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

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ABSTRACT

Ion-source temperature markedly affects the sensitivity for field ionization of saturated hydrocarbons relative to the sensitivity for FI of aromatic hydrocarbons. Increasing the ion-source temperature from *ca.* 100° to *ca.* 300°C reduces the dependence of saturate/aromatic relative FI sensitivities on mixture composition to within the limits of data precision. The decane/ethylbenzene relative FI sensitivity was found to be independent of field potential for a wide range in binary mixture composition at ion-source temperatures of 100°, 200°, and 300°C. Relative sensitivities for FI of saturated hydrocarbons determined in the absence of aromatic hydrocarbons and at 270°-300°C ion-source temperature do not exhibit a measurable dependence on the composition of the saturate mixture. Relative FI sensitivities were determined at an ion-source temperature of 270°C for 20 alkanes and naphthenes relative to decane. Excellent analytical data were obtained for a test mixture using these sensitivities. Based upon these results field-ionization mass spectrometry constitutes an ideal technique for group-type analysis of 1) saturated hydrocarbons and 2) mixtures of saturated and aromatic hydrocarbons providing FI/MS are obtained with adequate resolution.

Development of field desorption capability in our laboratory is essentially complete. This endeavor involved design and fabrication of the emitter probe, emitter holder, activation and etching cells, power supplies, and vacuum system. Considerable experience has been gained in emitter conditioning; especially the growth of carbon dendrites on the tungsten wire. Acquisition of FD/MS will be attempted in the near future.

Implementation of computer assisted data reduction, correlation, and interpretation has focused on converting mass spectral ion abundance data for a given gel-permeation chromatography (GPC) fraction into quantitative distributions and conversion of the data for the various fractions into distributions for the total sample.

High-resolution 70-eV electron-impact mass spectra were recorded for 56 fractions obtained from separation of a tar sand sample on photographic plates. High-resolution data have been grouped into qualitative distributions for 17 of the fractions.

OBJECTIVE AND SCOPE OF WORK

The objective of this program is to obtain qualitative and quantitative information concerning the composition of synthetic fuels and related materials using the technique of mass spectrometry. Special emphasis is placed upon the use of low- and high-resolution field-ionization mass spectrometry to obtain information relating to the compound types and/or compounds present in a sample. However, high-resolution electron-impact mass spectrometry and gas chromatography in combination with electron-impact and field-ionization mass spectrometry are also used. Our combination FI/EI source is being modified to operate in the field-desorption mode. The technique of FD/MS will be applied to the analysis of relatively nonvolatile high-molecular weight components. Known mixtures of compounds structurally related to those either believed or known to be present in these samples will be investigated with the view of 1) determining sensitivities towards field ionization and field desorption and 2) ascertaining for sample quantification the accuracy obtained by various techniques.

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

SUMMARY OF PROGRESS TO DATE

Field-ionization mass spectrometry is being used to analyze samples both qualitatively and quantitatively. Determination of field ionization sensitivity data for saturate analysis and modification of combination FI/EI ion source to operate in field desorption mode are on schedule, if not somewhat ahead.

During the past three months the percentage of time devoted by the principal investigator was 10%. Detailed analysis of fractions obtained from separation of tar sands sample is on schedule.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Development of Field-Ionization Mass Spectrometry as a Technique for the Quantitative Analysis of Saturates

Field-ionization mass spectrometry, FI/MS, (1), which produces virtually fragment-ion-free mass spectra (1b,2) is ideally suited to the quantitative analysis of the aromatic components of coal-derived liquids (3). The technique should be ideally suited to group-type quantitative analyses of saturates. In this regard, sensitivities have been reported and metastable spectra investigated for field ionization of a series of saturates using an ion-source temperature of 185°C (4). The utility of these data is not clear since FI sensitivities of saturates relative to low-molecular weight aromatic hydrocarbons determined at low ion-source temperatures using mixtures of the two compound classes exhibit a dependence on mixture composition (5). Since the technique of FI/MS would appear to be unsatisfactory for the routine analysis of saturate plus aromatic mixtures and possibly saturate mixtures and since composition independent relative sensitivities were obtained for aromatics using a ion-source temperature of *ca.* 270°C, a systematic investigation of the influence of factors such as ion-source temperature and field potential on relative sensitivities for FI of saturates both in the presence and absence of aromatics was initiated.

Gram sensitivities for FI of heptane relative to the gram sensitivities for FI of benzene, $s_H(g)/s_B(g)$, were determined as a function of both ion-source temperature and binary mixture composition (6). Values of $s_H(g)/s_B(g)$ were calculated by multiplying the ratio of the *m/e* 100 to the *m/e* 78 ion abundances by the ratio of the weight of benzene to the weight of heptane.

Table I presents $s_H(g)/s_B(g)$ values determined as a function of the weight percent heptane in the mixture and using ion-source temperatures $\leq 110^\circ\text{C}$. The

TABLE I. Dependence of FI Sensitivity for Heptane Relative to Benzene on Binary Mixture Composition at Ion-Source Temperatures $< 110^\circ\text{C}$

Weight Percent Heptane	Set 1 ^a [$s_H(g)/s_B(g)$] $\times 10^2$	Set 2 ^b
25	54	67
28	55	
51	50	63
60	48	63
74	41	64
80	37	62
90	27	55
97	20	39

^a Calculated from curves in Figure 6 of reference 5a. Ion-source temperature was either room temperature or 70–110°C. ^b Present work. Ion-source temperature was 100°C.

dependence of the m/e 78 and m/e 100 ion abundances on the percent partial pressures of benzene and heptane in the gas reservoir reported by Hippe and Beckey in Figure 6 (5a) was used to calculate the relative gram sensitivities in column 2. It is important to note that both the data in Figure 6 and the sensitivity factors for heptane and benzene reported in Table II of reference 5a for a binary mixture composed of 23.3 and 76.7 mole percent heptane and benzene, respectively, yield relative gram sensitivities of 0.55 for a binary mixture containing 28 weight percent heptane. Column 3 presents $s_H(g)/s_B(g)$ values determined in the present investigation. The experimental sensitivity data were obtained using ion-source temperatures of a) either room temperature or 70-110°C by Hippe and Beckey (5a) and b) 100°C in this study.

The agreement between the two sets of relative gram sensitivity data in Table I is reasonable although not quantitative. In this regard, the $s_H(g)/s_B(g)$ values in column 2 for binary mixtures containing weight percents of heptane ranging from greater than 79 to less than 100 could reflect the possibility that the m/e 100 and m/e 78 ion abundance curves in Figure 6 (5a) for gaseous mixtures containing mole percents of heptane in excess of 75 but less than 100 are based upon interpolations rather than upon experimental points. However, the data in both columns 2 and 3 show that the gram sensitivity for FI of heptane relative to the gram sensitivity for FI of benzene determined at ion-source temperatures of *ca.* 100°C decreases as the weight percent heptane in the binary mixture increases. The decrease in $s_H(g)/s_B(g)$ is most dramatic for mixtures containing in excess of 80 weight percent heptane.

Relative field-ionization gram sensitivities determined as a function of ion-source temperatures of 100°, 150°, and 200°C and in Table III for an ion-source temperature of 270°C. As shown in the footnotes to Tables II and III, the $s_H(g)/s_B(g)$ values are based upon 1 to 6 determinations for gaseous-binary-mixture pressures in the ion source ranging from *ca.* 1.1×10^{-5} torr to *ca.* 9.0×10^{-5} torr. The standard deviation in any given average relative sensitivity is based upon the individual $s_H(g)/s_B(g)$ values calculated from 3 to 18 FI/MS. The percent standard deviations for the 35 average $s_H(g)/s_B(g)$ values produces an average percentage uncertainty of 6.3 ± 3.0 . Relative sensitivities were determined as a function of the pressure of the gaseous binary mixture in the ion source (pressures are specified in the appropriate footnotes in Tables II and III) for mixtures containing the following weight percents of heptane at the indicated ion-source temperatures: 25% at 200° and 270°C, 51% at 150° and 270°C, 74% at 150°C, 80% at 100°C, 90% at 100°, 150°, 200°, and 270°C, and 97% at 100°, 150°, 200°, and 270°C. The average percent standard deviation for the 15 average relative sensitivities measured as a function of ion-source pressure is 8.3 ± 2.5 . The average percent standard deviation for the remaining 20 average $s_H(g)/s_B(g)$ values is 4.8 ± 2.5 . Although the average percent standard deviation in the relative sensitivities determined over a range in ion-source pressures is on the average slightly greater than the corresponding value calculated for the relative sensitivities measured at essentially a single ion-source pressure, the difference is clearly within the limits of data precision. In fact, the former and latter values of 8.3 ± 2.5 and 4.8 ± 2.5 , respectively, are not statistically different from the average percentage uncertainty of 6.3 ± 3.0 obtained for all determinations. The statistical uncertainty in the present data is commensurate with that obtained for the relative sensitivities for field ionization of aromatic compounds (3a).

