MASS SPECTROMETRIC ANALYSIS OF STREAMS FROM COAL GASIFICATION AND LIQUEFACTION PROCESSES

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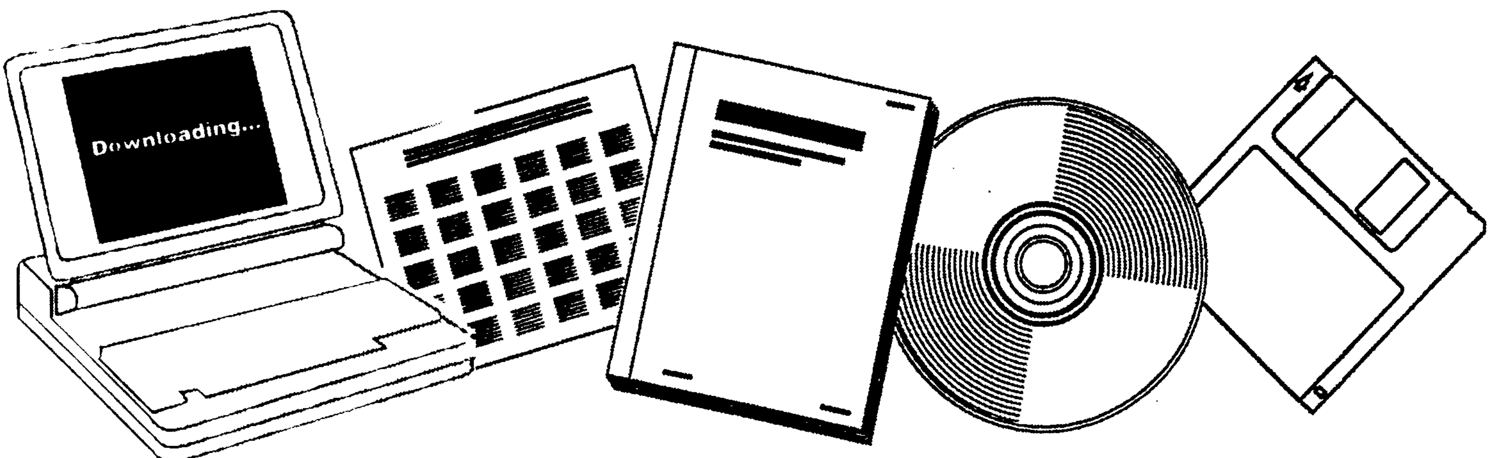

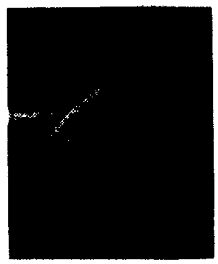

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MASS SPECTROMETRIC ANALYSIS OF STREAMS FROM COAL GASIFICATION AND LIQUEFACTION PROCESSES

By

A. G. Sharkey, Jr.[1], J. L. Shultz[2], C. E. Schmidt[3], and R. A. Friedel[4]

ABSTRACT

The increased effort in developing coal hydrogenation and coal gasification processes has emphasized the need for additional methods to analyze coal-derived fuels. Mass spectrometry is playing a major role in analyzing many of the streams from the Pittsburgh Energy Research Center's SYNTHANE and SYNTHOIL processes. Streams from coal gasification and coal hydrogenation processes are outlined and examples given for the analysis of coal, gas, oil, tar, and process water. Deficiencies in current mass spectrometric methods as applied to coal-derived fuels are reviewed and needs for future analytical research are discussed.

INTRODUCTION

Hydrocarbon-type analysis and other mass spectrometric techniques have provided analytical data in petroleum laboratories for many years and it is only natural that an attempt is being made to extend these established techniques to coal derived fuels. Certain of the methods for gas analysis, including techniques for trace and minor components, will be directly applicable. Currently available hydrocarbon-type analysis methods in which the total concentrations of various structural types such as paraffins, naphthenes, and aromatics are determined in petroleum products, cannot for the most part be applied directly to coal-derived oils because of the difference in the nature of the organic material (2, 5, 9, 12).

Samples from process streams that must be considered for analysis include the coal, product oil, asphaltenes, gas from both the reactor and gasifer, and process water (3, 4, 13). The catalyst must also be analyzed to assist with regeneration and problems such as deactivation. Process pollutants and hazardous compounds associated with any of the streams must also be included in the analytical scheme. Carbonaceous residues and ash that might have to be disposed of will have to be analyzed.

Mass spectrometric techniques can be applied to the analysis of gas, liquid, and solid samples. The five types of information that can be derived from

---

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the analysis of various organic components in the gas and liquid streams are:

1. Determination of total hydrocarbons in gas streams
2. Analysis for hydrocarbon types
3. Carbon number distribution
4. Compound identification
5. Structure elucidation.

