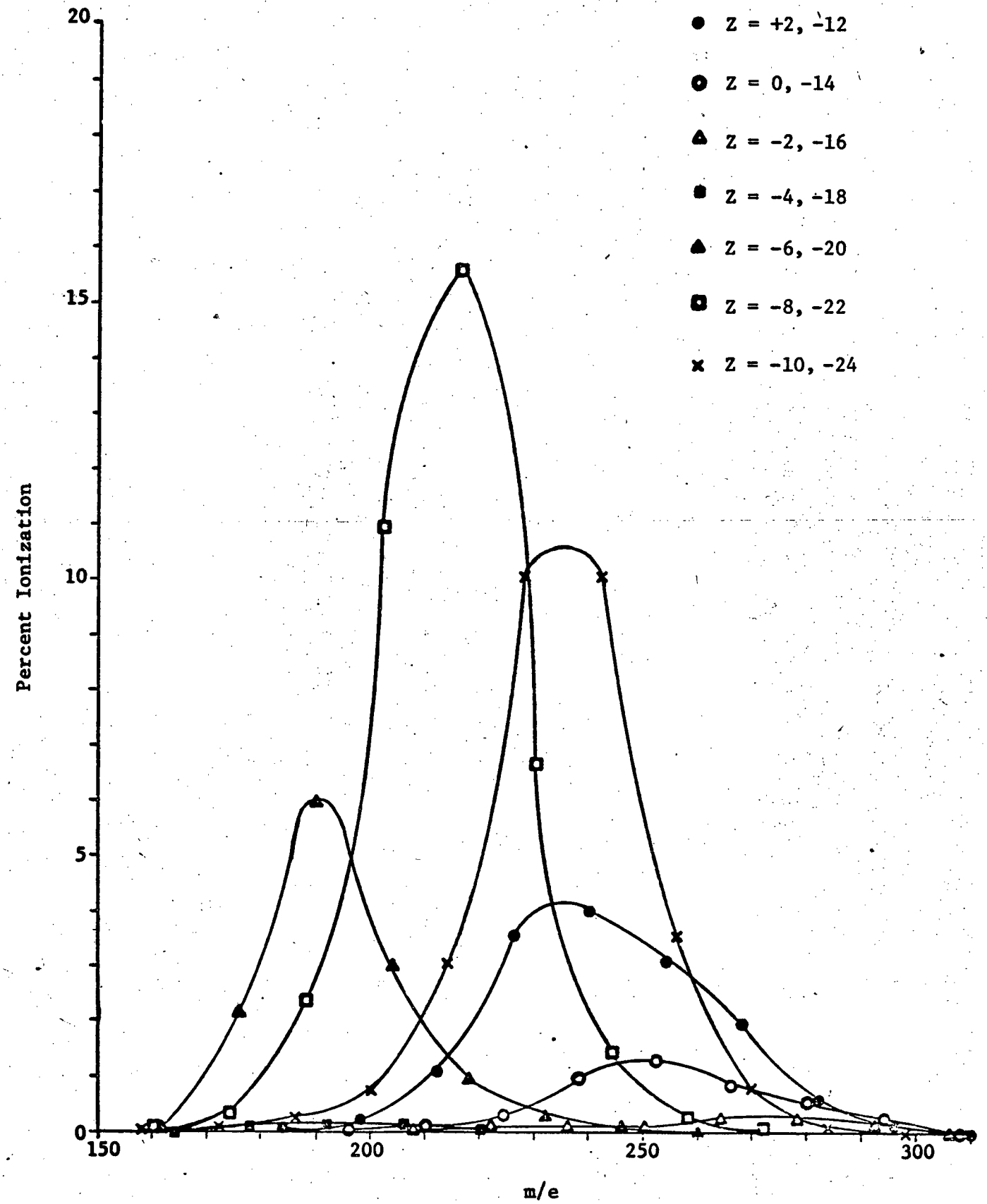


Figure 4. Z Class Characterization of Synthoil Sample 172-15 Using FI Percent Ionization

