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

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ABSTRACT

Medium- and low-resolution field-ionization and high-resolution 70-eV electron-impact mass spectral data were obtained for thirty-eight GPC fractions obtained from an HRI coal-derived liquid by members of the Separation and Characterization group at the Bartlesville Energy Research Center. This group was supplied with empirical formulas deduced from the high-resolution electron-impact data. The field-ionization data were acquired for eventual calculation of quantitative distributions for the HRI coal-derived liquid.

The field-ionization mass-spectral data obtained for the GPC fractions from a Synthoil sample are being converted into quantitative compositional data for this coal-derived liquid. In conjunction with subcommittee ASTM D-2, we analyzed a blend of aromatic hydrocarbons obtained from twelve crude oils. A paper describing our investigations of field-ionization sensitivities has been submitted for publication to Analytical Chemistry,

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 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 50% of his time to the project in the next quarter.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Analysis of Samples for Bartlesville Energy Research Center (BERC)

Mr. J. E. Dooley's Separations and Characterization group at BERC provided us with 38 fractions obtained from separation of a HRI coal-derived liquid. For each of these GPC fractions, low-resolution field-ionization (FI) mass spectra were obtained and high-resolution (*ca.* 18,000) 70-eV electron-impact mass spectra were recorded on photographic plates. "Exact" masses for approximately 3000 molecular ions derived from these fractions were obtained from the spectra recorded on the photographic plates by computer processing the line positions for each ion measured with respect to lines corresponding to ions from perfluorokerosene. The "exact" masses for these ions were computer processed to obtain best-fit compositions and empirical formulas (1). The best-fit compositions were computer compared (1) with some 1200 formulas of compounds known or believed to be present in materials derived from fossil fuels. The "exact" masses and best-fit compositions were supplied to the appropriate individuals at BERC.

Quantitative Compositions from Field Ionization Ion Abundances

Low-resolution field-ionization mass spectra were previously obtained (2) for selected gel permeation chromatographic (GPC) fractions obtained from high- and low-boiling monoaromatic and diaromatic and high-boiling polyaromatic polar (PAP) concentrates from Synthoil. During this quarter medium-resolution FI spectra were recorded for these fractions and for the low-boiling PAP; in addition, low-resolution FI/MS were recorded for the low-boiling PAP. Sufficient resolution was used to resolve ions of a given nominal but different exact masses resulting from ionization of aromatic hydrocarbons and heteroaromatic compounds. The intensities of the individual ions in each multiplet were then used to factor the total intensity at that *m/e* value in the low-resolution FI/MS into contributions from each of the component molecular ions.

The ion intensities in the low-resolution FI/MS of each GPC fraction were converted to weight percents as a function of compound nominal mass assuming unit relative sensitivities. Where necessary, the weight percent at a given nominal mass was factored into contributions for hydrocarbons, and aromatic compounds containing sulfur and oxygen using the medium-resolution FI data (see above). The resultant weight percents for the hydrocarbons, sulfur-containing compounds, and the oxygen-containing compounds were ordered according to the *Z* values appropriate for each class of compounds. The analysis of the high- and low-boiling PAP concentrates was more difficult since one must consider the consequences of nitrogen-containing aromatics in addition to oxygen- and sulfur-containing aromatics. Consequently, compositional data are being obtained for the polyaromatic polar concentrates as follows.

- 1) The weight percents of aromatic hydrocarbons, and sulfur- and oxygen-containing compounds at each nominal mass are obtained and ordered as a function of their corresponding *Z* number (see above).
- 2) Since the high-resolution data (3,4) are consistent with the presence of compounds containing only one nitrogen atom,

molecular ions corresponding to ionization of nitrogen-containing compounds appear at only odd nominal masses. Consequently, the peak heights of the ions having odd nominal masses in the low-resolution FI mass spectra are corrected for contributions from heavy-isotope peaks of the adjacent lower even mass.

- 3) The weight percents of the nitrogen-containing compounds at each mass are calculated assuming unit-relative sensitivities and ordered according to Z number.
- 4) The weight percents corresponding to aromatic hydrocarbons, sulfur-, oxygen-, and nitrogen-containing components at each nominal mass are then factored according to the percent of aromatic hydrocarbons and sulfur- and oxygen-containing compounds and the percent of nitrogen-containing compounds in each GPC fraction.