TABLE II. Dependence of FI Sensitivity for n-Heptane Relative to Benzene on Mixture Composition at Various Ion-Source Temperatures

Weight Percent Heptane	Relative Gram Sensitivities ($\times 10^2$) ^{a,b} at an Ion-Source Temperature of		
	100°C ^c	150°C	200°C
25	67.0 $\pm$ 1.6	47.6 $\pm$ 4.2	24.5 $\pm$ 1.4 ^m
51	62.9 $\pm$ 5.6 ^d	47.9 $\pm$ 2.4 ⁱ	27.1 $\pm$ 0.5
60	63.4 $\pm$ 5.0	46.1 $\pm$ 2.1	29.6 $\pm$ 0.8
74	64.0 $\pm$ 3.4 ^e	48.5 $\pm$ 3.2 ^j	34.4 $\pm$ 1.3
80	62.3 $\pm$ 5.1 ^f	50.1 $\pm$ 2.3	30.4 $\pm$ 1.3
90	55.1 $\pm$ 5.2 ^g	43.1 $\pm$ 3.0 ^k	30.4 $\pm$ 2.6 ⁿ
97	39.0 $\pm$ 5.0 ^h	35.8 $\pm$ 4.1 ^l	25.7 $\pm$ 2.5 ^o

^aValue represents a single determination based upon 3 FI/MS recorded at an ion-source pressure of $1.8\text{--}2.2 \times 10^{-5}$ torr unless otherwise noted. ^bDeviations are standard deviations. ^cUnless otherwise noted, values represent the average of two determinations on two different days. ^dAverage of four determinations at $2.0\text{--}2.2 \times 10^{-5}$ torr ion-source pressure. ^eAverage of three determinations at $2.0\text{--}2.2 \times 10^{-5}$ torr ion-source pressure. ^fAverage of five determinations at *ca.* 2.2, 3.0, and 4.8×10^{-5} torr ion-source pressure. ^gAverage of five determinations at *ca.* 3.3, 4.6, and 7.1×10^{-5} torr ion-source pressure. ^hAverage of five determinations at *ca.* 4.0, 4.6, 7.2, and 7.6×10^{-5} torr ion-source pressure. ⁱAverage of six determinations at *ca.* 1.1, 2.2, 2.6, 3.2, and 5.0×10^{-5} torr ion-source pressure. ^jAverage of five determinations at *ca.* 1.6, 2.2, 2.8, 4.8, and 7.6×10^{-5} torr ion-source pressure. ^kAverage of five determinations at 2.0, 3.0, 4.7, and 7.2×10^{-5} torr ion-source pressure. ^lAverage of four determinations at 2.2, 2.8, 4.6, and 9.0×10^{-5} torr ion-source pressure. ^mAverage of three determinations at 2.0, 2.8, and 4.8×10^{-5} torr ion-source pressure. ⁿAverage of four determinations at 2.1, 2.5, and 4.1×10^{-5} torr ion-source pressure. ^oAverage of four determinations at 4.2, 4.6, and 6.8×10^{-5} torr ion-source pressure.

TABLE III. Dependence of FI Sensitivity for n-Heptane Relative to Benzene on Mixture Composition at an Ion-Source Temperature of 270°C

Weight Percent Heptane	Relative Gram Sensitivity ($\times 10^2$) ^{a,b}	
	Day 1	Day 6
25	20.2 $\pm$ 0.7	24.2 $\pm$ 1.8 ^e
51	24.0 $\pm$ 1.8 ^c	24.6 $\pm$ 1.5
60	21.4 $\pm$ 0.1	23.4 $\pm$ 0.8
74	23.5 $\pm$ 1.2	26.8 $\pm$ 1.2
80	24.1 $\pm$ 0.7	26.7 $\pm$ 1.1
90	23.2 $\pm$ 3.0 ^d	25.1 $\pm$ 1.6 ^f
97	21.0 $\pm$ 2.1	26.0 $\pm$ 1.6 ^g

^aValue represents a single determination based upon 3 FI/MS recorded at an ion-source pressure of *ca.* $1.8\text{--}2.2 \times 10^{-5}$ torr unless otherwise noted.

^bDeviations are standard deviations. ^cAverage of five determinations at *ca.* 1.2, 2.4, 2.9, 4.9, and 7.6×10^{-5} torr ion-source pressure. ^dAverage of five determinations at *ca.* 1.2, 2.2, 2.8, 4.6, and 7.1×10^{-5} torr ion-source pressure. ^eAverage of two determinations at *ca.* 1.8 and 4.8×10^{-5} torr ion-source pressure. ^fAverage of two determinations at *ca.* 2.1 and 4.1×10^{-6} torr ion-source pressure. ^gAverage of two determinations at *ca.* 4.2 and 6.8×10^{-5} torr ion-source pressure.

For a given binary-mixture composition the data in Table II show that the FI sensitivity of heptane relative to the FI sensitivity of benzene decreases as the ion-source temperature is increased from 100° to 200°C. Furthermore, the variation in $s_H(g)/s_B(g)$ with change in the weight percent heptane in the binary mixture is seen to decrease as the ion-source temperature is increased from 100° to 200°C. The data in column 4 of Table II suggest that an ion-source temperature of 200°C is not quite high enough to reduce the dependence of $s_H(g)/s_B(g)$ on mixture composition to within the limits of data precision. The decrease in the relative sensitivities upon increasing the ion-source temperature from 100°C to 200°C appears to be greatest for binary mixtures containing either less than *ca.* 50% or greater than *ca.* 90% heptane.

The data in Table III reveal that increasing the ion-source temperature to 270°C results in $s_H(g)/s_B(g)$ values which are independent of binary mixture composition within the limits of experimental precision. It is encouraging to note that the relative sensitivities for each binary mixture measured over a six day interval agree in all cases within 2σ . Averaging the 14 $s_H(g)/s_B(g)$ values without regard to the standard deviation in each value leads to an average relative gram sensitivity of $(23.8 \pm 2.0) \times 10^{-2}$. Comparison of the data in Tables II and III suggests that increasing the ion-source temperature from 200° to 270°C has the greatest effect on the relative sensitivities for mixtures containing between *ca.* 50 to *ca.* 90 weight percent heptane.

Preliminary studies were made of the dependence of both the *m/e* 78 and *m/e* 100 ion abundances on the quantities of benzene and heptane injected into the batch-inlet system. Samples were introduced into the batch-inlet system using a 1 μ l zero dead-volume Hamilton syringe because the present inlet system does not permit introduction of precisely known volumes (quantities) of highly volatile materials. Consequently, the results are unavoidably subject to experimental imprecision. For ion-source temperatures of 100° and 270°C Figure 1 shows that, within the limits of data precision, the intensity of the benzene molecular ion (*m/e* 78) is a linear function of the quantity of benzene injected. Furthermore, it is important to note that doubling the moles of benzene in the ion source doubles the intensity of the *m/e* 78 ion at both ion-source temperatures within the limits of experimental precision. The dependence of the intensity of the heptane molecular ions (*m/e* 100) on the quantity of heptane injected is shown in Figure 2 for ion-source temperatures of 100° and 270°C. At both ion-source temperatures the intensity at *m/e* 100 exhibits either a negative departure from a linear dependence or two different linear dependences on the moles (volume) of heptane injected. However, at the lower ion-source temperature a linear dependence between moles (volume) of heptane injected and molecular ion peak height appears to attain when the volume of heptane injected into the inlet system exceeds *ca.* 0.8 μ l. At the higher ion-source temperature, the onset of a clear linear dependence of the *m/e* 100 intensity on moles of heptane occurs at heptane pressures 2-3 times lower than at the lower ion-source temperature. The linear segments of the curves in Figure 2, when extrapolated to zero volume of heptane, intersect the ion intensity axis at values greater than zero. However, the intercept is seen to be considerably greater for an emitter temperature of 100°C than for an emitter temperature of 270°C.

Equation 1 through 3 illustrate the implications of these results on the sensitivity for FI of heptane. In Equation 1, $S_H(m)$ is the FI mole sensitivity,

$$S_H(m) = I(H)_j / m(H)_j \quad (1)$$

Figure 1. Variation in Ion Abundance for Benzene Molecular Ion as a Function of µl Benzene Injected at Ion Source Temperatures of 100° and 270°C

Figure 2. Variation in Ion Abundance for Heptane Molecular Ion as a Function of µl Heptane Injected at Ion Source Temperatures of 100° and 270°C

$I(H)_j$ is the intensity at m/e 100 produced by m_j moles of heptane. Equation 2 is applicable for the region of both curves in Figure 2 in which the $C_7H_{14}^+$ intensity varies linearly with moles of C_7H_{14} injected. The first-order

$$I(H)_j = a(H)m(H)_j + b(H) \quad (2)$$

polynomial which describes this variation has a slope $a(H)$ in units of ion intensity mole⁻¹ and an intercept $b(H)$ in intensity units. Equation 3 is obtained by substituting Equation 2 into Equation 1. For $b(H) = 0$, Equation 3

$$S_H(m) = \frac{a(H)m(H)_j + b(H)}{m(H)_j} \quad (3)$$

shows that $S_H(m)$ is independent of the moles of heptane injected. For non-zero values of the intercept, i.e., $0 \leq b(H) \leq 0$, Equation 3 shows that the sensitivity is rigorously dependent on the moles of heptane injected. However, the observable dependence of the sensitivity on moles of heptane injected will depend on the magnitude of $b(H)$ relative to the product of $a(H)$ and $m(H)_j$ and the experimental uncertainties in each of these quantities. As seen in Equation 2, the standard deviation in the slope and intercept reflects the ion statistics, the accuracy of injection, and either the rate of effusion of heptane out of the reservoir into the ion source or the reproducibility in the time before sampling the ion intensity following injection.

