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TO SUPPORT COAL-LIQUID CHARACTERIZATION RESEARCH

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ABSTRACT

Modification of our combined FI/EI ion source to permit operation in the FD mode is underway. Oxidation-reduction and activation cells were fabricated and assembly of the vacuum system for the activation cell is in progress. High- and low-voltage power supplies needed for emitter preparation were constructed.

The sensitivity for field ionization of decane relative to that for ethylbenzene was measured as a function of binary mixture composition, ion-source temperature, and field strength. A gallium frit is being added to our all-glass inlet system. The purity of 25 saturates and naphthenes and 10 single-ring aromatics substituted with alkyl groups was checked using FID/GC.

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

Commitments to provide high-resolution mass spectral data and assignments of elemental compositions based upon these data are being met. 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 DESCRIPTION OF TECHNICAL PROGRESS

Modification of FI/EI Ion Source to Operate in Field Desorption Mode

Modification of the combined FI/EI ion source to permit operation in the field-desorption (FD) mode and construction of auxiliary equipment is underway. This endeavor represents the combined effort of Dr. C. S. Hsu and Messrs. G. J. Greenwood, N. B. Perreira and is supported under ERDA contracts E(34-1)-0020, E(49-18)-2537, and E(49-18)-2011.

Preparation of an emitter requires uniform etching of the surface of the 8 μ m tungsten wire (1) followed by its activation in the presence of benzonitrile (2). An oxidation/reduction cell was fabricated for etching the tungsten wire. The design allows heating of the wire to 1300°C in a hydrogen atmosphere. After the surface is cleaned the temperature is reduced to ca. 750°C. A mixture of hydrogen and water vapor is then admitted to the oxidation-reduction cell by sweeping hydrogen gas through the water bath. The oxide layer so formed is reduced in a hydrogen atmosphere and at a wire temperature of 1300°C. The etched wire is transferred to the activation cell (2,3) and its potential is increased to ca. 10-12 kV with respect to the cathode. Carbon dendrites are grown on the wire by heating in the presence of benzonitrile (ca. 10^{-3} torr).

The low-voltage/low-amperage DC power supply for the oxidation-reduction cell has been fabricated. A regulated high-voltage/low-amperage DC power supply for the activation cell was constructed. The vacuum system designed for the activation cell contains a mechanical forepump, an oil diffusion pump, and two cold traps. The pressure in the activation cell will be monitored using a cold-cathode vacuum gauge; repair of the procured controller was necessary. The electrometer for measuring the ion current during the activation process has been obtained.

Determination of Field Ionization Sensitivities for Saturates

Use of FI/MS to determine compositional data for saturates requires knowledge of the sensitivities of these compounds towards ionization by high electric fields. Sensitivities have been reported and metastable spectra investigated for field ionization of a series of saturates (4). The significance of this investigation is not clear since other determinations of FI sensitivities for mixtures of saturates and saturates plus low-molecular weight aromatics indicates that these sensitivities are dependent on mixture composition (5-7). It is important to note that low ion-source temperatures were used in these latter studies. In this regard, studies in our laboratory (8) show that relative sensitivities for field ionization of aromatic compounds obtained at high ion-source (emitter) temperature are independent of mixture composition. Consequently, a systematic investigation of saturate FI sensitivities as a function of mixture composition, emitter temperature, the average thermal energy of the neutral molecules, ion-source pressures, and emitter potential has been initiated. The purpose of these investigations is to determine the applicability of FI/MS for the quantitative analysis of 1) saturate mixtures and 2) saturate and aromatic mixtures which would negate the need for separation of such mixtures

into saturates and aromatics. In order to expedite this research, we have combined research efforts under ERDA projects E(34-1)-0020, E(49-18)-2011, and E(49-18)-2537. Preliminary results obtained from our investigations of benzene-heptane mixtures have been summarized (9,10) and will be discussed in detail in a manuscript to be submitted to *Anal. Chem.*.

The sensitivity for field ionization of a series of saturates relative to the sensitivity for field ionization of ethylbenzene was reported (7) to be dependent upon mixture composition for an ion-source temperature of 120°C. Assuming that the sensitivity for decane relative to ethylbenzene to be independent of the presence of other saturates, relative sensitivities can be predicted for binary mixtures whose compositions are specified (7) by the weight percents of ethylbenzene and decane in these multicomponent mixtures. The results so obtained are presented in Table I. It should be noted, that in the absence of ethylbenzene the relative sensitivities for the various saturates appear to be composition independent (7). As noted by Ryska, Kuras, and Mostecky (7) the relative sensitivity becomes essentially independent of mixture composition for weight percents of ethylbenzene in excess of *ca.* 30%.

