

APPLICATIONS OF HIGH RESOLUTION MASS SPECTROMETRY IN COAL RESEARCH

A. G. Sharkey, Jr., J. L. Shultz, T. Kessler,
and R. A. Friedel

U.S. Department of the Interior, Bureau of Mines
Pittsburgh Coal Research Center, Pittsburgh, Pa.

INTRODUCTION

The Pittsburgh Coal Research Center of the Federal Bureau of Mines is attempting to determine which specific organic structures are most influential in enhancing desirable properties in commercially important fractions of coal tars such as road tar and electrode binder pitch. The current emphasis is on a survey of the types of hydrocarbon structures in coal-tar pitch detectable by high-resolution mass spectrometry. This information will provide the basis for an investigation of weathered road tar and other altered fractions of coal tar.

E. J. Greenhow and G. Sugowdz summarized the literature on pitch chemistry to 1961 by stating that less than 100 organic compounds in pitch have been isolated and identified¹. In these investigations quantitative data were obtained for only a few of the structures identified.

In a previous investigation at our laboratory, mass spectrometric analyses were obtained for three fractions of pitch from the high-temperature carbonization of coal². Semiquantitative data were reported for 34 structural types as well as carbon number distribution data for alkyl derivatives. Approximately 70 percent of the 80° to 85° C softening point pitch was investigated. An average molecular weight of approximately 250 and a value of 4.5 for the mean structural unit (number of aromatic rings per cluster) were derived from the mass spectrometric data. An aromaticity value of 0.94 (aromatic carbon/total carbon) calculated from these data is in excellent agreement with measurements by nuclear magnetic resonance.

Changes in the characteristics of road tar during weathering and in the carbonization properties of various coals following storage possibly involve alteration of certain organic constituents by reactions with oxygen, nitrogen, and sulfur. In our previous investigations of pitch by mass spectrometry only the hydrocarbon portion could be studied in detail as structures containing the heteroatoms nitrogen, oxygen, and sulfur have, in many instances, the same nominal molecular weights as hydrocarbons. Procedures commonly used to study the chemical constitution of coal-tar pitches, such as solvent fractionation, result in a separation according to molecular size but not chemical type as is required to detect changes in heteroatom concentrations.

High-resolution mass spectrometry offers a new approach to studies of species containing heteroatoms. Separation of the components is not necessary if the instrument has sufficient resolution and sensitivity. The addition of a heteroatom results in a slight change in the precise molecular weight of the species producing distinctive peaks for the various combinations of atoms.

In this preliminary study of the high-resolution mass spectrum of coal-tar pitch the investigation consisted of:

(1) Obtaining spectra by fractionating the pitch directly in the mass spectrometer ion source to effectively concentrate species in particular molecular weight ranges.

(2) Making precise mass determinations and deriving empirical formulas for components in the 150 to 320 mass range. This mass range includes components comprising approximately 70 percent by weight of the pitch.

(3) Showing that many of the high molecular weight species detected for the first time could arise from the condensation of radicals.

EXPERIMENTAL PROCEDURE

A Consolidated Electrodynamics Corp. Model 21-110B double focusing mass spectrometer was used for this study of a Koppers 80° to 85° C softening point pitch. A direct insertion probe was used to introduce the pitch into the region of ionization for the fractionation experiment. The mass spectrum and the weight of the sample vaporized were determined at the following probe temperatures: 100°, 175°, 250°, 290°, and 325° C.

A conventional umbrella-type glass introduction system was used for the precise mass study.

Mass measurements on standards were accurate to $\pm .003$ amu. The peak matching technique with perfluorokerosene as a standard was used for all mass assignments. For most of the high-resolution determinations, the instrument was operated with a resolving power of approximately 1 part in 8 to 10 thousand and with an inlet and source temperature of 300° C. The resolution was high enough to permit accurate mass assignments to approximately mass 300 and represented a compromise between sensitivity and desired resolving power. The resolving power required at mass 300 for complete separation of several of the mass doublets of interest is shown in table 1; however, complete separation is not generally required for precise mass assignments. In many instances 50 percent of the theoretical resolving power is adequate.

RESULTS AND DISCUSSION OF RESULTS

A. Mass Spectra of Pitch Fractionated in Mass Spectrometer.

Data obtained for the fractional distillation of the 80°-85° C softening point pitch in the mass spectrometer ion source are shown in table 2. Fractionation of the sample by increasing the temperature of the direct introduction probe was effective in concentrating species in a limited molecular weight range. Precise mass determinations, made as a second part of this investigation, substantiated structural assignments to about molecular weight 350.