Detailed numerical analysis of the data in Equations 1-3 in the units specified is unwarranted because of the inaccuracy presently associated with sample injection. Because of the method used to determine relative heptane/benzene FI sensitivities it is not possible to quantitatively relate the data in Figures 1 and 2 to the $s_H(g)/s_B(g)$ values in Tables II and III. However, a qualitative comparison is possible by using both the data given and the units specified in Figure 2 to calculate first estimates of the volume sensitivity for FI of heptane as a function of the volume of C_7H_{14} injected into the inlet system. The slope and intercept calculated for the straight line drawn through the linear portion of the curve for each ion-source temperature is given in Table IV and were used in Equation 3 to calculate volume sensitivities as a function of the volume of heptane injected. The values so obtained are presented in Table IV. The dependence of the sensitivity on the volume of heptane is seen to be considerably greater at the lower emitter temperature. As noted above, the sensitivity for FI of benzene is independent of the volume of C_6H_6 injected within the limits of data precision. Consequently, the variation in the relative heptane/benzene sensitivity calculated from the individually determined sensitivities will reflect the change in the heptane sensitivity over the range in the volume injected in relation to experimental factors such as the reproducibility in the ion intensities and the accuracy of sample injection. For example, the typical volumes of binary mixtures used to determine the benzene/heptane relative sensitivities shown in Table III for an ion-source temperature of 270°C were such that the variation in heptane sensitivity is

TABLE IV. Dependence of Volume Sensitivities on Volume of Heptane Injected at Emitter Temperature of 100° and 270°C

Volume (μ l)	Sensitivity (mm/ μ l) at Emitter Temperature of	
	100°	270°
0.5	-	163
0.9	258	135
1.0	-	131
1.25	205	125
1.50	182	120
1.75	166	117
2.00	154	115
2.25	145	113
2.50	137	112
2.75	131	111
3.0	-	110
Slope (mm/ μ l)		69
Intercept (mm)		32

estimated to be ca. 15-20%. Since this variation in the C_7H_{14} sensitivity approximates the imprecision which can be expected from all factors influencing the determination of the C_7H_{14}/C_6H_6 relative sensitivities in Table III, the $s_H(g)/s_B(g)$ values determined at this ion-source temperature could appear to be essentially independent of binary mixture composition. On the other hand, comparison of relative sensitivities determined experimentally and calculated from individually determined sensitivities implicitly assumes that each component in the gaseous mixture field ionizes independently of the other ones. Consequently, both relative and individual sensitivities will be determined using precisely known quantities of sample. These data will thus permit a detailed numerical comparison of experimentally determined and calculated relative saturate and saturate/aromatic sensitivities. Such data are necessary for developing FI/MS for the quantitative analysis of saturates and for predictive purposes.

Table V presents sensitivities for FI of decane relative to the sensitivity for FI of ethylbenzene at ion-source temperature of 100° and 300°C as a function of both mixture composition and the microamperes of current flowing in the high-voltage power supply for the emitter; this current is termed the emitter current and is proportional to the field potential. At both ion-source temperatures the decane relative sensitivity is seen to be independent of field potential for each binary mixture within the limits of precision. The decane

TABLE V. Decane/Ethylbenzene Relative FI Gram Sensitivity as a Function of Sample Composition, Ion-Source Temperature, and Field Strength

T°C	C ₈ H ₁₀ C ₁₀ H ₂₂	Emitter Current (μA)				
		90	100	optimum	110	120
100	80:20	0.63 ± 0.01	0.53 ± 0.14	0.55 ± 0.10	0.67 ± 0.03	0.70 ± 0.03
	50:50	0.57 ± 0.01	0.52 ± 0.00	0.52 ± 0.07	0.59 ± 0.01	0.64 ± 0.04
	35:65	0.55 ± 0.02	0.50 ± 0.03	0.49 ± 0.05	0.60 ± 0.01	0.61 ± 0.03
	20:80	0.50 ± 0.06	0.55 ± 0.04	0.43 ± 0.08	0.59 ± 0.04	0.61 ± 0.00
	10:90	0.37 ± 0.02	0.33 ± 0.01	0.35 ± 0.02	0.40 ± 0.03	0.47 ± 0.01
	5:95	0.29 ± 0.01	0.31 ± 0.02	0.33 ± 0.04	0.36 ± 0.01	0.41 ± 0.01
300	80:20	0.15 ± 0.01	0.14 ± 0.01	0.10 ± 0.02	0.12 ± 0.01	0.12 ± 0.02
	50:50	0.14 ± 0.01	0.12 ± 0.01	0.11 ± 0.02	0.11 ± 0.02	0.12 ± 0.01
	35:65	0.13 ± 0.02	0.12 ± 0.00	0.09 ± 0.01	0.10 ± 0.00	0.10 ± 0.00
	20:80	0.11 ± 0.01	0.11 ± 0.01	0.10 ± 0.03	0.08 ± 0.01	0.10 ± 0.01
	10:90	0.09 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	0.09 ± 0.01	0.09 ± 0.01
	5:95	0.08 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.02	0.08 ± 0.01

relative sensitivity decreases with increasing weight percent decane at an ion-source temperature of 100°. Increasing the ion-source temperature from 100° to 300°C decreases the decane relative sensitivity. At 300°C there is some indication that the decane relative sensitivity may be slightly lower for mixtures containing in excess of 80 weight percent decane than for mixtures containing less decane. However, it is pragmatically important to note that this difference, if it does indeed exist, is most probably within the limits of experimental reproducibility. Hence, a single value for the relative gram sensitivity for decane can be used for ion-source temperatures in the range 270-300°C.

Mixtures were prepared which closely approximate in composition those used by Ryska, Kuras, and Mostecky (5b). Relative sensitivities reported by these authors using an ion-source temperature of 120°C and determined in this investigation using an ion-source temperature of 100°C are tabulated in Table VI. Ryska, Kuras, and Mostecky (5b) did not report standard deviations in their sensitivity data. However, based upon the standard deviation in our relative sensitivities, it is important to note that only 4 out of the 28 individual sensitivity determinations in the 5 mixtures differ by more than 2σ from their corresponding values. Our results quantitatively support the contention of these authors that 1) relative sensitivities for saturates depend upon the weight percent ethylbenzene in the mixture for mixtures containing up to ca. 33% ethylbenzene and 2) the *n*-alkane relative gram sensitivities approach each other in magnitude when ethylbenzene comprises at least 30% of the mixture.

Table VII presents relative sensitivities determined at an ion-source

2, 3, and 4 in Tables VI and VII shows that the increase in ion-source temperature 1) enhanced the sensitivity of hexane, heptane, octane, nonane, and ethylbenzene and 2) depressed the sensitivity of undecane relative to the sensitivity for

TABLE VI. The Variation of Relative Gram-Sensitivities of n-Alkanes in Hydrocarbon Mixtures at Low Ion-Source Temperature^a

Compound	Mixture #1		Mixture #2		Mixture #3		Mixture #4		Mixture #5a	
	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b
	Our Work ^a									
Hexane	14.4	0.36 ± 0.04	12.2	0.54 ± 0.11	15.8	0.53 ± 0.05	10.5	0.78 ± 0.06		
Heptane	16.6	0.55 ± 0.05	13.9	0.71 ± 0.08	14.6	0.72 ± 0.05	10.8	0.94 ± 0.11	16.2	0.39 ± 0.04
Ethylbenzene			10.2	1.49 ± 0.08	17.8	1.42 ± 0.13	32.3	1.29 ± 0.13		
Octane	16.5	0.65 ± 0.06	15.6	0.76 ± 0.06	12.3	0.79 ± 0.05	12.1	0.90 ± 0.06	12.5	0.58 ± 0.05
Nonane	20.2	0.82 ± 0.07	15.9	0.88 ± 0.04	13.3	0.92 ± 0.06	11.5	0.97 ± 0.04	13.6	0.80 ± 0.07
Decalin									31.6	1.04 ± 0.05
Decane	16.0	1.00	15.7	1.00	12.7	1.00	11.8	1.00	13.0	1.00
Undecane	16.3	1.16 ± 0.07	16.5	1.06 ± 0.06	13.4	1.04 ± 0.05	11.0	1.06 ± 0.08	13.1	1.09 ± 0.07
	Previous Work ^{a,c}									
	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b	wt. %	S/S _{decane} ^b
Hexane	16.5	0.29	14.3	0.67	14.9	0.81	11.4	0.94		
Heptane	16.7	0.45	14.9	0.82	13.5	0.96	11.1	1.01	17.3	0.48
Ethylbenzene			9.3	1.16	19.6	1.18	33.2	1.26		
Octane	15.7	0.59	15.6	0.83	12.0	1.10	10.9	0.93	12.4	0.61
Nonane	17.8	0.80	15.1	0.94	13.0	0.87	11.2	0.96	12.5	0.78
Decalin									32.2	0.93
Decane	17.1	1.00	14.9	1.00	13.5	1.00	11.3	1.00	12.7	1.00
Undecane	16.3	1.12	15.9	1.04	13.5	0.97	11.0	0.94	13.0	1.15

^aFor our work, the ion-source temperature was at ca. 100°C and the inlet temperature was ca. 300°C; for the previous work done by Ryska et al., the ion-source temperature was ca. 120°C and the inlet temperature was ca. 270°C.

