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

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ABSTRACT

Interfacing of a Perkin Elmer model 3920 gas chromatograph to the CEC 21-110B mass spectrometer has been completed and the GC/MS system is operational. Detailed descriptions of the heated probe assembly and the rapid mass-scanning module are given. Initial emphasis has been placed on the utilization of GC/MS in conjunction with the technique of field ionization (FI). Satisfactory results have been obtained from simple mixtures of aromatic hydrocarbons.

The FI source for the CEC 21-110B mass spectrometer is routinely operational. Familiarity with its operation has improved ion-abundance reproducibility. For a mixture containing aromatic hydrocarbons, thiophenes, and furans, the average percent standard deviation in the average percent ionizations is 3.55% from three spectra.

Application of the technique of FI mass spectrometry to quantitative analysis of coal type mixtures has been explored. The consequences of sensitivity data on the analytical results have been considered. Relative weight and mole sensitivities have been determined for 30 aromatic hydrocarbons, 20 thiophenes, and 7 heteroatom (oxygen and nitrogen) containing compounds with respect to ethylbenzene. Excellent analytical data has been obtained from three known mixtures using these sensitivities.

To date, fifty three coal-liquid samples have been processed for the Bartlesville Energy Research Center. Empirical formulas for ca. 5000 ions have been determined from the high-resolution (70 eV) spectra recorded on photographic plates. FI spectra have been recorded for ca. 20 synthoil samples. Percent ionizations obtained from these spectra have been used to characterize the mixtures according to Z numbers.

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 to the CEC 21-110B mass spectrometer has been completed and the GC/MS system is operational. The major difficulties encountered in interfacing the two instruments were the incorporation of a jet separator into the GC and construction of the heated inlet system. As shown in Figure I, a single jet glass 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 to both the flame-ionization detector and mass spectrometer. The split ratio was maximized by installing a splitting loop between the tee and flame-ionization detector. The loop was varied for maximum sensitivity to the mass spectrometer without appreciable peak distortion in the gas chromatograms. A Nupro high-vacuum--high-temperature valve preceeds the separator. The valve permits 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 II. 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 to 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 III. 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).

Other auxillary equipment which has either been constructed or purchased for the GC/MS system includes a Keithley 417 picoammeter, Leeds and Northrup duel-pen recorder (at no charge to this grant), and a resistance divider network for interfacing of the picoammeter and recorder.

Figure I. GC Manifold Oven and Molecular Separator Assembly

Figure II. Gas Chromatographic Probe Assembly

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

Initial emphasis has been placed on the utilization of GC/MS in conjunction with the technique of field ionization (FI). To date satisfactory results have been obtained from simple mixtures of aromatic hydrocarbons. During the next quarter, analysis will concentrate on coal-liquid samples.

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 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 FI electrode, and various operating voltages of the mass spectrometer. For a fraction of a Synthoil oil obtained by gel permeation chromatography (3), preliminary data indicated the average percent standard deviation in the percent ionizations for three spectra to be 8.90% (2). However, continuing use and development of the FI source has resulted in improved reproducibility. For example, Table I presents percent ionization data for three scans of the FI mass spectrum of a mixture of aromatic hydrocarbons, thiophenes, and furans (Test Mixture #1; see below). The average percent standard deviation is seen to be 3.55%. It is thus encouraging to note that the reproducibility of the FI ion abundances compares well with the reproducibility of the EI abundances we have obtained from the CEC 21-110B and CEC 21-103 mass spectrometers.

Use of Field Ionization Mass Spectrometry for Semiquantitative Analysis

Before discussing 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

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

TABLE I
FI PERCENT TOTAL IONIZATION FOR TEST MIXTURE #1

m/e	Percent Total Ionization from			% Std. Dev. in % Total Ionization
	Scan #1	Scan #2	Scan #3	
118	8.68	8.56	7.68	6.57
120	6.79	6.42	6.26	4.19
128	4.90	5.04	4.98	1.41
132	5.23	5.18	5.69	5.24
134	3.04	3.11	2.96	2.47
142	12.13	12.19	12.56	1.89
148	4.53	4.28	4.34	2.98
154	3.23	3.38	3.41	2.89
156	10.01	10.12	9.53	3.17
158	7.12	7.38	7.32	1.87
166	4.23	3.73	3.98	6.28
168	3.89	3.59	3.77	4.03
178	4.19	4.35	4.41	2.63
180	8.57	8.97	8.96	2.58
184	1.93	2.07	2.13	5.02
192	3.34	3.45	3.48	2.15
202	5.68	5.87	6.04	3.07
206	0.74	0.74	0.71	2.37
228	1.78	1.59	1.80	6.73
Average				3.55