Information from the above analyses ranges from the least specific to the most specific that can be derived by mass spectrometry. In the above analysis, the electron impact source is used in combination with low ionizing voltage, combined gas chromatography-mass spectrometry and high resolution mass spectrometry (1). Spark-source mass spectrometry can be used for the analysis of trace elements in various streams including the product oil, tar, water, and also for studies of the catalysts and various residues. Sensitivities in the ppb range are commonly achieved and, while data for many elements are not as precise as by other techniques, survey analyses for over 65 elements can be obtained in a single determination.

RESULTS AND DISCUSSION

Analyses of several streams from the Pittsburgh Energy Research Center's SYNTHOIL and SYNTHANE processes are used to illustrate the application of mass spectrometry to coal liquefaction and gasification products.

Coal

Analysis of the starting coal is important in evaluating the coal hydrogenation processes and such factors as hydrodesulfurization to remove the organic sulfur. Detailed analysis of the organic material associated with coal and also the trace element content of many coals have been investigated at PERC for many years (6, 10). Organic material extracted from coal with various solvents using ultrasonic techniques has been studied by mass spectrometry (9). Major differences are apparent in the material extracted from coals of various rank. Trace elements associated with 13 major coal seams in the United States have been investigated by spark-source mass spectrometry (Table 1) (7).

Gas

The major gaseous components from coal gasification are H_2, CO, CO_2, and the light hydrocarbons. In addition, there are a number of minor and trace components in the gas including H_2S, COS, thiophenes, alkylbenzenes, SO_2, and CS_2. Analyses for the major and trace components in gas from the gasification of an Illinois #6 coal are given in Tables 2 and 3. Neutron activation analysis has been used to investigate trace elements in the gas.

Table 1.—Analyses of Trace and Minor Elements in Coals.

Coals - Thirteen coals from 10 seams in 5 states.

Elements and range of concentration - Sixty-three elements ranging from 0.01 - 41,000 ppm.

Frequency of occurrence

43 elements in all samples.

15 additional elements in >75 percent of samples.

5 additional elements in <50 percent of samples.

9 additional elements checked but not detected.

Table 2.--Major Components in Gas from Gasification of Coal.

Component	Percentage
H_2	30.0
CH_4	18.0
CO	18.0
C_2H_6	2.0
CO_2	32.0

Table 3.--Trace Components in Gas from Coal Gasification.

Compound	Concentration (ppm)
H_2S	6,500
COS	107
Benzene	480
Toluene	66
C_8 Aromatic	34
Thiophene	43
C_1-thiophene	24
C_2-thiophene	5
Methylmercaptan	80

Mercury was detected at the sub ppm level in gas from the gasifier, but none was detected in the final product. HCN is also present in the ppb range in gas from the gasifier.

Liquid Products

The centrifuged liquid product has been examined following solvent separation. Solvent separation into a heavy oil and asphaltene fraction using benzene and pentane is used. Low-ionizing voltage mass spectrometry, high resolution mass spectrometry, and combined gas chromatography-mass spectrometry are used to examine the heavy oil and asphaltene fractions. Type-analysis methods are under development but have not reached the stage where data can be processed by this technique. Carbon number distribution data can be obtained by the low-ionizing technique. A summary of the major structural types and total for each type detected in the heavy oil and asphaltene fractions from the liquefaction of a Kentucky coal are given on Table 4.

High-resolution mass spectrometry provides molecular formulas for the major components including the heteroatom species containing O, N and S (11). A typical heavy oil or asphaltene fraction produces several hundred formulas and represents an extremely complex mixture. While the particular isomeric form(s) present cannot be determined from the molecular formulas derived from high-resolution data, (1) the presence of heteroatom species is readily detected, (2) the carbon number range is determined for the various components and (3) considerable insight is provided into the structural types present, that is, the degree of saturation, etc. One method of summarizing these data is illustrated in Figures 1 and 2. The important part of the plot is the upper terminus of the lines for the various combinations of atoms and limiting values for the various structural types are shown in Figure 3. These limiting values can be used to interpret the plots resulting from sample analysis as shown in Figures 1 and 2. Hydrocarbons to C_{28} have been detected in both the heavy oil and asphaltene fractions. Formulas have been detected for components with the following combinations of atoms: C_xH_y, C_xH_yO, C_xH_yN, C_xH_yON, $C_xH_yO_2$, and $C_xH_yO_3$.

High-resolution mass spectrometry has been used to investigate organic sulfur compounds in the SYNTHOIL products. The decrease in the organic sulfur compounds was monitored by intermittent sampling of a multiple pass experiment. This technique has proven extremely valuable in evaluating catalyst and conditions for hydrodesulfurization. A list of the major sulfur compounds detected in product from the hydrodesulfurization of Kentucky coal are given in Table 5. Data in Table 6 illustrate how the concentration can be followed as a function of reaction time. Compounds containing the thiophene nucleus are the most persistent. The extent of hydrogenation can also be followed by mass spectrometry as shown in Table 7.