At a probe temperature of 100° C 25.5 percent of the pitch sample was vaporized. Masses 178 and 202 are the most intense peaks in this spectrum, indicating anthracene and/or phenanthrene and 4-ring peri-condensed structures such as pyrene distill preferentially at these temperature-pressure conditions. Species with molecular weights as high as 420 were detected. When the probe temperature was increased to 175° C an additional 22.4 percent of the pitch vaporized. The molecular weight of the species showing maximum intensity increased to 252, corresponding to a 5-ring, peri-condensed aromatic structure(s); the molecular weight range of the spectrum increased to mass 526. At 250° C an additional 20.1 percent of the pitch distilled. The mass with maximum intensity was

Table 1.- Major mass doublets in mass spectrum of coal-tar pitch

Doublet	ΔM (amu)	Resolution required to separate doublet at mass 300
C_2H_8-S	.0906	3,300
CH_4-O	.0364	8,200
CH_2-N	.0126	24,000
$C^{12}H-C^{13}$.0045	67,000

Table 2.- Fractional distillation of Koppers 80°-85° C softening point pitch in mass spectrometer ion source

Probe temperature, °C	Distillate, weight percent		Mass spectrum	
	Cumulative	Fractional	Mass with Max. intensity	Maximum mol. wt.
100	25.5	25.5	178-202	420
175	47.9	22.4	252	526 ^a
250	68.0	20.1	228	550 ^a
290	68.0 ^b	-	326	620 ^a
325	68.0	-	326	570 ^a

a. Accurate mass numbers could not be assigned to trace peaks appearing at higher molecular weights.

b. No change in weight of residue detectable at probe temperatures > 250° C.

Table 3.- Mass assignments for several perfluorokerosene (PFK) and polynuclear hydrocarbon peaks

Experimental	Calculated (amu)	ΔM	P.P.M.	
204.9888	204.9896	.0008	4	(P.F.K.)
218.9856	218.9852	.0004	2	do
230.9856	230.9847	.0009	4	do
242.9856	242.9855	.0001	0.4	do
254.9856	254.9854	.0002	0.8	do
268.9824	268.9810	.0014	5	do
280.9824	280.9811	.0013	5	do

202.0776	202.0783	.0007	4	4-ring, peri-condensed
228.0937	228.0939	.0002	1	4-ring, cata-condensed

228, corresponding to a 4-ring, cata-condensed aromatic hydrocarbon, and the molecular weight range of the spectrum increased to mass 550. At higher probe temperatures, 290° and 325° C, the spectra indicated that the average molecular weight and ring size of the components continued to increase. The mass with maximum intensity occurred at 326 at temperatures of 290° and 325° C. The spectra indicated components with molecular weights higher than 620. There was no weight change detectable at probe temperatures greater than 250° C. Thus, the spectra obtained at 290° and 325° C represent only a very small portion of the pitch. The total amount of pitch vaporized was 68 weight percent of the charge. This value agrees well with the 70 percent vaporization obtained in our previous studies of the same pitch.² The mass spectra obtained at probe temperatures greater than 100° C contained trace peaks whose masses could not be assigned; these ions indicated molecular weights up to about 800.

The increased molecular weight range of the material vaporized at higher probe temperatures is illustrated in figures 1 and 2. These figures, based on low-ionizing voltage mass spectra, were plotted at the University of Pittsburgh Computer Center using a program obtained through the courtesy of the Graduate School of Public Health at the University. The trace ions up to approximately mass 800, which could not be effectively reproduced in these figures, correspond in molecular weight to structures containing at least 12 aromatic rings.

B. Precise Mass Assignments.

Table 3 lists precise mass values obtained by the peak matching technique for several peaks in the perfluorokerosene marker spectrum and for the molecular ions of 4-ring peri- and cata-condensed aromatic hydrocarbons. These data show that mass assignments can be made to within a few parts per million by this technique.

Empirical formulas were derived from the measured masses in the 150 to 319 range of the 80°-85° C coal-tar pitch. Species having from 12 to 28 carbon atoms were observed. A total of 273 peaks were indicated, many resulting from doublets and triplets at nominal masses. In addition to the hydrocarbon species, the precise masses indicated the presence of at least 10 structural types containing oxygen, 9 containing sulfur, and 10 containing nitrogen. Measured and calculated masses showed agreement in general from a few tenths to 3 millimass units. Nineteen of these masses represent structural types not previously reported for coal tar.⁴

The nominal molecular weight and atomic species for each of the components detected is shown in figures 3 and 4. The ability of the instrument to resolve complex mixtures is illustrated at mass 212 where empirical formulas were obtained for structures containing carbon-hydrogen, carbon-hydrogen-oxygen, and carbon-hydrogen-sulfur, all having the same nominal molecular weight.