^bGram sensitivity values relative to decane.

^cSee Reference 5b.

TABLE VII. Relative Gram Sensitivities of n-Alkanes in Hydrocarbon Mixtures at an Ion-Source Temperature of 270°C^a

Compound	MIXTURE #1		MIXTURE #2		MIXTURE #3		MIXTURE #4		MIXTURE #5	
	wt.%	S/S _{decane}	wt.%	S/S _{decane}	wt.%	S/S _{decane}	wt.%	S/S _{decane}	wt.%	S/S _{decane}
Hexane	14.4	1.08 ± 0.14	12.2	1.78 ± 0.36	15.8	1.61 ± 0.20	10.5	1.96 ± 0.62		
Heptane	16.6	1.35 ± 0.14	13.9	1.92 ± 0.27	14.6	1.72 ± 0.25	10.8	2.05 ± 0.43	12.4	1.29 ± 0.25
Ethylbenzene			10.2	5.59 ± 0.71	17.8	4.80 ± 0.60	32.3	4.83 ± 0.84		
Octane	16.5	1.11 ± 0.12	15.6	1.27 ± 0.16	12.3	1.19 ± 0.14	12.1	1.44 ± 0.19	10.1	1.05 ± 0.17
Nonane	20.2	1.03 ± 0.09	15.9	1.13 ± 0.12	13.3	1.05 ± 0.18	11.5	1.21 ± 0.13	10.7	1.05 ± 0.14
Decalin									42.6	3.61 ± 0.32
Decane	16.0	1.00	15.7	1.00	12.7	1.00	11.8	1.00	12.4	1.00
Undecane	16.3	0.93 ± 0.12	16.5	0.85 ± 0.11	13.4	0.82 ± 0.08	11.0	0.82 ± 0.09	11.9	1.03 ± 0.12

^a All values relative to decane.

decane. For mixtures 1 and 5 which contain only saturated hydrocarbons, the relative sensitivities for compounds having lower and higher molecular weights than decane are also enhanced and depressed, respectively; a marked increase is seen in the relative sensitivity for field-ionization of decalin. The relative sensitivities obtained for the various components in mixtures 2, 3, and 4 demonstrate that increasing the ion-source temperature from 100° to 270°C eliminates the dependence of the *n*-alkane relative sensitivities on the weight percent of ethylbenzene in the mixture within the limits of data precision. Based upon the standard deviations in Table VII the dependence of relative sensitivity on mixture composition would have to be $\geq 14\%$ in order to be observable.

Comparison of the results for the saturate mixtures 1 and 5 in Tables VI and VII reveals that increasing the ion-source temperature from 100° to 270°C tends to equalize the relative gram sensitivities for the *n*-alkanes. In this regard, relative FI sensitivities were determined at an ion-source temperature of 270°C for 20 alkanes and naphthenes in 22 mixtures containing only saturated hydrocarbons. Table VIII presents relative sensitivities determined for 10 of these mixtures and the average value for each relative sensitivity. As seen in Table VIII, relative sensitivities were determined in a number of instances using a reference compound other than decane; these values were multiplied by the sensitivity of the particular reference compound relative to decane. The data in Table VIII clearly supports the contention that the relative gram sensitivity for field ionization of saturates are independent of mixture composition for mixtures containing *n*-alkanes, cycloalkanes, and alkylated cycloalkanes within the limits of experimental precision and at an ion-source temperature of 270°C.

Comparison of the data in columns 3 and 4 of Table IX reveals that the relative sensitivities for a variety of saturates in the absence of aromatics are within 2 σ identical to the values obtained in the presence of ethylbenzene and 1-ethylnaphthalene. The result for heptane (1.25 ± 0.13) is unexplainably different from the average value of 1.19 ± 0.17 from Table VI. The sensitivity for 1-ethylnaphthalene relative to ethylbenzene (1.02 ± 0.04) is consistent with previous data for methyl- and dimethylnaphthalene (3a).

Relative gram and mole sensitivity for saturates obtained with an ion-source temperature of 270°C are tabulated according to compound type in Table X. The data for the *n*-alkanes suggests that the relative mole sensitivity increases by *ca.* 0.11-0.12 per CH₂ group. Heptane appears to be an exception. The sensitivities for the parent naphthenes are seen to be considerably greater than the sensitivities for the *n*-alkanes containing the same number of carbons on a mole basis. The data for the cyclohexanes indicate that the structure of the alkyl substituent markedly effects the cross-section for field ionization of the parent compounds. The results obtained for cyclohexane, decalin, perhydrofluorene and perhydropyrene suggest that the mole sensitivity increases noncumulatively as the number of fused naphthene rings rises. However, additional sensitivity data are obviously required before attempting to formulate any correlations between the number of condensed naphthene rings and mole sensitivity.

Table XI presents analytical data obtained from FI/MS analysis of a five-component test mixture. Comparison of the known weight percents (column 3) with those calculated 1) assuming unit relative sensitivities (column 4) and 2) including sensitivity corrections (column 5) shows that including relative sensitivities into the conversion of ion abundance to weight percents significantly enhances the accuracy of the analysis.

The present results clearly indicate that mixture independent relative sensitivities for the field-ionization of saturates can be determined for mixtures

Table VIII. The Gram Sensitivities of Some Saturate Hydrocarbons Relative to Decane in Saturate Hydrocarbon Mixtures

Compound	M.W.	Mixture 6	Mixture 7	Mixture 8	Mixture 9	Mixture 10	Mixture 11	Mixture 12	Mixture 13	Mixture 14	Mixture 15	Average ^d
cyclohexane	84					2.07 ± 0.10					1.75 ± 0.26	1.89 ± 0.22
hexane	86	0.85 ± 0.07				0.93 ± 0.12						0.89 ± 0.09
methylcyclohexane	98	1.97 ± 0.05						1.74 ± 0.38			2.02 ± 0.26	1.88 ± 0.31
heptane	100	1.39 ± 0.10				1.25 ± 0.15						1.24 ± 0.13
octane	114	(1.01) ^a	1.00 ± 0.06			1.01 ± 0.06		0.99 ± 0.12				1.01 ± 0.10
nonane	128		1.08 ± 0.06			1.03 ± 0.06			1.09 ± 0.20			1.06 ± 0.10
decalin	138			3.65 ± 0.27			3.68 ± 0.44		3.46 ± 0.45	(3.60) ^b		3.60 ± 0.37
n-butylcyclohexane	140		2.78 ± 0.10					2.68 ± 0.21			2.90 ± 0.29	2.76 ± 0.23
decane	142		1.00	1.00		1.00	1.00	1.00	1.00			1.00
undecane	156			1.00 ± 0.08					1.05 ± 0.17			1.05 ± 0.12
n-hexylcyclohexane	168			2.58 ± 0.16				2.59 ± 0.13		2.64 ± 0.19	2.75 ± 0.19	2.62 ± 0.15
dodecane	170			1.04 ± 0.09			1.07 ± 0.09					1.02 ± 0.10
perhydrofluorene	178			2.46 ± 0.15	(2.53) ^c		2.76 ± 0.33	2.56 ± 0.23	2.45 ± 0.38	2.53 ± 0.22	(2.53) ^c	2.53 ± 0.27
3-methylcyclohexyl- cyclohexane	180				3.11 ± 0.17				2.86 ± 0.47		3.03 ± 0.19	3.00 ± 0.30
perhydropyrene	218				3.56 ± 0.30				3.33 ± 0.41			3.37 ± 0.35
hexadecane	226				1.08 ± 0.10		1.06 ± 0.18		1.17 ± 0.18	1.01 ± 0.10		1.06 ± 0.14

^a Average of 33 determinations in 4 mixtures.^b Average of 27 determinations in 3 mixtures.^c Average of 61 determinations in 5 mixtures.^d The average values were taken from 16 mixtures (not including mixtures 1 through 5b) made for this study. Sensitivities from 10 of these mixtures are shown.

TABLE IX. Relative Gram Sensitivities of n-Alkanes and Naphthenes in the Presence of Aromatic Components at an Ion-Source Temperature of 270°C

Compound	wt. %	S/S _{decane}	S/S _{decane} ^a
cyclohexane	8.1	1.99 ± 0.26	1.89 ± 0.22
heptane	11.1	1.25 ± 0.13	1.24 ± 0.13
ethylbenzene	6.0	4.73 ± 0.48	
n-butylcyclohexane	11.9	2.31 ± 0.22	2.76 ± 0.23
decane	12.7	1.00	1.00
1-ethylnaphthalene	7.7	4.83 ± 0.57	
n-hexylcyclohexane	8.7	2.22 ± 0.18	2.62 ± 0.15
dodecane	7.7	0.99 ± 0.14	1.02 ± 0.10
perhydrofluorene	8.7	2.04 ± 0.19	2.53 ± 0.27
hexadecane	17.3	0.81 ± 0.05	1.06 ± 0.14

^aValues determined from mixtures containing only saturates.

TABLE X. Relative Sensitivities for Saturate Hydrocarbons^a

<u>n</u> -Alkanes ^b	Gram Sensitivity	Mole Sensitivity	Δ/C^c	Naphthenes ^b	Gram Sensitivity	Mole Sensitivity
hexane (22)	0.89	0.54		cyclohexane (18)	1.89	1.12
heptane (34)	1.24	0.87	0.33	methylcyclohexane (26)	1.88	1.30
octane (33)	1.01	0.81	0.14	n-butylcyclohexane (24)	2.76	2.72
nonane (30)	1.06	0.96	0.14	n-hexylcyclohexane (41)	2.62	3.10
decane	1.00	1.00	0.12	n-nonadecylcyclohexane (18)	1.56	3.85
undecane (36)	1.06	1.16	0.12	3-methylcyclohexylcyclohexane (19)	3.03	3.84
dodecane (42)	1.03	1.23	0.12	decalin (27)	3.60	3.50
tridecane (27)	1.07	1.39	0.12	perhydrofluorene (61)	2.53	3.17
hexadecane (64)	1.05	1.67	0.11	perhydropyrene (21)	3.37	5.17
octadecane (18)	0.99	1.76	0.10			
nonadecane (18)	1.07	2.02	0.11			
tetracosane (18)	0.98	2.32	0.10			

^aAll values relative to decane; percent standard deviation in values is ca. 10.^bValues in parentheses are the number of determinations.^cChange in molar relative sensitivity per carbon number above hexane.

TABLE XI. Use of FI Relative Sensitivities in the Quantitative Analysis of a Saturate Mixture

Nominal Mass	Compound	Grams	Weight Percent by FI/MS	
			$S_i/S_j = 1$	S_i/S_j
138	decalin	10.7	19.8	9.9
142	decane	34.3	19.9	34.9
170	dodecane	17.0	12.4	17.9
178	perhydrofluorene	14.6	26.6	15.1
226	hexadecane	23.5	21.3	22.2

containing 1) only saturated hydrocarbons and 2) mixtures containing both saturated and aromatic hydrocarbons. These preliminary studies thus lead to the conclusion that field-ionization mass spectrometry can be developed as a technique for obtaining quantitative distributions for 1) mixtures containing saturated hydrocarbons and 2) for mixtures containing both saturated and aromatic hydrocarbons if the field-ionization mass spectra can be obtained with the requisite resolution. Consequently, the determination of relative sensitivities for the field-ionization of saturated hydrocarbons both in the absence and presence of aromatic hydrocarbons and the use of these relative sensitivities in the analysis of both known and unknown mixtures is being pursued vigorously.

Application of Field-Desorption Mass Spectrometry to the Analysis of Materials Derived from Fossil Fuels

Field-desorption mass spectrometry, FD/MS, (7) is a powerful method for obtaining mass spectra of relatively non-volatile high-molecular weight compounds (8). Since the technique should thus be ideally suited to the analysis of heavy ends obtained from various sources of fossil energy, considerable activity has been devoted during the past year to developing FD/MS capability in our laboratory. Task completion, which involved design and fabrication of the various components such as the emitter probe, emitter holder, power supplies, activation and etching cells, and vacuum system, was expedited by combining activities under ERDA contracts EY-76-S-02-0020, EX-76-S-01-2537, and EX-76-C-01-2011. Since component fabrication is essentially complete and since knowledge has been acquired concerning the operation of equipment necessary for activation of field-desorption emitters (9), these activities are discussed and instrument schematics are presented.

At the present time we do not possess a spot-welder which is appropriate for welding the 8 μ m tungsten wire to the tungsten emitter posts. However, a satisfactory spot-welder will be acquired with funds provided under the renewal of this contract. Fortunately a source for spot-welding of emitters on a temporary basis was located (10) and will continue to be used until a spot-welder is acquired.

The oxidation-reduction apparatus used to prepare the wire emitter surface for high-temperature activation is illustrated in Figure 3 (9b). To reduce the possibility of an explosion, the system is purged with argon for *ca.* 20 minutes before hydrogen is introduced. The surface of the wire is cleaned by raising the temperature of the wire to *ca.* 1300°C for 2-4 minutes in a hydrogen atmosphere; heating of the wire requires an output of 200 mA from the DC power supply. The current to the emitter is then reduced (170-190 mA) until the temperature of the wire falls just below the value required to make the wire glow. The three-way stopcock is then adjusted so that hydrogen gas saturated with water vapor can be passed over the wire for 4-5 seconds. The oxide layer on the surface of the wire which is formed in this step is then reduced to the metal by returning to a pure hydrogen atmosphere (three-way stopcock is repositioned) and by increasing the temperature of the wire to 1300°C. The oxidation-reduction procedure is repeated 2-5 times to ensure proper etching of the 8 μ m tungsten wire.

The cap containing the FD emitter is then transferred to the emitter-conditioning cell which is illustrated in Figure 4. The cell is then evacuated (*ca.* 10^{-5} torr) and gaseous benzonitrile is introduced until the pressure reaches 10^{-3} torr by means of the vacuum line and manifold shown in Figure 5. The potential of the emitter (anode) is then raised to 8-10 kV with respect to the cathode; the current flowing through the emitter is 28 mA. Crude emitters which

Figure 3. FD Emitter Oxidation-Reduction Apparatus

Figure 4. FD Emitter Conditioning Cell

Figure 5. Conditioning Cell Vacuum Line and Manifold

were fabricated by soldering an 8 μ m wire to the steel posts were used in initial applications of the apparatus. Application of high potentials to these crude emitters generally resulted in high-voltage discharges which unfortunately melted the solder joints holding the emitter wire to the posts. However it was encouraging to note that ion currents of 10^{-8} amperes were obtained with these soldered emitters before they were destroyed. It is important to note that this problem is not observed with spot-welded emitters. The occurrence of high-voltage discharges has been observed to decrease upon conditioning of the activation cell. This process involves, in part, the deposition of a brownish-black deposit on the inside surface of the activation cell. The material is formed by glow discharging the activation cell using a benzonitrile pressure of 100 microns and an emitter potential of 6-10 kV for 4 hours. Additional activation is counterproductive due to the occurrence of violent discharges which remove the deposited material. Initial attempts at growing carbon dendrites on the surface of the etched 8 μ m tungsten wire were unsuccessful. In this regard, a major experimental problem involves the careful control of the current flowing through the emitter wire in order to avoid rupturing the 8 μ m tungsten wire during the growth of carbon dendrites on it. After considerable experimentation, we have been able to obtain emitters which appear to exhibit a considerable growth of carbon dendrites. The validity of this conclusion will be ascertained at least in part by using these emitters in an attempt to obtain field-desorption mass spectra.

The 0-15 kV power supply which is used in operating the CEC 21-110B mass spectrometer in the field-ionization mode (11) was modified by addition of a DC power supply to provide current for heating the FD emitter. The schematic diagram for the modified power supply which permits operation of the mass spectrometer in either electron-impact, field-ionization, or field-desorption mode is reproduced in Figure 6. To convert from operation in the EI mode to operation in the FI mode the tip-jack plugs are moved from positions 1, 2, 3, and 5 to the corresponding prime positions. For operation in the FD mode, high voltage is applied to the block and to the counter electrode (referred to as either the cathode or in Figure 6 the slit) using either pins 1' or 6 and either 2' or 7, respectively. In order to supply current from the 0-50 mA power supply to the FD emitter the leads to the repellers are connected to plugs 8 and 9. The FD emitter probe has been designed to allow 1) rapid and reproducible exchange of emitters and 2) application of high voltage to the emitter and passage of an electric current through the emitter using the ion-source repellers for electrical contacts rather than wires passing from the emitter through the probe to a vacuum feedthrough. Both the modified FI/FD high-voltage power supply and the FD emitter probe have been tested using the soldered emitters and were found to be routinely operational.

The schematic for the high-voltage power supply in Figure 4 is reproduced in Figure 7. This power supply is equivalent in design to the one shown in Figure 6. The negative side of the power supply is referenced to ground and the positive terminal is connected to one side of the emitter. The other side of the emitter is connected to the negative side of the 0-50 mA power supply which is referenced to the positive terminal of the 0-15 kV power supply.

As seen in Figure 4, an electrometer is necessary for monitoring the ion-beam output from the emitter during the growth of carbon dendrites on it. Attempts at using the original equipment CEC 21-110B total ion current monitor which had been replaced with a Keithley 417 picoameter as the electrometer in Figure 4 were unsuccessful. Figure 8 shows the wiring diagram for the electrometer which was subsequently designed and built to measure ion-beam currents in the

Figure 6. Modified Cathode High Voltage Power Supply

Figure 7. Emitter Conditioning Power Supply

Figure 8. Schematic for Electrometer: Shown for Electrometer in Figure 4

10^{-4} to 10^{-7} amp range. As seen in Figure 8, the module is relatively simple in design and uses an inexpensive plug-in integrated circuit (IC) operational amplifier which is easily replaced if arcing occurs during growth of carbon dendrites on the emitter surface.