Table 4.--Major Structural Types in Heavy Oil and Asphaltene Fractions from SYNTHOIL product.

Structural types[a]	Heavy Oil	Asphaltene
	Percent of Total Ionization	
Alkylbenzenes	11	9
Indenes	7	4
Indans	9	2
Naphthalenes	6	2
Acenaphthylenes	12	8
Biphenyls	21	11
Anthracenes; Phenanthrenes	6	4
Phenylnaphthalenes	5	6
4-rings, peri-condensed	5	11
4-rings, cata-condensed	3	9
5-rings, peri-condensed	4	15
5-rings, cata-condensed	1	5
6-rings, peri-condensed	1	10
Phenols	9	4

a/ Including alkyl derivatives.

Table 5.--Organic Sulfur Compounds in the Products of Coal Hydrogenation.

	m/e	Molecular Formula	Identification[a]
Light Oil	134	C_8H_6S	Benzothiophene
	148	C_9H_8S	Methylbenzothiophene
	162	$C_{10}H_{10}S$	Dimethylbenzothiophene
Heavy Oil	98	C_5H_6S	Methylthiophene
	138	$C_8H_{10}S$	Tetrahydrobenzothiophene
	174	$C_{11}H_{10}S$	Benzylthiophene
	184	$C_{12}H_8S$	Dibenzothiophene
	198	$C_{13}H_{10}S$	Methyldibenzothiophene
	208	$C_{14}H_8S$	Benzo(def)dibenzothiophene
	234	$C_{16}H_{10}S$	Naphthobenzothiophene
	248	$C_{17}H_{12}S$	Methylnaphthobenzothiophene
	284	$C_{20}H_{12}S$	Dinaphthothiophene

a/ Based upon molecular formula determined by high-resolution mass spectrometry. Other isomeric forms possible in some instances.

Table 6.--Sulfur Compounds in the Products for Multi-Pass Hydrogenation of Indiana #5 Coal with Co-Mo/SiO_2-Al_2O_3 Catalyst.

A. Operating Pressure: 2,000 psi

Compound	Concentration, as percent of ionization I Pass	II Pass	III Pass	IV Pass	F Pass
Benzothiophene	0.26	0.15	0.13	0.12	0.04
Dibenzothiophene	1.67	0.70	0.70	0.49	0.27
Naphthobenzothiophene	0.09	0.02	None	None	None

B. Operating Pressure: 4,000 psi

Compound	Concentration, as percent of ionization I Pass	II Pass	III Pass	IV Pass[a]
Benzothiophene	trace	trace	trace	trace
Dibenzothiophene	0.30	0.17	0.08	0.07

a/ Only 4 passes were conducted at 4,000 psi.

Table 7.--Catalytic Hydrodesulfurization: Evidence for Hydrogenation of Vehicle Oil.

(Distribution of Ionization)

Mass	Compound	Pass 1	Pass 3	Pass 5
128	Naphthalene	55	42	42
130	Dihydronaphthalene	18	24	27
132	Tetralin	16	24	31
134	Hexalin	3	5	4
136	Octalin	8	5	5