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

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

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

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

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

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

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

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

Thus, in addition to any contributions from instrumental factors, the accuracy of an analysis is determined by the availability of sensitivity data or parenthetically the validity of assuming that $S_j/S_i = 1$ 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. In the present instance sensitivities for compounds in known mixtures were obtained relative to ethylbenzene.

Determination of Relative Weight and Mole Sensitivities

Sensitivities relative to ethylbenzene have been determined for 30 aromatic hydrocarbons, 20 thiophenes, and 7 heteroatom (oxygen and nitrogen) containing compounds. Samples of all thiophenes, 1,6-dimethylnaphthalene, 1,2,3,4,5,5a-hexahydroacenaphthylene, 1,2,3,9,10,10a-hexahydropyrene, 2,6-dimethylantracene, 9,10-dihydroanthracene, and dibenzofuran were obtained from the Bartlesville Energy Research Center (4). Remaining samples were obtained either from Professor E. J. Eisenbraun (4) or from commercial sources. All samples were analyzed for purity by both GC and FI mass spectrometry. In sensitivity determinations, the weights of samples with purities less than 97%, i.e. 2,3-dihydro-1H-indene (95.8%),

1,2,3,4-tetrahydronaphthalene (93.7%), 2,3-dihydro-5-methyl-1H-indene (95.4%), 1,2,3,4,5,6,7,8-octahydrophenanthrene (92.6%), and chrysene (81.0%) were corrected for impurities. In all cases the nominal masses of the impurities did not contribute to the intensities of other components in a mixture.

Fourteen hydrocarbon, 9 thiophene, and 4 heteroatom compound mixtures were prepared using weighed quantities of standard compounds. For each mixture the weights (moles) and FI relative ion abundances (average of three determinations) were used to obtain weight (mole) sensitivities for each compound relative to the sensitivity for ethylbenzene. To investigate the effect of mixture composition on sample sensitivity, the sensitivities for each sample in most instances were determined from more than one mixture. Within experimental error, variations in sensitivities due to mixture composition are not discernable. Since only molecular ions were used to obtain the FI relative ion abundances, sensitivities have also been calculated using weights (moles) which have been corrected for the presence of isotopically labelled molecules. The results are presented for the hydrocarbons, thiophenes, and heteroatom compounds in Tables II, III, and IV, respectively.

To investigate the neglect of sensitivities on the weight percents obtained by both GC and FI, three additional mixtures, each containing a variety of hydrocarbons, thiophenes, and heteroatom compounds, were analyzed by GC and by FI. In the latter analysis, weight percents were determined including and excluding sensitivities. The results are presented in Tables V, VI, and VII. As seen, the accuracy of the FI analysis is generally improved by including the sensitivities.

Routine Sample Analysis

During the first three quarters, fifty three coal-liquid samples (17 Western Kentucky and 36 Synthoil) have been processed for the Bartlesville Energy Research Center. 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 5000 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, FI spectra have been recorded for approximately twenty Synthoil samples (3). Using the FI percent ionizations, these mixtures have been characterized according to Z numbers. A computer program has been written which calculates the percent ionizations for each even-numbered nominal mass in the spectra, correlates all percent ionizations for each nominal mass with Z numbers, and produces a plot of percent ionization versus nominal mass as a function of Z number. Plots of Synthoil samples 172-18 and 172-21 generated by this program are presented in Figures IV and V. Presently, these data are being compared in detail to those obtained by low-voltage electron-impact mass spectrometry at Bartlesville.