The analytical data for the GPC fractions are being combined to obtain compositional data for the various high- and low-boiling concentrates, distillate cuts, and the crude Synthoil, as follows. Since only every third GPC fraction was analyzed, the weight percents of compounds in each Z series for the analyzed fractions were summed and the resultant values assumed to be the same for adjacent unanalyzed GPC fractions. The weight of components in a given Z series for each fraction was obtained from the weight of each GPC fraction (5) and the summed weight percents for that Z series. Using the total weight of all GPC fractions (5) and the weight of components in each Z series, the weight percent according to compound class (Z number) was determined for each concentrate. Similarly, the weight percent a) of each concentrate from a given distillate cut (5), b) of each distillate cut relative to the Synthoil sample (5), and c) according to compound class for the concentrate, are being combined to obtain weight percents as a function of compound type for each distillate and for the crude coal-liquid. All computations are being performed using a general computer program for such analyses which is being developed by T. D. Marriott and P. L. Grizzle.

Other Research Activities

Low-Voltage EI Sensitivities

Preliminary measurements of low-voltage EI sensitivities were made for approximately 30 aromatic hydrocarbons, 20 thiophenes, and 7 heteroatom (oxygen and nitrogen)-containing compounds relative to ethylbenzene. Mass spectra of known mixtures (2) were obtained for nominal ionizing energies of 7.8 and 11.0 eV by P. W. Woodward and G. P. Sturm using the modified CEC 21-102 mass spectrometer at BERC. The ion intensities were both recovered off of the oscillographic recordings and converted to relative gram-and mole-sensitivities and relative cross-sections (2) by our group at OSU. Use of these sensitivities in quantitative analysis of synthetic blends greatly improves the accuracy of analysis. However, these preliminary studies have raised a number of important questions concerning factors which influence the reproducibility of low-voltage sensitivities and their variation with ionizing energy. Since these factors have important pragmatic consequences for quantitative analysis of complex mixtures using low-voltage EI mass spectrometry, several additional experiments will be conducted. A paper presenting the ensemble of results and our

conclusions will then be jointly authored by P. L. Grizzle, S. E. Scheppele, P. W. Woodward, G. P. Sturm, and J. E. Dooley and, hence, submitted jointly from BERL and OSU.

Manuscript Preparation and Submission

Relative gram-and mole-sensitivities and relative cross-sections for field ionization of a variety of compound types encountered in analysis of coal-derived liquids have been presented in previous quarterly progress reports (2,4) submitted under this ERDA project. These reports also summarized the significance of our studies and their applicability by analysis of synthetic blends (2). A summary of the results and conclusions was also presented in the Symposium on the Characterization of Synthetic Fuels sponsored by the American Society for Mass Spectrometry in San Diego in May 1976 (6). A paper (7) which presents these relative FI sensitivities and relative cross-sections and which discusses their a) variation with molecular structure, b) correlation with low-voltage EI cross-sections, c) predictability given $-Z$ values, and d) utility in terms of analysis of synthetic blends has been submitted to *Anal. Chem.* The consequences of omitting sensitivity corrections in quantitative analysis is evaluated for field-ionization and low-voltage electron-impact mass spectrometry. The paper also presents and discusses relative flame-ionization detector sensitivities.

Activities in Behalf of ASTM Subcommittee D2

In conjunction with subcommittee ASTM d-2, our group analyzed a blend of aromatic hydrocarbons obtained from twelve crude oils. Semiquantitative and qualitative analysis of the blend were performed by high- and low-resolution low-voltage electron impact (EI) and low-resolution FI and high-resolution high-voltage EI mass spectrometry, respectively. Percent total ionizations were obtained for all semiquantitative techniques and reported for the most abundant specified ions. Empirical formulas obtained from line positions on photographic plates were reported for specified ions; see Tables I and II.

GC/MS System

Minor improvements in the interface between the Perkin-Elmer 3920 gas chromatograph and the CEC 21-110B mass spectrometer have been (are being) made. A high-temperature probe holder for insertion of the GC probe into the conventional solid-introduction system has been constructed. Thus, the interface can now be maintained at higher temperatures. To further increase our temperature capability, components for new AC power supply have been obtained and fabrication has begun.