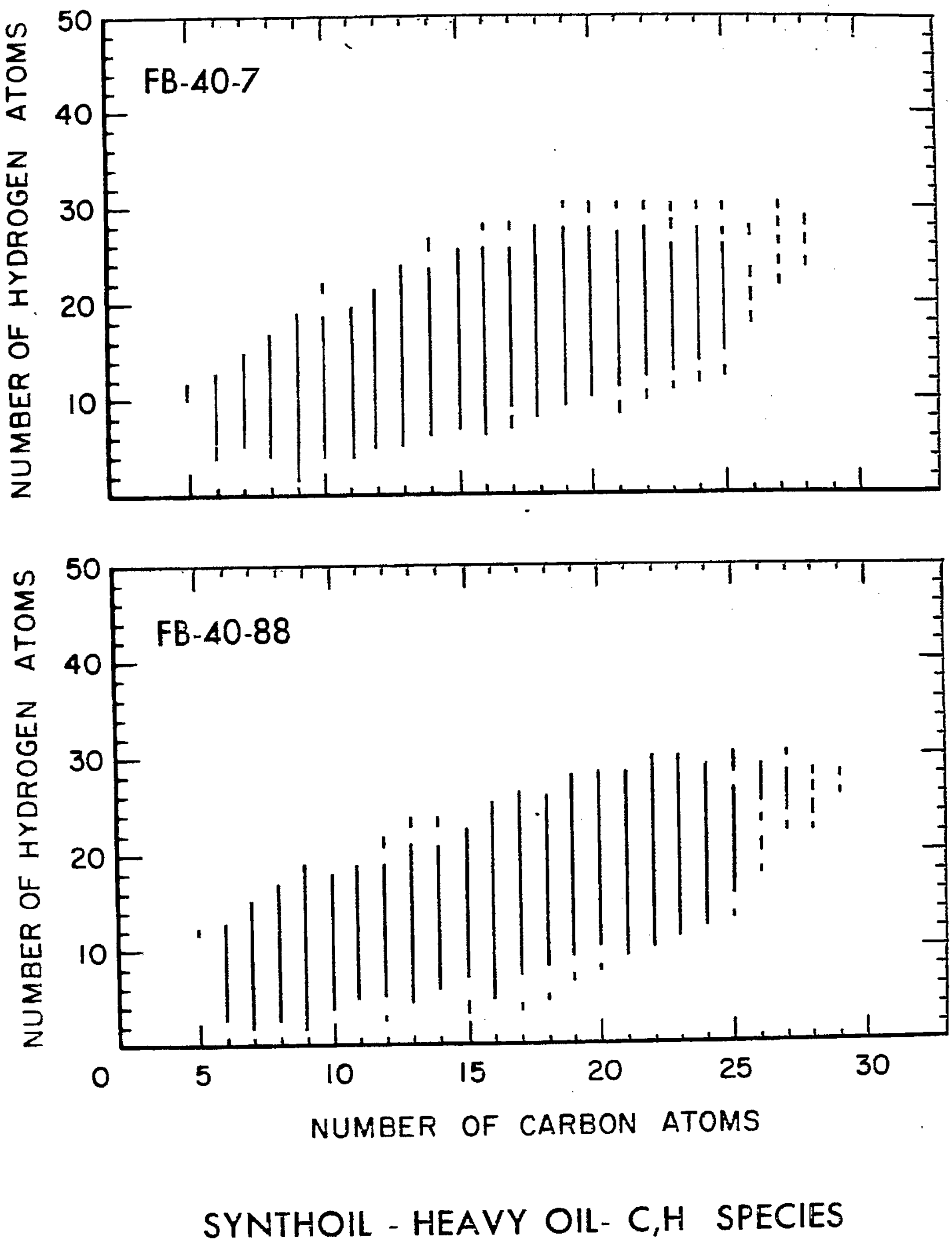

Fig. 1. Distribution of hydrocarbons (C_xH_y) in SYNTHOIL product.