TABLE II
RELATIVE FI SENSITIVITIES FOR HYDROCARBONS^a

Compd.	m/e	Z	<u>Relative Sensitivities</u>			
			<u>Excluding heavy atom Correction</u>		<u>Including heavy atom Correction</u>	
			weight	mole	weight	mole
benzene	78	-6	1.24 ± 0.02	0.91 ± 0.01	1.21 ± 0.02	0.89 ± 0.01
toluene	92	-6	1.18 ± 0.02	1.03 ± 0.02	1.17 ± 0.02	1.02 ± 0.02
ethylbenzene	106	-6	1.00	1.00	1.00	1.00
2,3-dihydro-1H-indene	118	-8	0.97 ± 0.01	1.08 ± 0.01	0.98 ± 0.01	1.09 ± 0.01
1,3,5-trimethylbenzene	120	-6	1.01 ± 0.02	1.14 ± 0.02	1.02 ± 0.02	1.15 ± 0.02
propylbenzene	120	-6	0.90 ± 0.01	1.02 ± 0.01	0.91 ± 0.01	1.03 ± 0.02
naphthalene	128	-12	1.04 ± 0.04	1.25 ± 0.05	1.06 ± 0.05	1.28 ± 0.06
1,2,3,4-tetrahydronaphthalene	132	-8	0.92 ± 0.01	1.14 ± 0.01	0.94 ± 0.01	1.17 ± 0.01
2,3-dihydro-5-methyl-1H-indene	132	-8	0.88 ± 0.02	1.10 ± 0.02	0.90 ± 0.02	1.13 ± 0.03
1-methylnaphthalene	142	-12	0.95 ± 0.03	1.27 ± 0.03	0.98 ± 0.03	1.31 ± 0.04
1,2-dihydroacenaphthylene	154	-14	0.96 ± 0.06	1.39 ± 0.09	1.00 ± 0.06	1.45 ± 0.09
1,6-dimethylnaphthalene	156	-12	0.98 ± 0.06	1.44 ± 0.09	1.02 ± 0.06	1.51 ± 0.09
2,3-dimethylnaphthalene	156	-12	1.05 ± 0.02	1.55 ± 0.03	1.10 ± 0.02	1.62 ± 0.03
1,2,3,4,5,5a-hexahydroacenaphthylene	158	-10	0.76 ± 0.03	1.13 ± 0.04	0.79 ± 0.03	1.18 ± 0.05
fluorene	166	-16	0.92 ± 0.06	1.44 ± 0.09	0.97 ± 0.06	1.53 ± 0.10
anthracene	178	-18	1.06 ± 0.09	1.78 ± 0.15	1.13 ± 0.10	1.90 ± 0.16
phenanthrene	178	-18	0.97 ± 0.08	1.63 ± 0.13	1.04 ± 0.08	1.74 ± 0.14

TABLE II (CONTINUED)

Compd.	m/e	Z	<u>Relative Sensitivities</u>			
			<u>Excluding heavy atom Correction</u>		<u>Including heavy atom Correction</u>	
			weight	mole	weight	mole
9,10-dihydrophenanthrene	180	-16	0.86 ± 0.01	1.46 ± 0.02	0.92 ± 0.01	1.56 ± 0.02
9,10-dihydroanthracene	180	-16	0.80 ± 0.04	1.36 ± 0.06	0.86 ± 0.04	1.46 ± 0.07
3-methylfluorene	180	-16	0.85 ± 0.01	1.44 ± 0.01	0.91 ± 0.01	1.54 ± 0.01
1,2,3,4-tetrahydrophenanthrene	182	-14	0.84 ± 0.02	1.45 ± 0.03	0.90 ± 0.02	1.55 ± 0.04
1,2,3,4,5,6,7,8-octahydro-phenanthrene	186	-10	0.82 ± 0.08	1.43 ± 0.14	0.87 ± 0.09	1.53 ± 0.15
4-methylphenanthrene	192	-18	0.84 ± 0.10	1.51 ± 0.18	0.90 ± 0.11	1.64 ± 0.19
pyrene	202	-22	0.82 ± 0.12	1.56 ± 0.22	0.89 ± 0.13	1.70 ± 0.25
fluoranthene	202	-22	0.89 ± 0.08	1.69 ± 0.16	0.97 ± 0.09	1.85 ± 0.18
2,6-dimethylantracene	206	-18	0.89 ± 0.07	1.73 ± 0.14	0.97 ± 0.08	1.89 ± 0.15
1,2,3,9,10,10a-hexahydropyrene	208	-16	0.85 ± 0.01	1.67 ± 0.02	0.93 ± 0.01	1.83 ± 0.02
2-methylpyrene	216	-22	0.81 ± 0.04	1.65 ± 0.07	0.90 ± 0.04	1.82 ± 0.08
5,6-dihydro-4H-Benz(de)anthracene	218	-20	0.83 ± 0.03	1.71 ± 0.06	0.92 ± 0.03	1.89 ± 0.07
chrysene	228	-24	0.74 ± 0.05	1.59 ± 0.10	0.82 ± 0.05	1.77 ± 0.11
2-ethylpyrene	230	-22	0.78 ± 0.01	1.68 ± 0.03	0.87 ± 0.02	1.88 ± 0.04