Data Processing

Numerical processing of both mass spectral data, obtained using the different ionization techniques and at various mass spectrometer operating resolutions, and information obtained from the separation of the sample prior to analysis constitutes an essential component of every characterization. Unfortunately conversion of experimental data to quantitative and qualitative distributions is exceedingly time consuming if done manually. However, high-speed digital computers are ideally suited to reduction, correlation, and interpretation of experimental mass spectral and separations data. In this regard, preliminary data processing programs have been developed for converting mass spectral ion abundance data for each fraction into quantitative distributions for that fraction and then for converting the quantitative distributions for the various fractions into distributions for the total sample (12). For samples possessing nitrogen compounds having odd molecular weights, the intensities of the ions having odd nominal masses in the low-resolution FI/MS are corrected for contributions from isotopically labelled ions corresponding to the adjacent lower-even-mass ion. The weight percent of the i th component in the j th Z series of each scan of the low-resolution FI/MS of the k th GPC fraction is computed assuming unit relative sensitivities. The weight percents at each nominal mass are averaged over all scans of the mass spectrum and the average weight percents are grouped according to nominal Z series.

The intensities of the resolved multiplets at a given nominal m/e value in the medium-resolution FI/MS of a given concentrate are used to factor the total average weight percent at that nominal mass into contributions from aromatic hydrocarbons and from heteroatom-containing components. Since compounds containing an even number of nitrogens are not generally observed, the average weight percents are thus obtained for aromatic hydrocarbons, $-Z$, and aromatic compounds containing oxygen, $-Z(O)$, and/or sulphur $-Z(S)$. The weight percents across each $-Z$, $-Z(O)$, $-Z(S)$, and $-Z(N)$ series are summed to obtain the total weight percents of aromatic CH, CHO, CHS, and CHN containing compounds, respectively, in a given GPC fraction.

Only every third GPC fraction is presently analyzed. Consequently, the total weight percent of each $-Z$ compound-type series is assumed to be identical for GPC fractions adjacent to the ones analyzed. The weights of an analyzed and its two adjacent GPC fractions are multiplied by the weight fractions for each Z series in the analyzed fractions to arrive at weights as a function of Z series for each fractions. The weights in each Z series are summed across all GPC fractions and the summations are then divided by the total weight of all GPC fractions to arrive at the distribution of weight percents according to compound class for a given concentrate. These weight percents are then multiplied by the weight fraction of 1) the concentrate in the distillate cut and 2) the concentrate in the crude to obtain weight percents as a function of $-Z$, $-Z(O)$, $-Z(S)$, $-Z(N)$ for each distillate cut in the total sample, respectively.

Additional program development is needed as follows. First, the quantitative distributions may reflect two types of overlaps. Since the resolution in any chromatographic separation is finite, overlap of compound classes will occur for the general case. For example, overlap generally occurs in the separation of mono- and diaromatics in the silica/alumina gel chromatography step of the separation. The second type of overlap reflects the simultaneous presence of compounds with different molecular formulas which will occur in the same nominal mass Z series. Examples of such overlapping are 1) hydrocarbons with different Z series, i.e., $Z_i = Z_j \pm 14$, 2) hydrocarbons and heteroatom-containing compounds. The use of GPC/MS correlations and high-resolution mass spectral data constitute approaches for correcting the distributions for such overlap. However, this procedure requires development of the appropriate computer programs. In determining the occurrence of overlap between hydrocarbons and certain types of sulfur compounds these approaches should be supplemented as follows. The percent sulfur should be calculated 1) from ion abundances for ions shown to contain sulfur and 2) for those m/e values where the possibility of overlap exists assuming that these ion abundances reflect only the presence of sulfur containing ions. The so obtained values will then be compared with the percent sulfur obtained from combustion measurements.

The second modification to the program involves the option of including sensitivity corrections in the conversion of ion intensities to quantitative distributions. The inclusion of sensitivity corrections is undoubtedly more important for low-voltage electron-impact ionization than for field ionization (3a). Presentation of the analytical data as weight percents as a function of carbon number for each Z series constitutes the third modification. The fourth modification involves incorporating the option of processing as many GPC fractions as desired.

Routine Analysis

High-resolution 70-eV electron-impact mass spectra were recorded on photographic plates for 56 of the 60 fractions obtained from separation of a Canadian Tar Oil Sand sample by the Separations and Characterization Group at the Bartlesville Energy Research Center. Insufficient amount of material precluded the acquisition of mass spectral data for GPC fractions 229-25, 204-8, 241-8, and 241-35. Because of high viscosity, samples of each fraction were introduced into the batch-inlet system of the CEC 21-110B as follows. After gentle warming of the sample, a pipet was used to transfer an aliquot to a small glass bulb. The neck of the bulb was then inserted through the hole in a rubber septum and the bulb plus septum was substituted for the rubber septum in the introduction port to the inlet system. Following evacuation of the introduction port, the contents of the bulb were heated with an auxiliary heater in order to introduce material into the glass-expansion volume. Mass spectra of the sample and the sample plus perfluorokerosene (PFK) were recorded on a photographic plate.

To date, high-resolution data have been recovered off of the photographic plates and processed for the saturate fractions, the total acids and total bases from the polyaromatic polar fraction, the polyaromatic silica/alumina concentrate, and at least one sample for each GPC series. Line positions for the ions in both the mass spectra of the sample and PFK were measured using a microdensitometer/comparator. The line positions were converted into exact ion masses for the m/e values in the mass spectrum of each sample and the exact masses were then computer processed to obtain molecular formulas.

Molecular formulas deduced from the high-resolution mass spectra processed to date are grouped according to Z values as a function of carbon number in Table XII. Both the nomenclature for each fraction and the boiling-point range is listed in column one. Columns two and three list the general formula of the compound type and the Z number, respectively. Note that the value of Z is determined based upon the elements present in each compound type. The last column lists the number of carbons in each Z series. Determination of the lowest molecular weight member in the various Z series for each fraction was difficult due to the unavailability of fragment-ion-free field ionization mass spectra. However, acquisition of the requisite FI/MS data is now possible due to the resolution of problems associated with the electron multiplier. Therefore, acquisition of the photoplate data was arbitrarily begun at the upper end of the half-mass region. The m/e value at which molecular formula determination commences in each Z series is given as a footnote in Table XII after each sample.

In the three saturate fractions, the molecular formulas of the compounds exhibit high Z numbers. The highest carbon number varies with the boiling-point range of the sample and the maximum carbon number is observed to increase as the boiling-point rises. The high-resolution mass spectral data for the first two saturate fractions provided no evidence for the presence of heteroatom-containing compounds. However, the present data are insufficient to exclude Z(S) compound types because the resolution required to resolve Z and Z(S) molecular ions at the same nominal mass generally exceeds the resolution attainable with our CEC 21-110B mass spectrometer. For example, the resolution required to resolve $C_7H_{12}S$ molecular ions from $C_{10}H_8$ molecular ions is 38,000 while the spectra were recorded at a resolution in excess of 13,000. Therefore, either elemental analysis or GPC/MS correlations or both should be used to either exclude or collaborate the presence of sulfur-containing compounds in these samples. In the mass spectrum of the third saturate fraction (489,490,491) molecular ions were observed at masses corresponding to $C_{10}H_8O$, $C_9H_8O_2$, $C_{11}H_{14}S$, $C_{14}H_8S$, and $C_{20}H_{10}S$. Since other homologues of these compound types were not observed, the presence of these ions was reconfirmed. The origin of these molecular ions is thus still open to question. Additional assignment of molecular formulas to a number of ionic species appears to be difficult assuming the presence of only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. Some of these ionic species have moderate intensities and exhibit sharp peak shapes which indicates that they are not metastable ions. Of the 17 samples presently analyzed, this phenomena has only been observed for the third saturate fraction. The possibility that a number of these ions can be produced from ionization of material from the silicone rubber septum in the inlet system is currently under investigation.