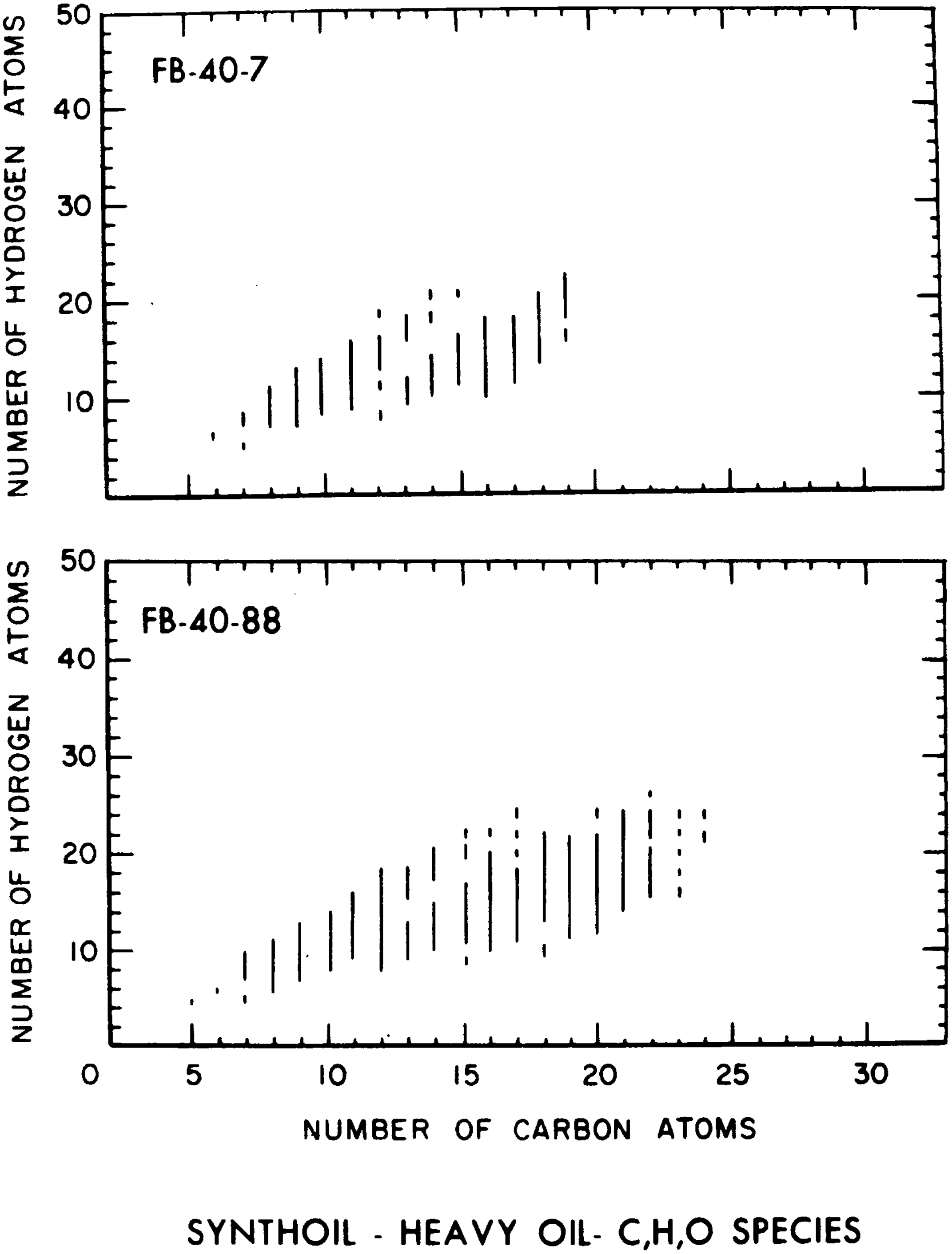

Fig. 2. Distribution of oxygenated compounds (C_xH_yO) in SYNTHOIL.

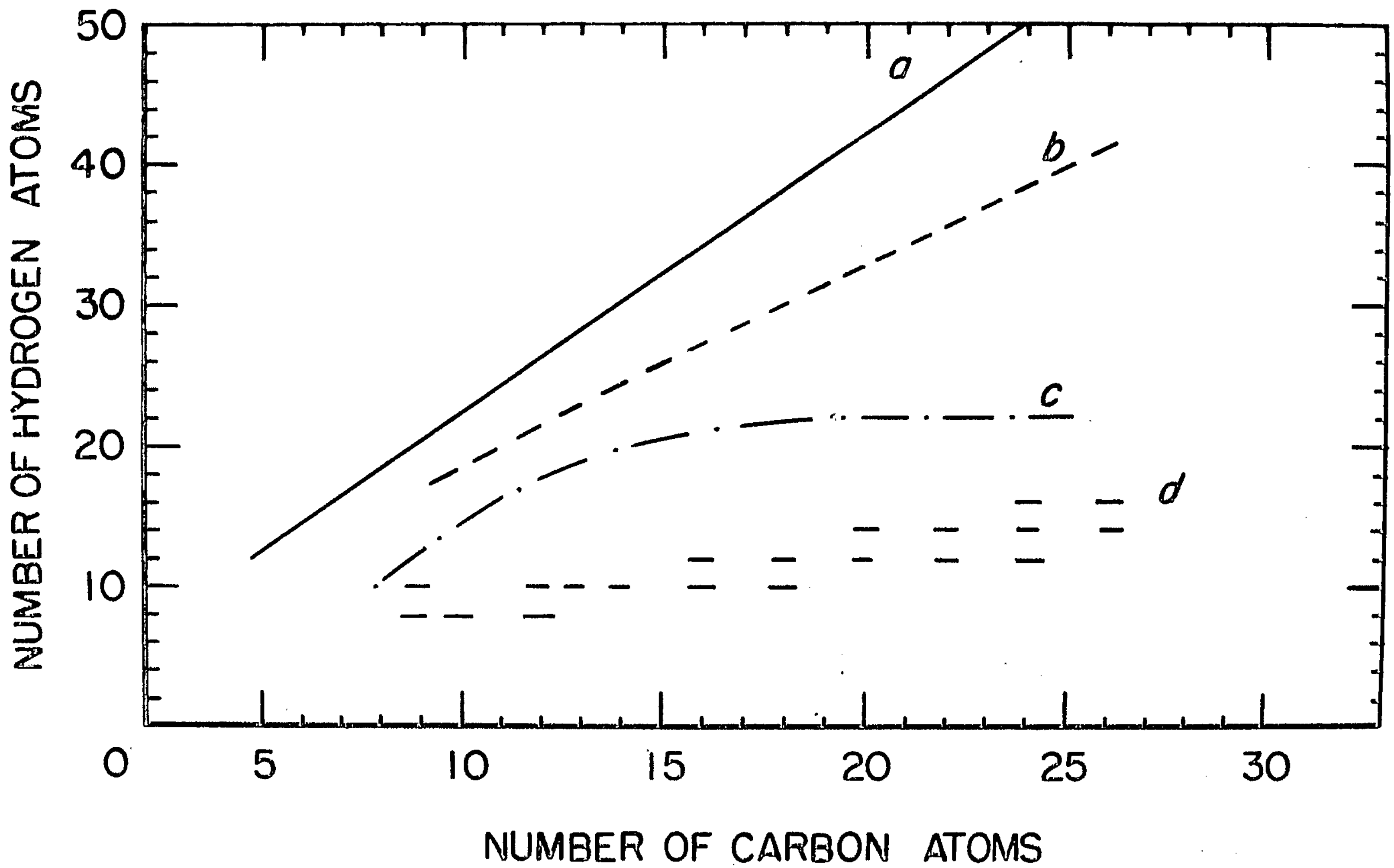

Fig. 3. Limiting values for several classes of hydrocarbon compounds.
a. aliphatic
b. perhydroaromatic
c. alkylated aromatic [assuming 5 alkyl carbon group(s)].
d. polynuclear aromatic.