Table 4 gives the formulas for 13 new high molecular weight species detected in the high-resolution mass spectrum of pitch. The formulas were derived from the observed precise masses. The particular structural type(s) cannot be identified as many isomeric variants are possible for each formula. Also shown are formulas and structures of several compounds containing (C,H), (C,H,O), (C,H,N), and (C,H,S) previously identified in coal tar.⁴ The last two columns of table 4 illustrate how the high molecular weight species, with molecular formulas determined in this investigation, can arise from condensation reactions.⁵ The addition of C₄H₄ or C₆H₅ radicals to radicals from previously identified structures will produce the molecular formulas shown.

Table 4.- Formation of high molecular weight components by condensation of radicals

Previously identified/ Compound	m/e (amu)	High molecular weight components detected this investigation			Possible origin of component Radical from Addition original structure required ^{b/}		
		Formula	Precise mass (amu) Observed	Theoretical		Δ	
Benzo[k]xanthene	218.0732	C ₂₀ H ₁₂ O	268.0894	268.0888	.0006	C ₁₆ H ₈ O	C ₄ H ₄
		C ₂₄ H ₁₄ O	318.1052	318.1045	.0007	C ₁₆ H ₈ O	2(C ₄ H ₄)
Naphtho[2,1,8,7- kilmn]xanthene	242.0732	C ₂₂ H ₁₂ O	292.0880	292.0888	.0008	C ₁₈ H ₈ O	C ₄ H ₄
Benzo[b]naphtho- [2,1-d]thiophene	234.0503	C ₂₀ H ₁₂ S	284.0657	284.0660	.0003	C ₁₆ H ₈ S	C ₄ H ₄
Dibenzo[b,def]- chrysene	302.1095	C ₂₈ H ₁₆	352.1161	352.1252	.0091	C ₂₄ H _{12}}	C ₄ H ₄
5H-Benzo[b]- carbazole	217.0891	C ₂₀ H ₁₃ N	267.1079	267.1048	.0031	C ₁₆ H ₉ N	C ₄ H ₄
		C ₂₄ H ₁₅ N	317.1250	317.1204	.0046	C ₁₆ H ₇ N	2(C ₄ H ₄)
4H-Benzo[def]- carbazole	191.0735	C ₂₂ H ₁₃ N	291.1077	291.1048	.0029	C ₁₄ H ₅ N	2(C ₄ H ₄)
Acridine	179.0735	C ₂₁ H ₁₃ N	279.1086	279.1048	.0038	C ₁₃ H ₅ N	2(C ₄ H ₄)
Phenanthrene	178.0783	C ₂₀ H ₁₄	254.1056	254.1095	.0039	C ₁₄ H ₉	C ₆ H ₅
Chrysene	228.0939	C ₂₄ H ₁₆	304.1205	304.1252	.0047	C ₁₈ H ₁₁	C ₆ H ₅
Benzo[ghi]perylene	276.0939	C ₂₆ H ₁₄	326.1116	326.1095	.0021	C ₂₂ H ₁₀	C ₄ H ₄
Coronene	300.0939	C ₂₈ H ₁₄	350.1122	350.1095	.0027	C ₂₄ H ₁₀	C ₄ H ₄

^{a/} Listed in "Properties of Compounds in Coal-Carbonization Products," ref. 4.

^{b/} M/e of added radical: C₄H₄ - 52; C₆H₅ - 77.

CONCLUSIONS

Approximately three times the number of components reported in previous investigations of coal-tar pitch by other techniques were detected in this study. While the identification of particular structural types is not possible, the precise masses indicate the atomic species present. This study shows that high-resolution mass spectrometry provides a means of detecting changes in either the concentration or composition of organic compounds in fractions of coal tar following exposure to various atmospheres. Such information should lead to a better understanding of the properties of road tars and other commercially important fractions of coal tar.

References

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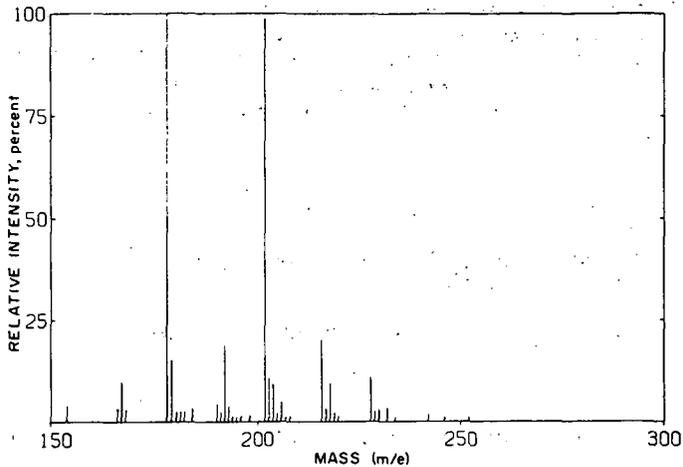


Figure 1.—Mass spectrum of 80°-85° softening point pitch fractionated at 100°C in spectrometer.