As mentioned above, the resolution capability of our CEC 21-110B is generally insufficient to resolve Z and Z(S) molecular ions. Consequently, the high-resolution mass spectral data alone are insufficient to define boundary conditions for the Z and Z(S) series. The following example illustrates the procedure arbitrarily adopted at the present time for cataloging the high-resolution mass spectral data for the remaining samples. For purposes of discussion, define Z, Z(H), and Z(S) as nominal mass, hydrocarbon compound type, and sulfur-containing compound type series. Both the -16(S) and the -26(H) series are members of the -26 series. The first member in the -26 Z(H) series ($C_{18}H_{10}$) occurs at mass 226. Sulfur-containing compounds which occur in the -16(S) series and which have a nominal mass of 226 possess the formula $C_{15}H_{14}S$. Thus, the -16(S) series intersects the -26(H) series at m/e 226. Consequently, molecular weights in the -26 Z series in GPC fraction 238-20 which are ≥ 226 are assigned to the -26(H) series and ≤ 212 are assigned to the -16(S) series. The equivalent procedure was applied where necessary

TABLE XII. Molecular Formulas Obtained from High Resolution 70-eV Mass Spectrometric Data

Fraction	General Formula	Z Number	Value of n
Saturates ⁽¹⁾ 480,481,482 (200-325°C)	$C_n H_{2n+Z}$	-12 -10 -8 -6 -4 -2 0 +2	10 8,9,10 8-13, 15-18 8-19 7-19 7-18 7-19 7-16
(1) The peaks below m/e 93 are not included.			
Saturates ⁽²⁾ 486,487,488 (325-425°C)	$C_n H_{2n+Z}$	-16 -14 -12 -10 -8 -6 -4 -2 0 +2	12 12 10-13 10-14, 16-26 10-28 9-28 9-27 9-26 9-24 9-12, 14,15
(2) The peaks below m/e 119 are not included.			
Saturates ⁽³⁾ 489,490,491 (425°C+)	$C_n H_{2n+Z}$	-16 -14 -12 -10 -8 -6 -4 -2 0 +2	12 12,13 12,13,14, 16 11-20, 22,23,25, 27-33 11-34 11-34 11-34 11-33 11-28 11-17, 23
(3) a. The peaks below m/e 143 are not included. b. The ionic species corresponding to $C_{10}H_8O$, $C_9H_8O_2$, $C_{11}H_{14}S$, $C_{14}H_8S$, $C_{20}H_{10}S$ and other ions (see text) were also observed.			
GPC 229-20 ⁽⁴⁾ Monoaromatics (200-325°C)	$C_n H_{2n+Z}$	-18 -16 -14 -12 -10 -8 -6	14 12,13,14 12-16 10-18 9-17 9-16 6-14

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
		-4	6-9
		-2	6-9
		0	6
	$C_n H_{2n+Z} O$	-12	10-16
		-10	9-15
		-8	8,9,10
		-6	8
(4) a. The peaks below m/e 78 are not included.			
b. The ionic species corresponding to C_5H_6S , C_6H_6S , and $C_{14}H_8S$ were also observed.			
GPC 230-20 ⁽⁵⁾	$C_n H_{2n+Z}$	-22	16
Di aromatics		-20	14-17
(200-325°C)		-18	14-18
		-16	12-18
		-14	12-18
		-12	10-18
		-10	10-17
		-8	10,11, 13,14,15
		-6	10,11
	$C_n H_{2n+Z} O$	-18	14,16
		-16	13-17
(5) a. The peaks below m/e 119 are not included.			
b. The ionic species corresponding to $C_{14}H_8S$ were also observed.			
GPC 231-17 ⁽⁶⁾	$C_n H_{2n+Z}$	-24	18
Monoaromatics		-22	16,17,18
(325-425°C)		-20	14,15, 17,18, 20
		-18	14-17, 19
		-16	12-27
		-14	12-27
		-12	10-27
		-10	9-26
		-8	9-25
		-6	6-23
		-4	6-13
		-2	6-13
		0	6-9
(6) a. The peaks below m/e 78 are not included.			
b. The ionic species corresponding to C_5H_6O , C_5H_8O , C_6H_6O , $C_{14}H_8S$, and $C_{14}H_{10}S$ were also observed.			

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
GPC 238-20 ⁽⁷⁾ Diaromatics (325-425°C)	$C_n H_{2n+Z}$	-28	20,21
		-26	18-23
		-24	18,19,20, 22,23
		-22	16-25
		-20	16-25
		-18	14-24
		-16	12-24
		-14	12-23
		-12	10-22
		-10	10-14, 18,19
		-8	10-13
		-6	9,10, 12
		-4	9,10
		$C_n H_{2n+Z} O$	-22
	-20		15-18, 22,23
	-18		14-23
	-16		13-21
	$C_n H_{2n+Z} S$	-20	14,15,16
		-18	14,15,16
		-16	12,13,14
		-14	12,13,14
		-12	11,12
		-10	10
		-8	10
(7) The peaks below m/e 119 are not included.			
GPC 239-14 ⁽⁸⁾ Monoaromatics (425°C+)	$C_n H_{2n+Z}$	-24	18
		-22	16,17
		-20	15-18
		-18	14-19, 32-36
		-16	13-22, 29-36
		-14	12-36
		-12	10-35
		-10	9-35
		-8	9-33
		-6	6-21, 26-32
		-4	6-16
		-2	6-13, 15
		0	6-10
		(8) The peaks below m/e 78 are not included.	

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
GPC 240-11 ⁽⁹⁾ Diaromatics (425°C+)	$C_n H_{2n+Z}$	-28	20,21,22, 24, 37, 39-43
		-26	18-24, 36-43
		-24	18-23, 37-43
		-22	16-23, 25, 33, 35-43
		-20	14-25, 27, 32-43
		-18	14-28, 30-42
		-16	12-41
		-14	12-40
		-12	11-23, 25,26, 30-38
		-10	11-23
		-8	10-23
		-6	10-20
		-4	10,11
		-2	10
		0	10
	$C_n H_{2n+Z} O$	-18	15,16,17, 19, 34
		-16	14-19, 33,34
	$C_n H_{2n+Z} S$	-22	14
		-20	14,15,16
		-18	14

(9) a. The peaks below m/e 131 are not included.

b. The ionic species corresponding to $C_{20}H_{10}S$ and $C_9H_{14}O$ were also observed.

GPC 240-17 ⁽¹⁰⁾ Diaromatics (425°C+)	$C_n H_{2n+Z}$	-32	22
		-30	22,23, 28-30
		-28	20-31
		-26	18-33
		-24	18-33
		-22	16-33
		-20	14-33
		-18	14-32
		-16	12-31
		-14	12-30
		-12	12-20, 25-28
		-10	11-19
		-8	11-17
		-6	11-16
		-4	11
	$C_n H_{2n+Z} O$	-24	25,26,27
		-22	16,17,18
		-20	15-21, 24-28
		-18	14-23, 25-28
		-16	12-19, 24-27

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
	$C_n H_{2n+Z} S$	-22	16,17,18
		-20	14-18
		-18	14,15,16
		-16	12,13,14
		-14	12,13,14
		-12	11,12
		-10	10
		-8	9,10
		-6	9
(10) a. The peaks below m/e 143 are not included.			
b. The ionic species corresponding to $C_{20}H_{10}S$ were also found.			
GPC 241-23 ⁽¹¹⁾	$C_n H_{2n+Z}$	-30	23
Polyaromatics		-28	20-24
Polar		-26	18-25
(325-425°C)		-24	18-23
		-22	16-23
		-20	14-23
		-18	14-22
		-16	12-22
		-14	12-18, 20
		-12	10-13
		-10	10,11,12
		-8	9,10,11
		-6	10
	$C_n H_{2n+Z} O$	-26	19,20
		-24	19-22
		-22	17-22
		-20	16-22
		-18	14-21
		-16	12-19
		-14	12, 18
	$C_n H_{2n+Z} S$	-24	20,21
		-22	16,17
		-20	14-17
		-18	14,15,16
		-16	12,13,14
		-14	12,13,14
		-12	11,12
		-10	9,10
		-8	9,10
		-6	7,8
		-4	7,8

(11) The peaks below m/e 119 are not included.

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
GPC 242-26 ⁽¹²⁾ Polyaromatics Polar (425°C+)	$C_n H_{2n+Z}$	-34	24,25
		-32	22-25
		-30	22-26
		-28	20-26
		-26	18-25
		-24	18-25
		-22	16-24
		-20	14-17
		-18	14,15,16
		-16	12-15
		-14	12,13
		-12	10,11,12
		-10	10,11
	$C_n H_{2n+Z} O$	-26	20-23
		-24	21,22
	$C_n H_{2n+Z} S$	-26	18,19
		-24	17-20
		-22	16,17,18
		-20	14-18
		-18	14,15,16
		-16	12,13,14
		-14	12,13,14
		-12	11,12
		-10	8, 10
		-8	8,9,10
		-6	7,8
		-4	7,8
	$C_n H_{2n+Z} N$	-27	23
		-25	23,24
		-23	22,23
		-21	17-23
		-19	16-23
		-17	15-22
		-15	14,15,16

(12) a. The peaks below m/e 119 are not included.

b. The ionic species corresponding to $C_{21}H_{16}O_2$ and $C_{21}H_{18}O_2$ were also observed.

GPC 242-32 ⁽¹³⁾ Polyaromatics Polar (425°C+)	$C_n H_{2n+Z}$	-32	22-26
		-30	22-25
		-28	20-24
		-26	18-23
		-24	18-21
		-22	16,17,18
		-20	14-17

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
		-18	14-18
		-16	12-17
		-14	12-15
		-12	10-14
		-10	10-13
		-8	11,12,13
		-6	9,10
		-4	9,10
	$C_n H_{2n+Z} O$	-36	23
		-30	22,23
		-28	20,21,22
		-26	20,21,22
	$C_n H_{2n+Z} S$	-30	20
		-28	20,21,22
		-26	18-22
		-24	17-22
		-22	16,17,18
		-20	14-18
		-18	14,15,16
		-16	12,13,14
		-14	12,13,14
		-12	11,12
		-10	8,9,10
		-8	8,9,10
		-6	7,8
		-4	7,8
	$C_n H_{2n+Z} S_2$	-26	20
	$C_n H_{2n+Z} N$	-27	21, 24
		-25	21,22,23
		-23	18, 20,21,22
		-21	18-21
		-19	17-20
	$C_n H_{2n+Z} N_2$	-34	21,22
	$C_n H_{2n+Z} NO$	-27	19
		-25	19,20
		-19	15
		-17	14
		-15	13

(13) The peaks below m/e 119 are not included.