Table I. EI LOW VOLTAGE-LOW RESOLUTION AND FI LOW RESOLUTION DATA

m/e	Percent of Total Ionization ^a		
	EI		FI
	Tuned at m/e 156 ^b	Tuned at m/e 288 ^b	Tuned at m/e 156 ^b
142	1.61 ± 0.07	1.35 ± 0.03	0.78 ± 0.05
156	4.20 ± 0.28	3.71 ± 0.19	2.32 ± 0.07
160	0.92 ± 0.08	0.84 ± 0.08	0.58 ± 0.04
162	1.04 ± 0.03	0.93 ± 0.03	0.67 ± 0.03
170	4.09 ± 0.07	3.74 ± 0.14	2.65 ± 0.13
174	1.30 ± 0.04	1.23 ± 0.09	1.04 ± 0.04
176	1.18 ± 0.04	1.10 ± 0.03	0.90 ± 0.06
182	0.87 ± 0.01	0.86 ± 0.03	0.86 ± 0.06
184	2.45 ± 0.14	2.38 ± 0.07	2.15 ± 0.11
188	1.28 ± 0.07	1.20 ± 0.03	1.25 ± 0.08
190	1.01 ± 0.02	0.99 ± 0.04	0.94 ± 0.07
192	0.79 ± 0.02	0.73 ± 0.01	0.82 ± 0.12
196	1.19 ± 0.09	1.14 ± 0.04	1.11 ± 0.03
198	1.73 ± 0.04	1.53 ± 0.04	1.50 ± 0.14
200	0.84 ± 0.03	0.80 ± 0.04	1.13 ± 0.01
202	1.00 ± 0.02	0.96 ± 0.05	1.32 ± 0.15
204	0.95 ± 0.04	0.90 ± 0.08	1.11 ± 0.07
206	1.15 ± 0.01	1.15 ± 0.02	1.14 ± 0.04
208	0.77 ± 0.04	0.78 ± 0.06	0.94 ± 0.03
210	1.24 ± 0.04	1.29 ± 0.04	1.44 ± 0.08
212	1.69 ± 0.06	1.59 ± 0.06	1.52 ± 0.16
214	0.83 ± 0.01	0.80 ± 0.05	1.18 ± 0.02
216	0.83 ± 0.01	0.81 ± 0.03	1.22 ± 0.01

Table I (Continued)

m/e	Percent of Total Ionization ^a		
	EI		FI
	Tuned at m/e 156 ^b	Tuned at m/e 288 ^b	Tuned at m/e 156 ^b
218	0.91 ± 0.07	0.87 ± 0.07	1.24 ± 0.06
220	1.01 ± 0.02	1.02 ± 0.01	0.94 ± 0.03
222	0.72 ± 0.01	0.75 ± 0.06	0.86 ± 0.03
224	1.16 ± 0.05	1.16 ± 0.02	1.30 ± 0.02
226	1.50 ± 0.06	1.45 ± 0.07	1.50 ± 0.09
228	0.76 ± 0.02	0.77 ± 0.02	1.20 ± 0.09
230	0.72 ± 0.07	0.70 ± 0.02	1.15 ± 0.03
232	0.87 ± 0.04	0.92 ± 0.05	1.28 ± 0.04
234	0.68 ± 0.04	0.69 ± 0.02	0.62 ± 0.02
236	0.78 ± 0.02	0.78 ± 0.02	0.83 ± 0.05
238	0.98 ± 0.02	1.02 ± 0.01	1.18 ± 0.04
240	1.18 ± 0.10	1.14 ± 0.10	1.32 ± 0.09
242	0.68 ± 0.03	0.68 ± 0.03	1.06 ± 0.07
244	0.72 ± 0.05	0.69 ± 0.01	1.13 ± 0.07
246	0.89 ± 0.06	0.89 ± 0.03	1.23 ± 0.15
250	0.75 ± 0.02	0.78 ± 0.03	0.83 ± 0.10
252	0.86 ± 0.01	1.00 ± 0.04	0.98 ± 0.09
254	0.95 ± 0.05	1.02 ± 0.10	1.10 ± 0.05
256	0.64 ± 0.05	0.67 ± 0.02	1.01 ± 0.08
258	0.71 ± 0.04	0.74 ± 0.05	0.94 ± 0.11
260	0.75 ± 0.04	0.79 ± 0.05	1.09 ± 0.07
266	0.72 ± 0.02	0.79 ± 0.05	0.83 ± 0.03
268	0.79 ± 0.01	0.82 ± 0.03	0.95 ± 0.04
274	0.68 ± 0.06	0.71 ± 0.04	0.85 ± 0.01
282	0.59 ± 0.03	0.60 ± 0.03	0.81 ± 0.06
288	0.54 ± 0.02	0.57 ± 0.01	0.82 ± 0.04

^a Average of three determinations. Deviations are standard deviations.

^b Instrument performance maximized on given m/e value.

Table II. EI LOW VOLTAGE-HIGH RESOLUTION DATA

Series ^b	C#	Nominal Mass	Percent of Total Ionization ^a	
			Tuned at m/e 156 ^c	Tuned at m/e 288 ^c
$C_n H_{2n-6}$	12	162	0.64 ± 0.09	0.77 ± 0.03
	13	176	0.77 ± 0.05	0.89 ± 0.05
	14	190	0.74 ± 0.10	0.90 ± 0.05
	16	218	0.68 ± 0.04	0.75 ± 0.11
	17	232	0.59 ± 0.06	0.68 ± 0.06
$C_n H_{2n-8}$	13	174	1.04 ± 0.07	1.12 ± 0.07
	14	188	1.00 ± 0.04	1.28 ± 0.15
	15	202	0.82 ± 0.07	1.09 ± 0.13
$C_n H_{2n-10}$	13	172	0.35 ± 0.07	0.38 ± 0.02
	14	186	0.58 ± 0.10	0.64 ± 0.14
$C_n H_{2n-12}$	11	142	1.04 ± 0.21	1.20 ± 0.11
	12	156	2.94 ± 0.16	3.57 ± 0.41
	13	170	3.34 ± 0.17	3.92 ± 0.39
	14	184	2.18 ± 0.14	2.45 ± 0.14
	15	198	1.36 ± 0.13	1.53 ± 0.24
	16	212	0.98 ± 0.07	1.05 ± 0.09
	17	226	0.77 ± 0.10	0.88 ± 0.03
	20	268	0.54 ± 0.06	0.61 ± 0.08
	23	310	0.38 ± 0.07	0.28 ± 0.03
	24	324	0.24 ± 0.02	0.23 ± 0.03
$C_n H_{2n-14}$	15	196	1.00 ± 0.03	1.07 ± 0.10
	16	210	1.04 ± 0.08	1.22 ± 0.08
	17	224	1.08 ± 0.12	1.04 ± 0.06
	18	238	0.86 ± 0.08	0.91 ± 0.04
	20	266	0.55 ± 0.04	0.51 ± 0.04
	21	280	0.54 ± 0.02	0.41 ± 0.10
	23	308	0.33 ± 0.04	0.24 ± 0.07
	24	322	0.27 ± 0.01	0.21 ± 0.06

Table II (Continued)

Series ^b	C#	Nominal Mass	Percent of Total Ionization ^a	
			Tuned at m/e 156 ^c	Tuned at m/e 288 ^c
$C_n H_{2n-16}$	16	208	0.76 ± 0.06	0.83 ± 0.03
	17	222	0.78 ± 0.10	0.71 ± 0.11
	18	236	0.76 ± 0.04	0.77 ± 0.10
	19	250	0.72 ± 0.10	0.66 ± 0.02
	20	264	0.58 ± 0.04	0.52 ± 0.08
	21	278	0.49 ± 0.02	0.44 ± 0.07
	22	292	0.41 ± 0.03	0.32 ± 0.03
	24	320	0.23 ± 0.06	0.16 ± 0.01
$C_n H_{2n-18}$	15	192	0.83 ± 0.08	0.90 ± 0.10
	16	206	1.23 ± 0.12	1.26 ± 0.15
	17	220	0.97 ± 0.08	0.93 ± 0.08
	18	234	0.76 ± 0.13	0.54 ± 0.07
	19	248	0.42 ± 0.05	0.40 ± 0.08
	21	276	0.30 ± 0.04	0.28 ± 0.04
	22	290	0.31 ± 0.07	0.20 ± 0.04
$C_n H_{2n-20}$	19	246	0.42 ± 0.03	0.39 ± 0.06
	20	260	0.40 ± 0.04	0.31 ± 0.03
	21	274	0.33 ± 0.04	0.29 ± 0.05
	22	288	0.29 ± 0.04	0.22 ± 0.03
	23	302	0.21 ± 0.04	0.15 ± 0.04
$C_n H_{2n-16}^S$	14	212	0.98 ± 0.11	1.03 ± 0.10
	15	226	0.95 ± 0.04	0.90 ± 0.03

^a Average of three determinations. Deviations are standard deviations.

^b Determined from photographic plate data.

^c Instrument performance maximized on given m/e value.

References

- 1) We wish to thank Mr. Alan Robertson for supplying us with a copy of the computer program he developed for Mr. Mynard Hamming of the Research and Development Department of Continental Oil Company, Ponca City, Oklahoma; see A. L. Robertson and M. C. Hamming, "Computer Program for the Selection of Formulas from High-Resolution Mass-Spectral Data, to be submitted to *Fuel*.
- 2) See Quarterly Progress Report BERC-0020-3 submitted under ERDA contract no. E(34-1)-0020.
- 3) See Quarterly Progress Report BERC-0020-1 submitted under ERDA contract no. E(34-1)-0020.
- 4) See Quarterly Progress Report BERC-0020-2 submitted under ERDA contract no. E(34-1)-0020.
- 5) Obtained from the separations and characterizations group at BERC.
- 6) S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, and N. B. Perreira, "Mass Spectrometric Analysis of Coal Liquids and Their Hydrogenation-Hydrogenolysis Products," Proceedings 24th Annual Conference on Mass Spectrometry, San Diego, California, May 1976, in press.
- 7) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, "Determination of Field Ionization Sensitivities for the Analysis of Coal-Derived Liquids and Their Correlation with Low-Voltage Electron Impact Sensitivities," submitted to *Anal. Chem.*