^aDeviations are standard deviations.

TABLE III
RELATIVE FI SENSITIVITIES FOR THIOPHENES^a

Compd.	m/e	Relative Sensitivities			
		Excluding heavy atom Correction		Including heavy atom Correction	
		weight	mole	weight	mole
thiophene	84	0.92 ± 0.01	0.73 ± 0.01	0.93 ± 0.01	0.74 ± 0.01
2-butylthiophene	140	0.74 ± 0.02	0.98 ± 0.02	0.78 ± 0.02	1.03 ± 0.03
2-(2-methylpropyl)thiophene	140	0.76 ± 0.02	1.00 ± 0.02	0.80 ± 0.02	1.05 ± 0.02
2-(1,1-dimethylethyl)thiophene	140	0.70 ± 0.01	0.92 ± 0.01	0.73 ± 0.01	0.97 ± 0.01
2-(1-methylbutyl)thiophene	154	0.61 ± 0.05	0.89 ± 0.07	0.65 ± 0.05	0.95 ± 0.07
2-(2-ethylbutyl)thiophene	168	0.63 ± 0.03	1.00 ± 0.05	0.68 ± 0.04	1.08 ± 0.06
2-(4-methylpentyl)thiophene	168	0.62 ± 0.04	0.98 ± 0.07	0.66 ± 0.05	1.05 ± 0.07
2-ethyl-5-(2-methylpropyl)thiophene	168	0.66 ± 0.04	1.04 ± 0.06	0.71 ± 0.04	1.12 ± 0.06
2-phenylmethylthiophene	174	0.70 ± 0.01	1.15 ± 0.01	0.77 ± 0.01	1.26 ± 0.01
2-ethyl-5-(3-methylbutyl)thiophene	182	0.63 ± 0.02	1.09 ± 0.03	0.69 ± 0.02	1.19 ± 0.03
2-(2-ethylhexyl)thiophene	196	0.59 ± 0.05	1.09 ± 0.09	0.65 ± 0.05	1.20 ± 0.09
2-(2-methylpropyl)-5-propylthiophene	196	0.61 ± 0.02	1.13 ± 0.04	0.67 ± 0.02	1.24 ± 0.04
2,5-bis(1,1-dimethylethyl)thiophene	196	0.58 ± 0.01	1.07 ± 0.01	0.64 ± 0.01	1.18 ± 0.01
2-hexyl-5-propylthiophene	210	0.62 ± 0.01	1.23 ± 0.02	0.70 ± 0.01	1.37 ± 0.03
2-decylthiophene	224	0.48 ± 0.04	1.02 ± 0.08	0.54 ± 0.04	1.15 ± 0.09
2-heptyl-5-propylthiophene	224	0.65 ± 0.02	1.38 ± 0.04	0.74 ± 0.02	1.56 ± 0.04
2-undecylthiophene	238	0.47 ± 0.02	1.06 ± 0.03	0.54 ± 0.02	1.21 ± 0.04
benzo[b]thiophene	134	0.86 ± 0.03	1.09 ± 0.04	0.91 ± 0.03	1.15 ± 0.04
6-methylbenzo[b]thiophene	148	0.88 ± 0.04	1.23 ± 0.05	0.94 ± 0.04	1.31 ± 0.05
dibenzothiophene	184	0.82 ± 0.03	1.43 ± 0.06	0.91 ± 0.04	1.57 ± 0.07

^aDeviations are standard deviations.