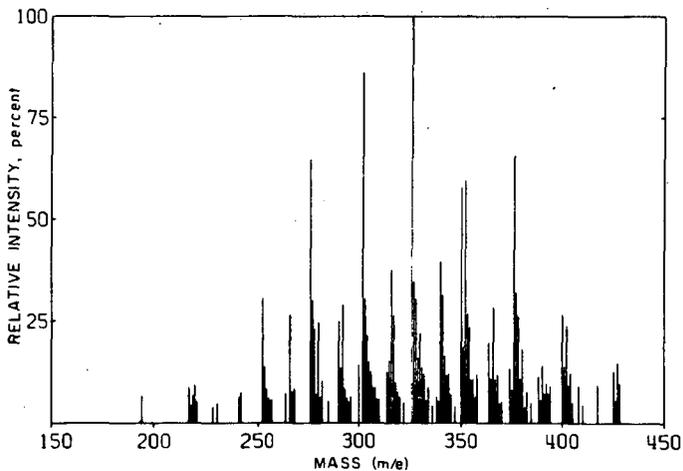
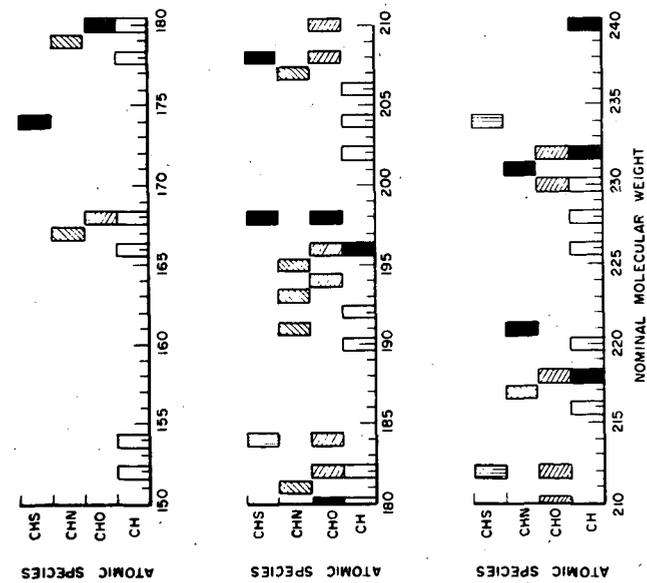


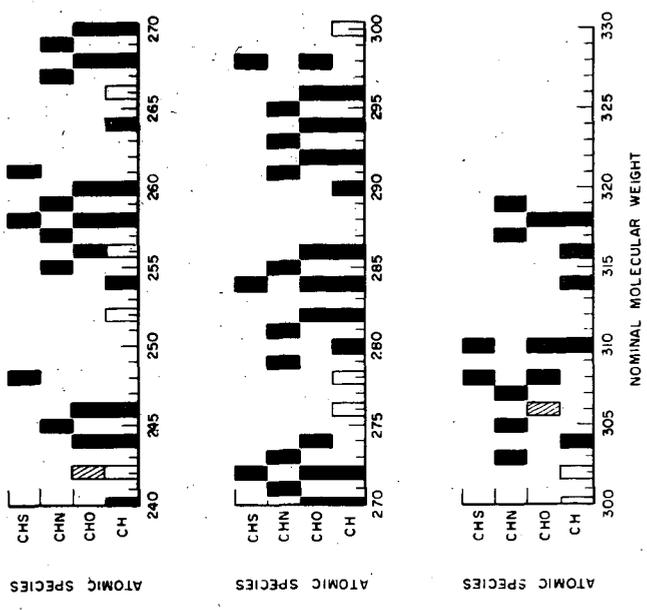
Figure 2.—Mass spectrum of 80°-85° softening point pitch fractionated at 325°C in spectrometer.



Molecular weight of and atomic species in components observed in 80°-85° C pitch by high-resolution mass spectrometry. Mass range 150-240

L-9942

Figure 3.



Molecular weight of and atomic species in components observed in 80°-85° C pitch by high-resolution mass spectrometry. Mass range 240-319.

L-9943

Figure 4.