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
PAP 480-482 ⁽¹⁴⁾ Polyaromatic Si-al Conc. (200-325°C)	$C_n H_{2n+Z}$	-26	19
		-22	16,17
		-20	14-17
		-18	14-18
		-16	12-19
		-14	12-18
		-12	10-16, 18
		-10	9-17
		-8	9-13
		-6	8-11
		-4	7-10
		-2	7,8,9
	$C_n H_{2n+Z} O$	-18	14, 16
		-16	12-16
		-14	12-17
		-12	10-17
		-10	9-14
		-8	8-11
		-6	6-9
		-4	6,7,8
		-2	7
	$C_n H_{2n+Z} O_2$	-16	15,16
		-14	16
	$C_n H_{2n+Z} S$	-16	12,13,14
		-14	12
		-12	11,12
		-10	8-11
		-8	8,9,10
		-6	6,7,8
		-4	6
		-2	6

(14) a. The peaks below m/e 93 are not included.

b. The ionic species corresponding to C_5H_6S and C_5H_8S are also observed.

PAP Acid ⁽¹⁵⁾ (425°C+)	$C_n H_{2n+Z} O$	-28	20-23
		-26	18, 20-26
		-24	18-26
		-22	16-24
		-20	16-23
		-18	14-19, 21,22
		-16	12-17
		-14	12,13,14
		-12	10-13
		-10	9-12

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
		-8	8-11
		-6	8,9
		-4	8,9
		-2	8
	$C_n H_{2n+Z} O_2$	-26	20-25
		-24	19-25
		-22	18, 22, 23, 24
		-12	11
		-10	10
		-8	9, 10
	$C_n H_{2n+Z}$	-32	22, 23
		-30	22-28
		-28	20-29
		-26	18-29
		-24	18-28
		-22	16-27
		-20	14-27
		-18	14-26
		-16	12-18, 20
		-14	12-15
		-12	10-15
		-10	10-13
		-8	10, 11, 12
		-6	9, 10, 11
		-4	9, 10
		-2	9, 10
		0	9, 10
	$C_n H_{2n+Z} S$	-22	16, 17
		-20	14-18
		-18	14, 15, 16
		-16	13, 14
		-14	13, 14
		-12	11, 12
	$C_n H_{2n+Z} N$	-31	24, 25

(15) The peaks below m/e 119 are not included.

PAP Base ⁽¹⁶⁾ (325-425°C)	$C_n H_{2n+Z} N$	-25	18, 19
		-23	17-23
		-21	16-24
		-19	15-26
		-17	14-26
		-15	12-26
		-13	12-25
		-11	10-25

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
		-9	9-23
		-7	9-21
		-5	9-14
		-3	9
	$C_n H_{2n+Z} NO$	-19	19
		-17	18, 19
		-15	18
		-13	17
		-11	11, 12
		-9	9-12
		-7	8, 9
		-5	8
	$C_n H_{2n+Z}$	-28	20, 21, 22
		-26	18-22
		-20	14
		-18	14
		-16	12, 13
	$C_n H_{2n+Z} S$	-20	14, 15
		-18	14, 15, 16
		-16	12, 13, 14
		-14	12, 13
		-12	11, 12, 13
		-10	8, 10
		-8	9, 10
		-6	8
(16) The peaks below m/e 131 are not included.			
PAP Base (17) (425°C+)	$C_n H_{2n+Z} N$	-29	22
		-27	21-25
		-25	18-28
		-23	17-28
		-21	16-29
		-19	15-29
		-17	14-28
		-15	12-26
		-13	13-17
		-11	14, 15
	$C_n H_{2n+Z} NO$	-23	18, 22
		-21	17, 19-24
		-19	15, 19-25
		-17	12, 13, 14, 17-24
		-15	13, 14, 21, 22, 23
		-13	14, 15
		-11	11, 12
		-9	11

TABLE XII. (Cond.)

Fraction	General Formula	Z Number	Value of n
	$C_n H_{2n+Z}$	-32	22
		-28	20, 21
		-26	18, 19
		-24	16
		-22	15, 16, 17
		-20	14, 15
		-18	12, 13, 14
		-16	11, 12, 13
		-14	11, 12
		-12	10, 11, 12
		-10	10, 11, 12
		-8	10, 11, 12
		-6	9, 10, 11
		-4	9, 10
		-2	9
		0	9
	$C_n H_{2n+Z} O$	-16	12
		-14	12
		-4	8, 10
	$C_n H_{2n+Z} O_2$	-16	12
		-14	12
	$C_n H_{2n+Z} S$	14	
(17) The peaks below m/e 119 are not included.			

to the remaining compound types in this GPC fraction and to the other samples presently analyzed. GPC/MS correlations, HR/MS data, analysis of the distribution of ion abundances in a given nominal mass Z series, and comparison of the weight percent elemental sulfur determined by combustion and calculated from ion abundances should be employed in obtaining analytical data for the sulfur-containing compounds.

As seen in Table XII a number of nitrogen containing compounds are observed in the polyaromatic polar GPC fractions 242-26 and -32 which are not observed in the polyaromatic polar GPC 241-23.

Two major compound types were observed in the acid fraction from the polyaromatic polars boiling above 425°C. The first type consists of oxygen-containing compounds and the second type has molecular formulas consistent with hydrocarbons. It will be interesting to see if this phenomena is also observed for the acid fraction for the polyaromatic polars boiling between 325-425°C.

The major compound types in the base fractions from the polyaromatic polars boiling from 325-425°C and above 425°C contain either nitrogen or nitrogen and oxygen.

REFERENCES

- 1) a) M. G. Inghram and R. Gomer, *J. Chem. Phys.*, 22, 1279 (1954); b) H. D. Beckey, "Field Ionization Mass Spectrometry", Pergamon Press, Oxford, England, 1971.
- 2) H. D. Beckey in "Biochemical Applications of Mass Spectrometry", G. R. Waller, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 30.
- 3) a) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, 48, 2105 (1976); b) S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, and N. B. Perreira, 24th Annual Conference on Mass Spectrometry and Allied Topics, 481 (1976); c) S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, C. S. Hsu, N. B. Perreira, P. A. Benson, K. N. Detwiler, and G. M. Stewart, *Preprints, Div. Petrol. Chem., Am. Chem. Soc.*, 22(2), 665 (1977).
- 4) G. G. Wanless and G. A. Glock, Jr., *Anal. Chem.*, 39, 2 (1967).
- 5) a) H. G. Hippe and H. D. Beckey, *Erdoel, Kohle, Erdgas, Petrochem.*, 24, 620 (1971); b) M. Ryska, M. Kuras, and J. Mostecky, *Int. J. Mass Spectrom. Ion Phys.*, 16, 257 (1975).
- 6) S. E. Scheppele, G. J. Greenwood, and P. A. Benson, *Anal. Chem.*, in press.
- 7) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 2, 500 (1969).
- 8) For a number of leading references of FD/MS applied to a variety of compound types and molecular weights see: a) H. R. Schulten and H. D. Beckey, *Org. Mass Spectrom.*, 7, 861 (1973); b) H. M. Fales, G. W. A. Milne, H. U. Winkler, H. D. Beckey, J. N. Damico, and R. Barron, *Anal. Chem.*, 47, 207 (1975); c) D. F. Barofsky, R. Held, and E. Barofsky, *Proc. 24th. Ann. Conf. Mass Spectrom. and Allied Topics*, 279 (1976); d) H. R. Schulten and H. D. Beckey, *ibid.*, 282 (1976); e) R. C. Charlton, K. L. Kan, P. Y. Lau, L. Lennill, G. N. S. Rao, and G. W. Wood, *ibid.*, 390 (1976).

- 9) a) H. D. Beckey, A. Hendricks, E. Hilt, M. D. Migahed, H. R. Schulten, and H. U. Winkler, *Messfchnik*, 79, 196 (1971); b) D. F. Barofsky and E. Barofsky, *Int. J. Mass Spectrom. Ion Phys.*, 14, 3 (1974).
- 10) We thank D. F. Barofsky and E. Barofsky for spot-welding emitters.
- 11) G. J. Greenwood, "Characterization of Coal-Derived Liquids Using Mass Spectrometry", Ph.D. Thesis, Oklahoma State University, 1977.
- 12) J. E. Dooley, S. E. Scheppele, and G. J. Thompson, "Characterizing Syncrudes from Coal" in "Analytical Methods for Coal and Coal Products", Ed. C. Karr, Jr., Academic Press, Inc., Chapter 32, in press.