TABLE IV

RELATIVE SENSITIVITIES FOR OXYGEN AND NITROGEN CONTAINING COMPOUNDS^a

Compd.	m/e	<u>Relative Sensitivities</u>			
		<u>Excluding heavy atom Correction</u>		<u>Including heavy atom Correction</u>	
		weight	mole	weight	mole
1,3-benzenediol	110	1.32 ± 0.02	1.37 ± 0.02	1.30 ± 0.02	1.35 ± 0.02
1-naphthalenol	144	1.05 ± 0.04	1.42 ± 0.05	1.07 ± 0.04	1.46 ± 0.05
dibenzofuran	168	0.90 ± 0.01	1.42 ± 0.02	0.94 ± 0.01	1.49 ± 0.02
diphenylether	170	0.91 ± 0.04	1.45 ± 0.07	0.95 ± 0.04	1.52 ± 0.07
indole	117	1.42 ± 0.02	1.57 ± 0.02	1.42 ± 0.02	1.57 ± 0.02
quinoline	129	1.30 ± 0.03	1.58 ± 0.03	1.32 ± 0.03	1.61 ± 0.03
carbazole	167	1.07 ± 0.06	1.68 ± 0.10	1.12 ± 0.06	1.77 ± 0.10

^aDeviations are standard deviations.

TABLE V
WEIGHT PERCENTS OF COMPONENTS IN TEST MIXTURE #1^a

Compd.	Grams	GLC ^{b,c}	Weight Percent by	
			FI ^d	
			Excluding Sensitivities	Including Sensitivities
1,3,5-trimethylbenzene	8.28	7.89 ± 0.14	6.31 ± 0.43	7.73 ± 0.52
2,3-dihydro-1H-indene	6.28	6.66 ± 0.67	5.02 ± 0.22	5.83 ± 0.25
naphthalene	4.46	5.25 ± 0.51	4.10 ± 0.06	4.34 ± 0.06
1,2,3,4-tetrahydronaphthalene	5.46	7.76 ± 0.30	4.56 ± 0.22	5.30 ± 0.27
benzo[b]thiophene	3.21		2.62 ± 0.07	3.18 ± 0.08
1-methylnaphthalene	11.78	14.93 ± 0.49	11.25 ± 0.19	11.78 ± 0.21
6-methylbenzo[b]thiophene	4.35		4.17 ± 0.13	4.50 ± 0.14
1,2-dihydroacenaphthylene	3.06	3.17 ± 0.19	3.32 ± 0.09	3.16 ± 0.09
1,6-dimethylnaphthalene	9.43	9.66 ± 0.07	9.94 ± 0.34	9.15 ± 0.35
1,2,3,4,5,5a-hexahydroacenaphthylene	8.52	8.30 ± 0.08	7.40 ± 0.13	8.72 ± 0.16
fluorene	3.90	3.85 ± 0.03	4.25 ± 0.27	3.91 ± 0.25
dibenzofuran	3.54	3.18 ± 0.07	4.06 ± 0.17	3.78 ± 0.16
phenanthrene	4.05	4.58 ± 0.04	4.95 ± 0.12	4.02 ± 0.10
9,10-dihydrophenanthrene	9.11	9.79 ± 0.26	10.24 ± 0.25	9.29 ± 0.23
dibenzothiophene	2.13	2.04 ± 0.02	2.42 ± 0.12	2.25 ± 0.11
4-methylphenanthrene	3.47	3.68 ± 0.17	4.24 ± 0.09	3.71 ± 0.08
pyrene	6.36	6.31 ± 0.19	7.63 ± 0.22	6.50 ± 0.20
2,6-dimethylanthracene	0.63	0.68 ± 0.04	0.97 ± 0.03	0.74 ± 0.02
chrysene	1.97	2.34 ± 0.03	2.53 ± 0.17	2.12 ± 0.15

^aDeviations are standard deviations unless otherwise noted. ^bDeviations are average deviations.

^cAverage of two determinations. ^dAverage of three determinations.