Table I also presents relative sensitivities determined in our laboratory (11) and at an ion-source temperature of 270°C for quaternary mixtures composed of various weight percents of decane, ethylbenzene, toluene, and benzene. The sensitivities for benzene and toluene relative to the sensitivity for ethylbenzene are seen to be independent of mixture composition. Averaging the data for benzene and toluene without regard to the individual standard deviations yields grand averages of 1.14 ± 0.15 and 1.15 ± 0.07 for the relative gram sensitivities for benzene and toluene, respectively. Although the standard deviation in the grand average for benzene is somewhat large, the averages in Table I and the grand averages compare favorably with the sensitivities determined (8) for benzene (1.22 ± 0.07) and for toluene (1.17 ± 0.04) relative to the sensitivity of ethylbenzene in mixtures of aromatic compounds and at an ion-source temperature of 270°C. This agreement shows that the relative sensitivities for benzene and toluene are independent of the weight percent decane in the mixture within the limits of data precision. Furthermore, at an ion-source temperature of 270°C the sensitivity of decane relative to the sensitivity of ethylbenzene in the quaternary mixtures is seen to be independent of both the total weight percent of aromatics and the composition of the aromatic blend.

In view of these results, a study of the dependence of the sensitivity of decane relative to the sensitivity of ethylbenzene on weight percents of each component in the binary mixture, ion-source temperature and field potential was initiated. A first set of results is shown in Table II. Relative gram sensitivities are presented as a function of microamperes of current in the high-voltage power supply for the emitter, this measured current is termed the emitter current, rather than as a function of the field potential. The optimum value of the emitter current was approximately 106-108 μA at all ion-source temperatures.

The relative sensitivities as a function of binary mixture composition and obtained at an ion-source temperature of 300°C and at the optimum emitter current are in excellent agreement with our previous values shown in Table I. At this emitter temperature the relative sensitivity for each binary mixture is independent of emitter current within the limits of experimental precision. At 300°C there is some indication that the average relative sensitivity for decane may be slightly lower for mixtures containing in excess of 80 weight percent decane than for mixtures containing less decane. However, it is

TABLE I. FIELD IONIZATION RELATIVE SENSITIVITY DATA AS A FUNCTION OF MIXTURE COMPOSITION

Weight Percent of				Gram Sensitivities Relative to Ethylbenzene		
Ethylbenzene	Decane	Benzene	Toluene	S (Decane)	S (Benzene)	S (Toluene)
4.8 ^a	95.2 ^a			0.57 ^b		
13.2 ^a	86.8 ^a			0.67 ^b		
29.7 ^a	70.3 ^a			0.89 ^b		
38.4 ^a	61.6 ^a			0.86 ^b		
49.4 ^a	50.6 ^a			0.96 ^b		
53.5 ^a	46.5 ^a			0.89 ^b		
59.8 ^a	40.8 ^a			0.85 ^b		
74.7 ^a	25.3 ^a			0.80 ^b		
5.2 ^c	83.8 ^c	5.9 ^c	5.2 ^c	0.09 ± 0.01 ^c	1.13 ± 0.06 ^c	1.12 ± 0.09 ^c
8.2 ^c	73.0 ^c	9.6 ^c	9.1 ^c	0.10 ± 0.01 ^c	1.34 ± 0.06 ^c	1.25 ± 0.05 ^c
14.3 ^c	53.6 ^c	16.2 ^c	15.9 ^c	0.11 ± 0.01 ^c	0.98 ± 0.03 ^c	1.09 ± 0.02 ^c
25.0 ^c	23.0 ^c	25.1 ^c	26.9 ^c	0.11 ± 0.01 ^c	1.11 ± 0.03 ^c	1.14 ± 0.03 ^c

^aCalculated from the weight percents given in reference . ^bTypical of values given in reference .
 Ion-source temperature = 120°C. ^cPresent work. Ion-source temperature = 270°C.

TABLE II. GRAM SENSITIVITY FOR DECANE RELATIVE TO THE GRAM SENSITIVITY FOR ETHYLBENZENE AS A FUNCTION OF SAMPLE COMPOSITION, ION-SOURCE TEMPERATURE, AND FIELD STRENGTH