Use of combined gas chromatography-mass spectrometry in the analysis of heavy fractions is illustrated in Figures 4 through 7, showing the detailed analysis of a tar from the gasification of coal. Concentrations of the major structural types derived from the low-ionizing voltage mass spectrum for the gasification of Illinois #6 coal are given in Table 8.

Process Water

By-product water results from both coal gasification and liquefaction processes. Detailed analysis of the contaminants in the water are being provided to assist in devising a purification process for this stream (8). In the SYNTHANE gasification process it is anticipated that much of the purified condensate water will be used as a recycle cooling water. Water from coal gasification has been examined in detail by extraction with methylene chloride. From 0.6 to 2.4 percent (by weight) of extractable material has been detected of which 68 percent is phenolic. A summary of the compound types detected in product water from coal gasification is given in Figure 8.

Trace elements in the condensate from an Illinois #6 coal gasification run have also been examined by spark-source mass spectrometry and the analysis is given in Table 9 (4).

Catalysts

In studies of catalyst surfaces to determine changes that occur with catalyst aging, and in evaluating regeneration processes, spark-source mass spectrometry is being used to determine the trace elements. Direct imaging mass spectrometry can be used to determine the distribution of elements on the surface and also to obtain a depth profile of the first few layers of the material. Only preliminary data have been obtained thus far but spark-source mass spectrometry analyses indicate that many of the elements determined in the original coal can be found on the surface of used catalyst.

Pollutants and Hazardous Compounds

Many of the environmental concerns for coal liquefaction products were presented at the EPA Symposium on the Environmental Aspects of Fuel Conversion Technology held at St. Louis, MO, May 13-15, 1974. Analytical needs for the product oil included studies of the organic carcinogens, metal compounds and inhalable vapors. The inorganic residue that must be disposed of should be investigated because of leachable inorganic compounds. The process water is of concern because of the organic contaminants and also because of possible changes in elemental composition if the water is returned to streams.

Screening of the major streams from coal hydrogenation processes for pollutants is possible by mass spectrometric techniques. The oil product is