TABLE VI

WEIGHT PERCENTS OF COMPONENTS IN TEST MIXTURE #2^a

Compd.	Grams	GLC ^{b,c}	Weight Percent by	
			FI ^d	
			Excluding Sensitivities	Including Sensitivities
ethylbenzene	46.46	48.86 ± 0.51	38.11 ± 0.70	47.01 ± 0.82
naphthalene	11.67	12.22 ± 0.26	11.64 ± 0.59	11.47 ± 0.57
fluorene	9.83	10.13 ± 0.10	11.73 ± 0.47	10.03 ± 0.40
carbazole	5.04	5.20 ± 0.43	6.17 ± 0.36 ^e	4.52 ± 0.27 ^e
dibenzofuran	13.89	11.44 ± 0.27	15.74 ± 0.08 ^e	13.65 ± 0.09 ^e
phenanthrene	7.03	7.01 ± 0.13	9.43 ± 0.28	7.13 ± 0.22
dibenzothiophene	6.08	5.13 ± 0.13	7.17 ± 0.04	6.19 ± 0.03

^aDeviations are standard deviations unless otherwise noted. ^bDeviations are average deviations.^cAverage of two determinations. ^dAverage of three determinations. ^ePeak intensity of molecular ion mass corrected for contribution from isotope peaks at lower nominal mass.

TABLE VII

WEIGHT PERCENTS OF COMPONENTS IN TEST MIXTURE #3^a

Compd.	Gram	GLC ^{b,c}	Weight Percent by	
			FI ^d	
			Excluding Sensitivities	Including Sensitivities
thiophene	8.76	5.77 ± 0.19	5.55 ± 0.13	8.60 ± 0.19
2,3-dihydro-5-methyl-1H-indene	11.40	12.06 ± 0.03	10.48 ± 0.34	10.81 ± 0.34
2-butylthiophene	7.28	6.85 ± 0.04	6.12 ± 0.19	7.09 ± 0.21
2-(1-methylbutyl)thiophene	8.16	7.41 ± 0.02	6.62 ± 0.10	8.41 ± 0.13
2-(4-methylpentyl)thiophene	8.15	7.80 ± 0.02	7.17 ± 0.11	8.31 ± 0.11
2-phenylmethylthiophene	6.52	6.24 ± 0.21	6.33 ± 0.20	6.21 ± 0.19
anthracene	1.72	2.47 ± 0.02	2.51 ± 0.11	1.60 ± 0.07
3-methylfluorene	2.30	1.94 ± 0.04	2.99 ± 0.10	2.35 ± 0.07
1,2,3,4-tetrahydrophenanthrene	6.80	7.96 ± 0.08	9.07 ± 0.26	7.11 ± 0.19
1,2,3,4,5,6,7,8-octahydrophenanthrene	5.20	6.30 ± 0.15	6.11 ± 0.17	4.83 ± 0.14
2-(2-ethylhexyl)thiophene	7.45	7.56 ± 0.10	6.94 ± 0.13	7.22 ± 0.15
fluoranthene	0.99	1.27 ± 0.02	1.61 ± 0.23	1.08 ± 0.16
1,2,3,9,10,10a-hexahdropyrene	2.77	3.33 ± 0.03	3.81 ± 0.17	2.58 ± 0.11
2-hexyl-5-propylthiophene	7.43	6.93 ± 0.14	7.98 ± 0.24	7.37 ± 0.23
5,6-dihydro-4H-Benz(de)anthracene	2.84	3.32 ± 0.08	4.13 ± 0.13	2.74 ± 0.09
2-decylthiophene	6.39	7.23 ± 0.27	6.71 ± 0.18	7.47 ± 0.18
2-undecylthiophene	5.86	5.62 ± 0.02	5.85 ± 0.26	6.23 ± 0.28

^aDeviations are standard deviations unless otherwise noted. ^bDeviations are average deviations.^cAverage of two determinations. ^dAverage of three determinations.

Figure IV. Z Number Characterization of Synthoil Sample 172-18 Using FI Percent Ionization

Figure V. Z Number Characterization of Synthoil Sample 172-21 Using FI Percent Ionization

References

- 1) Research supported by ERDA under contract number E(49-18)-2011.
- 2) Related material is also presented in quarterly progress reports FE 2011-2, Dist. Category UC 90d for period 9/9/75-12/8/75 and BERC-0020-2 for period 9/9/75-12/8/75.
- 3) Synthoil samples supplied by Mr. J. E. Dooley at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.
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