T°C	wt. % C ₈ H ₁₀ C ₁₀ H ₂₂	Emitter Current (μA)						
		80	90	100	optimum ^a	110	120	130
100	80:20	0.49 ± 0.02	0.63 ± 0.01	0.53 ± 0.14	0.55 ± 0.10	0.67 ± 0.03	0.70 ± 0.03	0.67 ± 0.02
	50:50	0.53 ± 0.01	0.57 ± 0.01	0.52 ± 0.00	0.52 ± 0.07	0.59 ± 0.01	0.64 ± 0.04	0.64 ± 0.02
	35:65	0.50 ± 0.05	0.55 ± 0.02	0.50 ± 0.03	0.49 ± 0.05	0.60 ± 0.01	0.61 ± 0.03	0.62 ± 0.02
	20:80	0.48 ± 0.04	0.50 ± 0.06	0.55 ± 0.04	0.43 ± 0.08	0.59 ± 0.04	0.61 ± 0.00	0.60 ± 0.02
	10:90	-	0.37 ± 0.02	0.33 ± 0.01	0.35 ± 0.02	0.40 ± 0.03	0.47 ± 0.01	0.51 ± 0.02
	5:95	-	0.29 ± 0.01	0.31 ± 0.02	0.33 ± 0.04	0.36 ± 0.01	0.41 ± 0.01	0.43 ± 0.01
200	80:20	0.33 ± 0.01	0.36 ± 0.00	0.34 ± 0.05	0.28 ± 0.04	0.32 ± 0.04	0.33 ± 0.02	0.32 ± 0.01
	50:50	0.31 ± 0.01	0.34 ± 0.01	0.27 ± 0.03	0.32 ± 0.02	0.32 ± 0.01	0.33 ± 0.00	0.32 ± 0.01
	35:65	0.26 ± 0.04	0.30 ± 0.01	0.29 ± 0.01	0.27 ± 0.02	0.29 ± 0.03	0.31 ± 0.00	0.31 ± 0.00
	20:80	0.22 ± 0.02	0.24 ± 0.02	0.24 ± 0.01	0.24 ± 0.03	0.27 ± 0.00	0.29 ± 0.01	0.28 ± 0.02
	10:90	0.17 ± 0.02	0.19 ± 0.03	0.21 ± 0.06	0.17 ± 0.02	0.21 ± 0.02	0.23 ± 0.02	0.24 ± 0.02
	5:95	-	0.14 ± 0.01	0.13 ± 0.06	0.16 ± 0.03	0.17 ± 0.01	0.20 ± 0.01	0.23 ± 0.00
300	80:20	0.16 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.10 ± 0.01	0.12 ± 0.01	0.12 ± 0.02	0.12 ± 0.02
	50:50	0.15 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	0.11 ± 0.02	0.11 ± 0.02	0.12 ± 0.01	0.10 ± 0.01
	35:65	0.13 ± 0.01	0.13 ± 0.02	0.12 ± 0.00	0.09 ± 0.01	0.10 ± 0.00	0.10 ± 0.00	0.10 ± 0.01
	20:80	0.11 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.10 ± 0.03	0.08 ± 0.01	0.10 ± 0.01	0.09 ± 0.01
	10:90	0.05 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.07 ± 0.03
	5:95	0.08 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.07 ± 0.02	0.08 ± 0.01	0.07 ± 0.02

^aThe optimum emitter current which gives a symmetrical flat-top peak for ethylbenzene with maximum intensity.

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 emitter temperatures in the range 270-300°C.

For emitter temperatures of 100 and 200°C the relative sensitivity of decane is seen to be independent of emitter current for each binary mixture within the limits of precision. Relative sensitivities were not determined for an emitter current of 80 μ A at ion-source temperatures of 100 and 200°C for mixtures containing 90 and 95% and 95% ethylbenzene, respectively, because of the low intensity at m/e 106. The sensitivity of decane relative to the sensitivity of ethylbenzene decreases with increasing weight percent decane at an emitter temperature of 100°C. However, the present results suggest that two average relative decane sensitivities can be used at this temperature; for mixtures containing more than and less than *ca.* 80 weight percent decane the values based upon the data for the optimum emitter current are about 0.35 and 0.52, respectively.

The agreement between the relative sensitivity data obtained at an ion-source temperature of 100°C in Table I and those calculated for a source temperature of 120°C from the data of Ryska, Kuras, and Mostecky in Table II is reasonable, although not quantitative. Table II shows that increasing the ion-source temperature from 100 to 200°C decreases the sensitivity of decane relative to ethylbenzene by *ca.* a factor of two for all binary mixtures. The extent to which this decrease in the relative decane sensitivity with increasing ion-source temperature reflects variations in the absolute sensitivity of either decane or ethylbenzene or both is presently unknown. The observed phenomena will be further investigated by redetermination of the relative decane sensitivities as a function of both binary mixture composition and ion-source temperatures using the optimum field strength and by measuring absolute sensitivities for field ionization of decane and ethylbenzene. Consequently, a gallium frit is being incorporated into our all-glass inlet system and lambda pipets are being acquired to permit introduction of known volumes of liquids.

Samples of 25 saturates and naphthenes and 10 monoaromatic hydrocarbons with aliphatic side chains have been acquired. The purity of these samples has been checked using FID/GC. Low-resolution FI/MS will be acquired to further establish the purity of each sample. Relative sensitivities will be determined for various saturate and aromatic mixtures and for mixtures of saturates and aromatics. Absolute sensitivities will also be measured.

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- 9) See Quarterly Progress Report BERC-0020-5 submitted under ERDA contract E(34-1)-0020.
- 10) See Quarterly Progress Report FE-2011-6, Dist. Cat. UC-90d submitted under ERDA contract E(49-18)-2011.
- 11) Unpublished results of S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira.