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ABSTRACT

Field-ionization relative sensitivities were determined at an ion-source temperature of *ca.* 270°C for 16 saturates and naphthenes in 18 mixtures containing only saturated and naphthenic hydrocarbons, and for 14 saturates and naphthenes in 5 mixtures containing aromatic hydrocarbons. Variations in the relative gram sensitivities for 6 saturates in the presence of ethylbenzene (3 mixtures) and in the absence of ethylbenzene (2 mixtures) at an ion-source temperature of *ca.* 100°C were compared with literature values for similar mixture compositions determined at an ion-source temperature of *ca.* 120°C.

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 DESCRIPTION OF TECHNICAL PROGRESS

Determination of Relative Sensitivities for Field Ionization of Saturates

Ryska, Kuras, and Mostecky (1) observed that the relative gram sensitivities for field ionization of saturated hydrocarbons in the presence of ethylbenzene were ethylbenzene dependent for mixtures containing up to *ca.* 30 weight percent ethylbenzene. These results were obtained using an ion-source temperature of 120°C. In contrast, the sensitivities for field ionization of decane, benzene, and toluene relative to the sensitivity for FI of ethylbenzene were found to be independent of quaternary mixture composition using an ion-source temperature of 270°C within the limits of experimental precision (2). Determination of the FI gram sensitivity of decane relative to the value of ethylbenzene at an ion-source temperature of 270°C revealed that any dependence of the relative sensitivity on binary mixture composition or field strength was within the limits of experimental reproducibility (3). However, the relative sensitivities determined at an ion-source temperature of 100°C exhibited a dependence on the weight percent ethylbenzene in the mixtures (3). The agreement between these decane relative sensitivities and those calculated from the data for multicomponent mixtures of Ryska, Kuras, and Mostecky was reasonable although not quantitative (3). In view of these results FI sensitivities were determined for mixtures equivalent to those used by Ryska, Kuras, and Mostecky at both 100° and 270°C ion-source temperatures.

Table I presents gram sensitivities for field ionization of various hydrocarbons relative to the corresponding value for decane, S/Sdecane, and determined for the specified mixtures at an ion-source temperature of 100°C. Relative sensitivities determined for the same mixture compositions at an emitter temperature of 270°C are presented in Table II. Table III contains gram sensitivities for field ionization of various saturates relative to the corresponding value for decane determined at an ion-source temperature of 270°C. The average relative gram sensitivities in column 13 of Table III are based upon data obtained for 15 mixtures; columns 3 through 12 present results for 10 of the mixtures. In general, difficulty was experienced with the reproducibility in the relative sensitivities for hexane and heptane. This problem assumably reflects, in part, the volatility of these low-molecular weight hydrocarbons.

For purposes of comparison, Table I also includes relative sensitivities determined at an ion-source temperature of 120°C by Ryska, Kuras, and Mostecky (1). These authors did not report standard deviations in their sensitivity data. However, based upon the standard deviations 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 the corresponding values reported by Ryska, Kuras, and Mostecky (1). Our results 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 weight percent of the mixture.

Table II reveals that an increase in the ion-source temperature from 100° to 270°C has a marked effect on the relative sensitivities. Comparison of the

TABLE I. 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}										
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 1.

TABLE II. RELATIVE GRAM SENSITIVITIES OF n-ALKANES IN HYDROCARBON MIXTURES AT AN ION-SOURCE TEMPERATURE OF 270°C^a

Mixture		Hexane	Heptane	Ethyl Benzene	Octane	Nonane	Decalin	Decane	Undecane
1	wt. %	14.4	16.6		16.5	20.2		16.0	16.3
	S/S _{C₁₀}	1.08 ± 0.14	1.36 ± 0.14		1.11 ± 0.12	1.03 ± 0.09		1.00	0.93 ± 0.12
	wt. %	12.2	13.9	10.9	15.6	15.9		15.7	16.5
	S/S _{C₁₀}	1.78 ± 0.36	1.92 ± 0.27	5.59 ± 0.71	1.27 ± 0.16	1.13 ± 0.12		1.00	0.85 ± 0.11
3	wt. %	15.8	14.6	17.8	12.3	13.3		12.7	13.4
	S/S _{C₁₀}	1.61 ± 0.20	1.72 ± 0.25	4.80 ± 0.60	1.19 ± 0.14	1.05 ± 0.18		1.00	0.82 ± 0.08
4	wt. %	10.5	10.8	32.3	12.1	11.5		11.8	11.0
	S/S _{C₁₀}	1.96 ± 0.62	2.05 ± 0.43	4.83 ± 0.84	1.44 ± 0.19	1.21 ± 0.13		1.00	0.82 ± 0.09
5b	wt. %		12.4		10.1	10.7	42.6	12.4	11.9
	S/S _{C₁₀}		1.29 ± 0.25		1.05 ± 0.17	1.05 ± 0.14	3.61 ± 0.32	1.00	1.03 ± 0.17

^aAll values relative to decane.

TABLE III. 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 ± 0.23	(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.

data for Mixtures 2, 3, and 4 in Tables I and II shows that the increase in the 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 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. The increase in ion-source temperature is seen to result in a marked increase in the relative sensitivity for decalin; compare data for mixtures 5a and 5b in Tables I and II, respectively.

The results obtained for Mixtures 2, 3, and 4 which contain ethylbenzene 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 II the variation in these relative sensitivities is $\leq 14\%$.

Comparison of the results for the saturate Mixtures 1 and 5 in Tables I and II reveals that increasing the ion-source temperature from 100° to 270° tends to equalize the relative gram sensitivities for the *n*-alkanes. These results and those in Table III determined with an emitter temperature of 270°C for mixtures containing different weight percents of *n*-alkanes, cycloalkanes, and alkylated cycloalkanes show that the relative gram sensitivities for saturates are independent of mixture composition, within the limits of experimental precision. In this regard, it is important to note that relative sensitivities were determined for a number of the mixtures using a reference compound other than decane, e.g., Mixtures 6, 9, 14, and 15 in Table III. However, as seen for Mixtures 6, 9, 14, and 15 in Table III multiplication of these experimental relative sensitivities by the sensitivity of the particular reference compound relative to decane yields sensitivities relative to decane which are in good agreement with the corresponding values obtained from mixtures containing decane.

Comparison of the data for Mixtures 1 and 5 with those for 2, 3, and 4 in Table II indicates that incorporating ethylbenzene into the saturate mixture alters the relative sensitivity for field ionization of these compounds. For example, the relative sensitivities for hexane and heptane are increased on the average by 65 and 28%, respectively, upon addition of *ca.* 10 to 32 weight percent ethylbenzene. The effect of ethylbenzene on the *n*-alkane relative sensitivities is seen to decrease as the molecular weight of the alkane increases.

The data in Tables II and III indicate that within the limits of experimental precision composition independent sensitivities for saturates can be determined for analysis of hydrocarbon mixtures containing 1) only saturates and 2) saturates plus aromatics. Consequently, analysis of mixtures containing both saturated and aromatic hydrocarbons would seemingly require either separation of the two compound classes prior to analysis or determination of relative sensitivities for field ionization of the former in the presence of the latter. However, from a pragmatic viewpoint it is seen that the relative sensitivities for nonane and undecane are similar in the absence and presence of ethylbenzene. If this phenomenon were general for the higher-molecular weight alkanes than the use of a single set of relative sensitivities for saturated hydrocarbons would not be expected to introduce major distortion into the quantitative distributions obtained for mixtures containing both compound classes.

Table IV presents relative sensitivity data for Mixture 16 which contains a variety of saturated hydrocarbons, ethylbenzene, and 1-ethylnaphthalene. For ease of comparison, relative sensitivities from Table III are also presented.

TABLE IV. 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
Mixture 16			
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
Mixture 17			
ethylbenzene	37.5	6.06 ± 0.31	
decalin	32.0	3.77 ± 0.22	3.60 ± 0.37
decane	30.5	1.00	1.00

^aValues taken from Table III.

Within the limits of experimental precision the relative sensitivities obtained for Mixture 16 do not differ from the values obtained for mixtures possessing no aromatic hydrocarbons. For heptane Mixture 16 yields a relative sensitivity of 1.25 ± 0.13 which is significantly different from the average value of 1.90 ± 0.17 obtained from Mixtures 2, 3, and 4; see Table II. The origin of this difference is not clear although it assumably reflects differences in the compounds present in and the composition of the former mixture compared to the latter 3 mixtures. It is important to note that the sensitivity of 1-ethylnaphthalene relative to ethylbenzene (1.02 ± 0.04) is consistent with previous results obtained for methyl- and dimethylnaphthalene (4).

Table IV also contains relative sensitivity data for a mixture containing ethylbenzene, decalin, and decane. Comparison of these values with data in Table III reveals that the relative sensitivity of decalin is increased from 3.60 ± 0.37 to 3.77 ± 0.22 by the incorporation of ethylbenzene into the mixture. However, the difference between the two values is less than the standard deviation in either one.

Relative gram and mole sensitivities for saturates obtained with an ion-source temperature of 270°C are tabulated according to compound type in Table V. The data for the *n*-alkanes suggest that the relative mole sensitivity increases by 0.11-0.12 per CH_2 group. Heptane appears to be an exception. The sensitivities for the parent naphthenes are seen to be considerably greater than the sensitivities for *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 affects the cross section for field ionization of the parent compound. These phenomenon are under investigation. The mole sensitivities of perhydropyrene and decalin relative to cyclohexane are 4.62 and 3.13, respectively. Consequently, the mole sensitivity appears to increase noncumulatively as the number of fused 6-membered naphthene rings rises. Additional sensitivity data are obviously required before attempting to formulate any correlations between the number of condensed naphthene rings and mole sensitivity.

TABLE V. RELATIVE SENSITIVITIES FOR SATURATE HYDROCARBONS AT AN ION-SOURCE TEMPERATURE OF 270°C^a

<u>n-alkanes</u>			<u>cyclohexanes</u>		
	Gram Sensitivity	Mole Sensitivity		Gram Sensitivity	Mole Sensitivity
hexane	0.89	0.54	cyclohexane	1.89	1.12
heptane	1.24	0.87	methylcyclohexane	1.88	1.30
octane	1.01	0.81	n-butylcyclohexane	2.76	2.72
nonane	1.06	0.96	n-hexylcyclohexane	2.62	3.10
decane	1.00	1.00	3-methylcyclohexyl- cyclohexane	3.03	3.84
undecane	1.05	1.15			
dodecane	1.02	1.22			
hexadecane	1.06	1.69			
			<u>naphthenes</u>		
				Gram Sensitivity	Mole Sensitivity
			decalin	3.60	3.50
			perhydrofluorene	2.46	3.08
			perhydropyrene	3.37	5.17

^a All values relative to decane.

REFERENCES

- 1) M. Ryska, M. Kuras, and J. Mostecky, *Int. J. Mass Spectrom. Ion Phys.*, 16, 237 (1975).
- 2) Unpublished results of S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira. Data are presented in Table I of Reference 3.
- 3) See Quarterly Progress Report BERC-0020-6 submitted under ERDA Contract E(34-1)-0020.
- 4) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, 47, 2105 (1976).