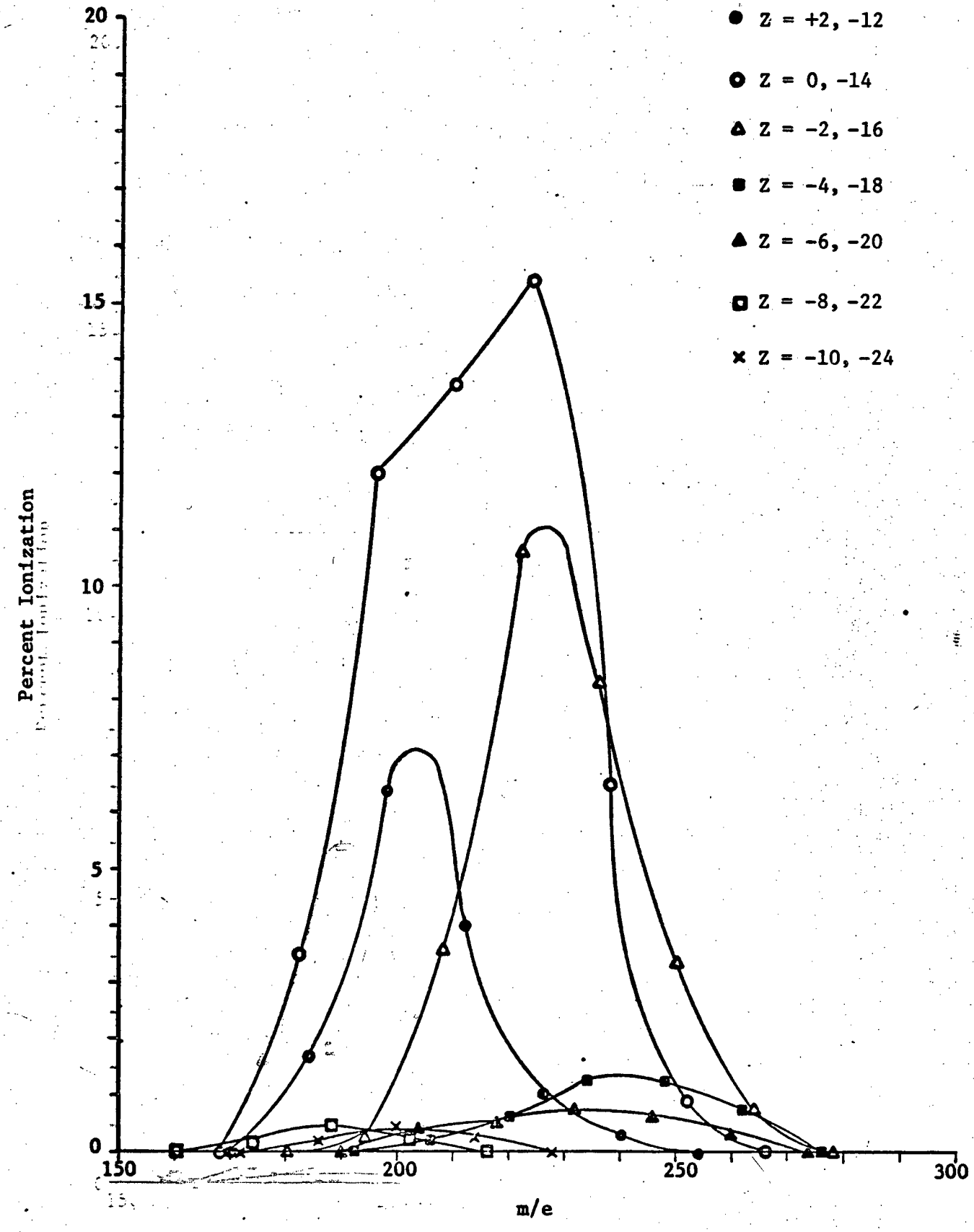


Figure 5. Z Class Characterization of Synthoil Sample 173-18 Using FI Percent Ionization

References

1) Research supported by ERDA under contract number E(49-18)-2011.

2) This material is also presented in quarterly progress report FE 2011-2, Dist. Category UC 90 d for period 9/9/75-12/8/75.

3) See quarterly progress report FE 2011-1, Dist. Category UC 90 d for period 6/9/75-9/9/75.

4) Synthoil samples supplied by Mr. J. E. Dooley at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.

5) We thank Professor E. J. Eisenbraun and his colleagues at Oklahoma State University for graciously supplying us standard reference compounds. Some samples were kindly provided by Mr. J. E. Dooley at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.

6) These data were obtained using the CEC 21-103 mass spectrometer at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.