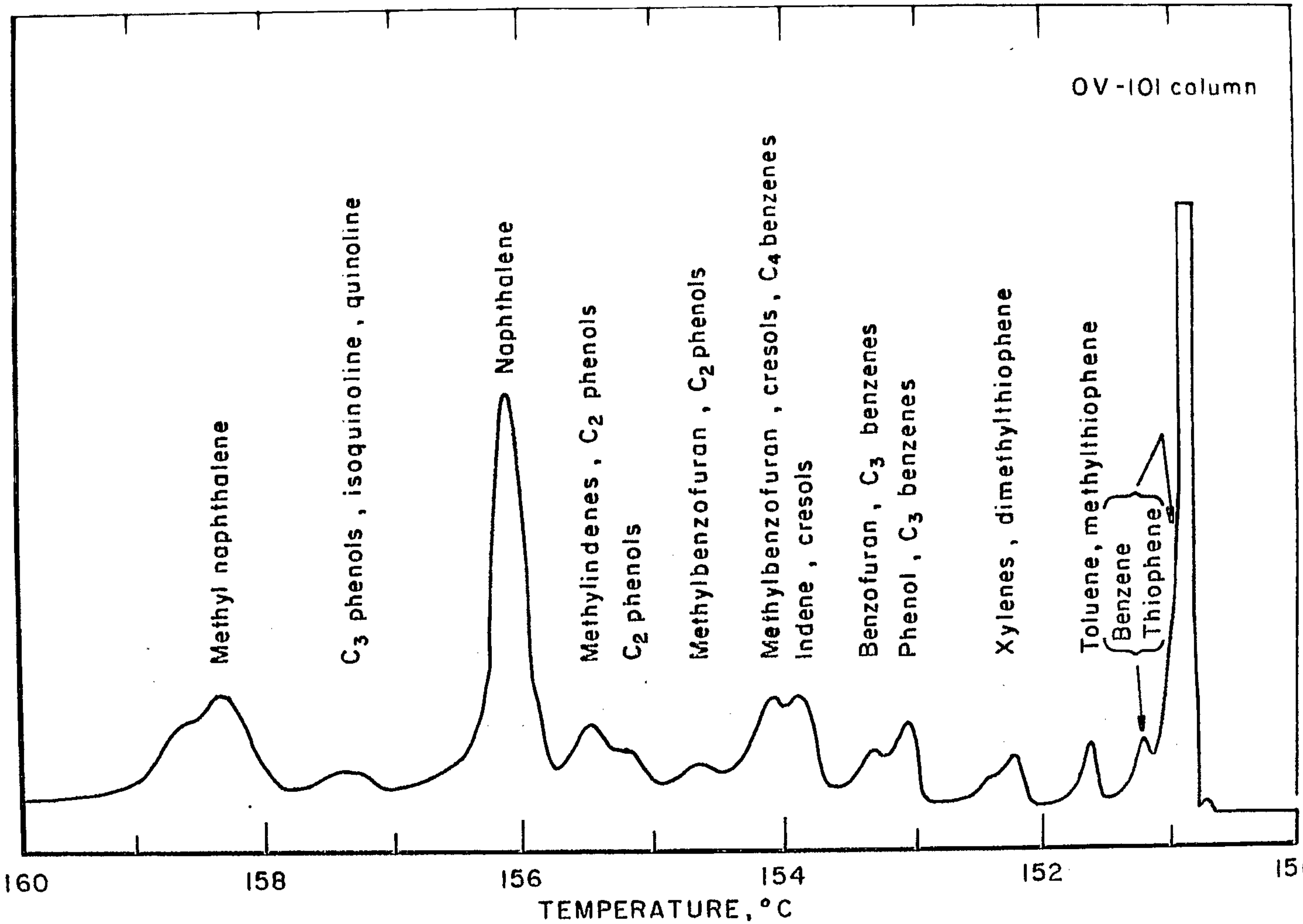

Fig. 4. - Analysis of light-ends of gasifier tar HP-183 by combined gas chromatography mass spectrometry.

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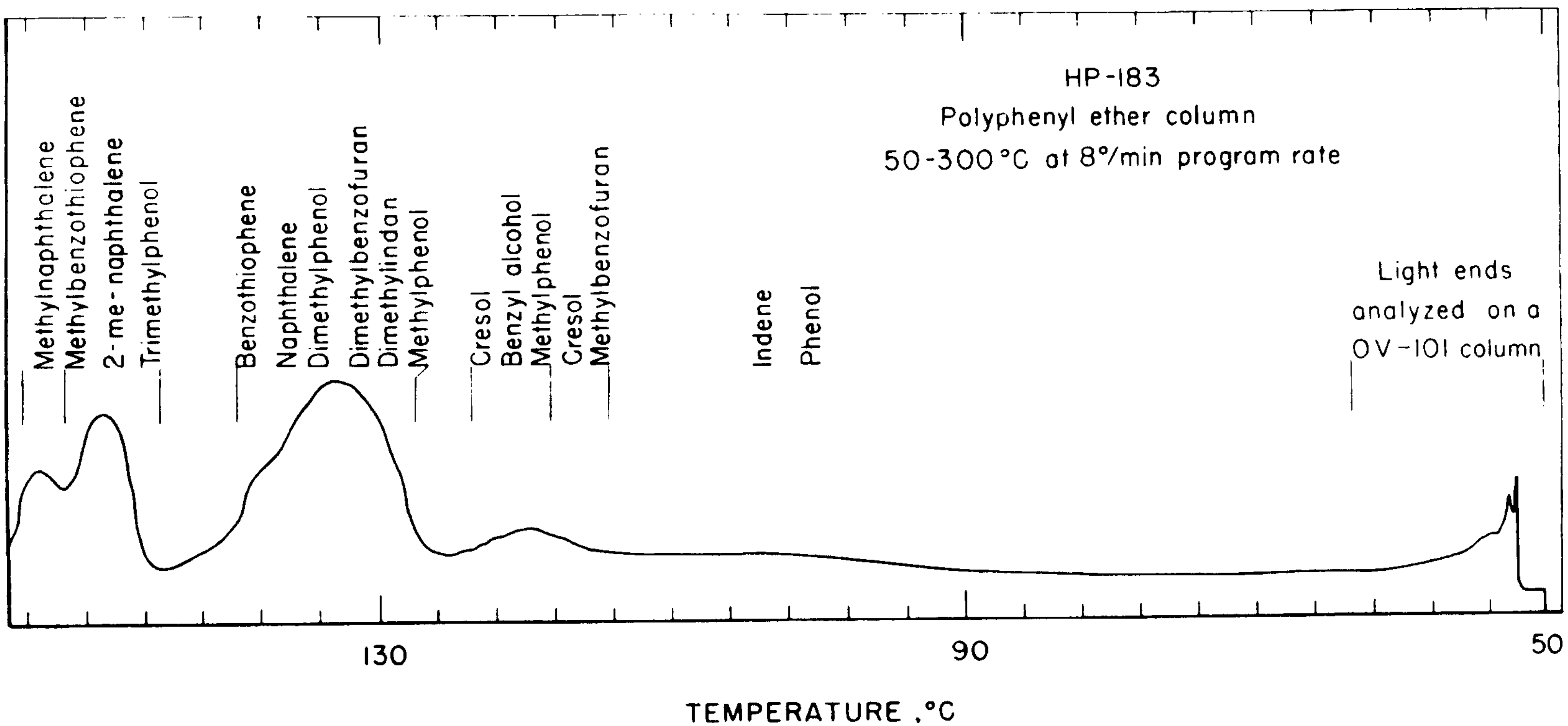

Fig. 5. - Analysis of gasifier tar HP-183 by combined gas chromatography-mass spectrometry (50°-150°C).

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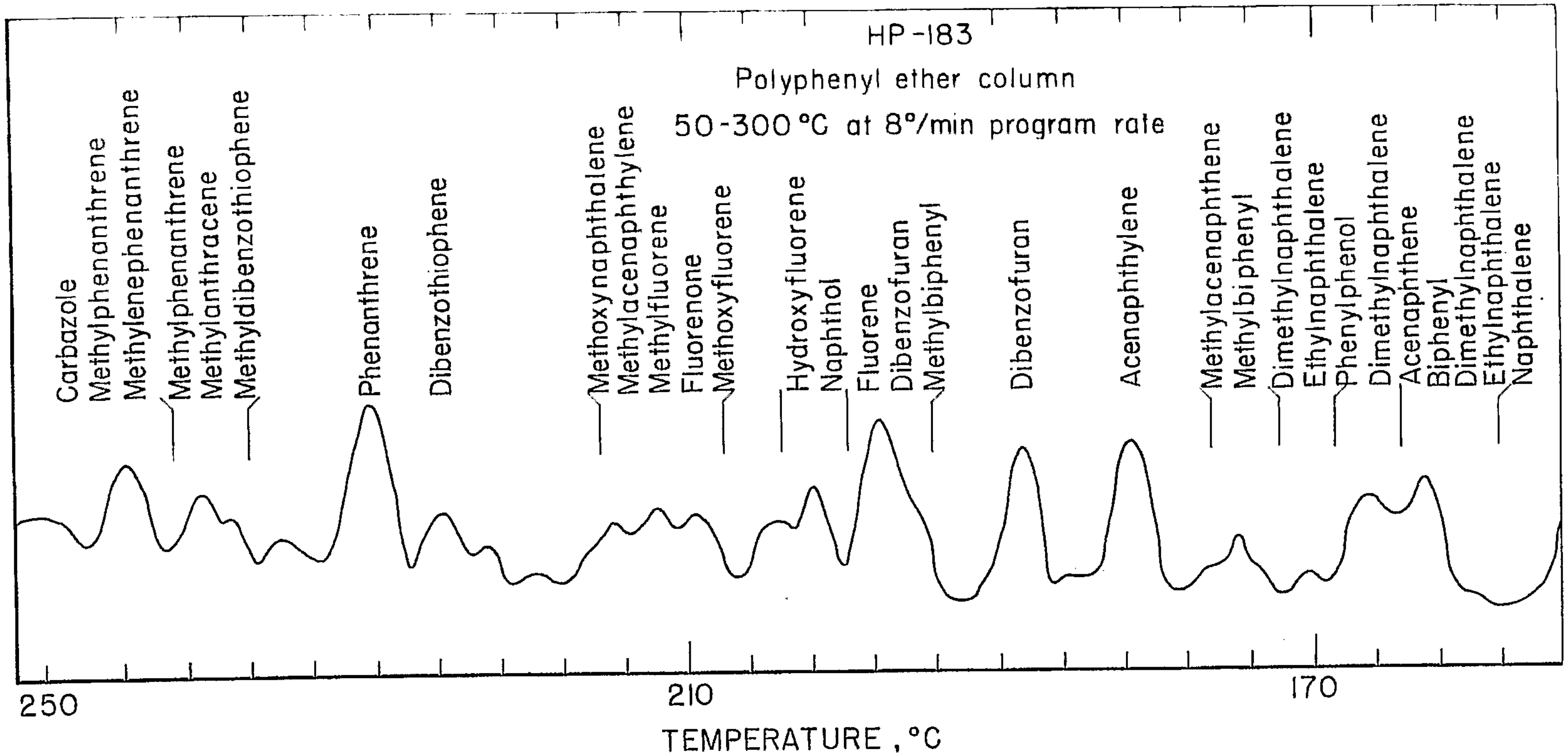

Fig. 6. Analysis of gasifier tar HP-183 by combined gas chromatography-mass spectrometry. (150°-250° C).

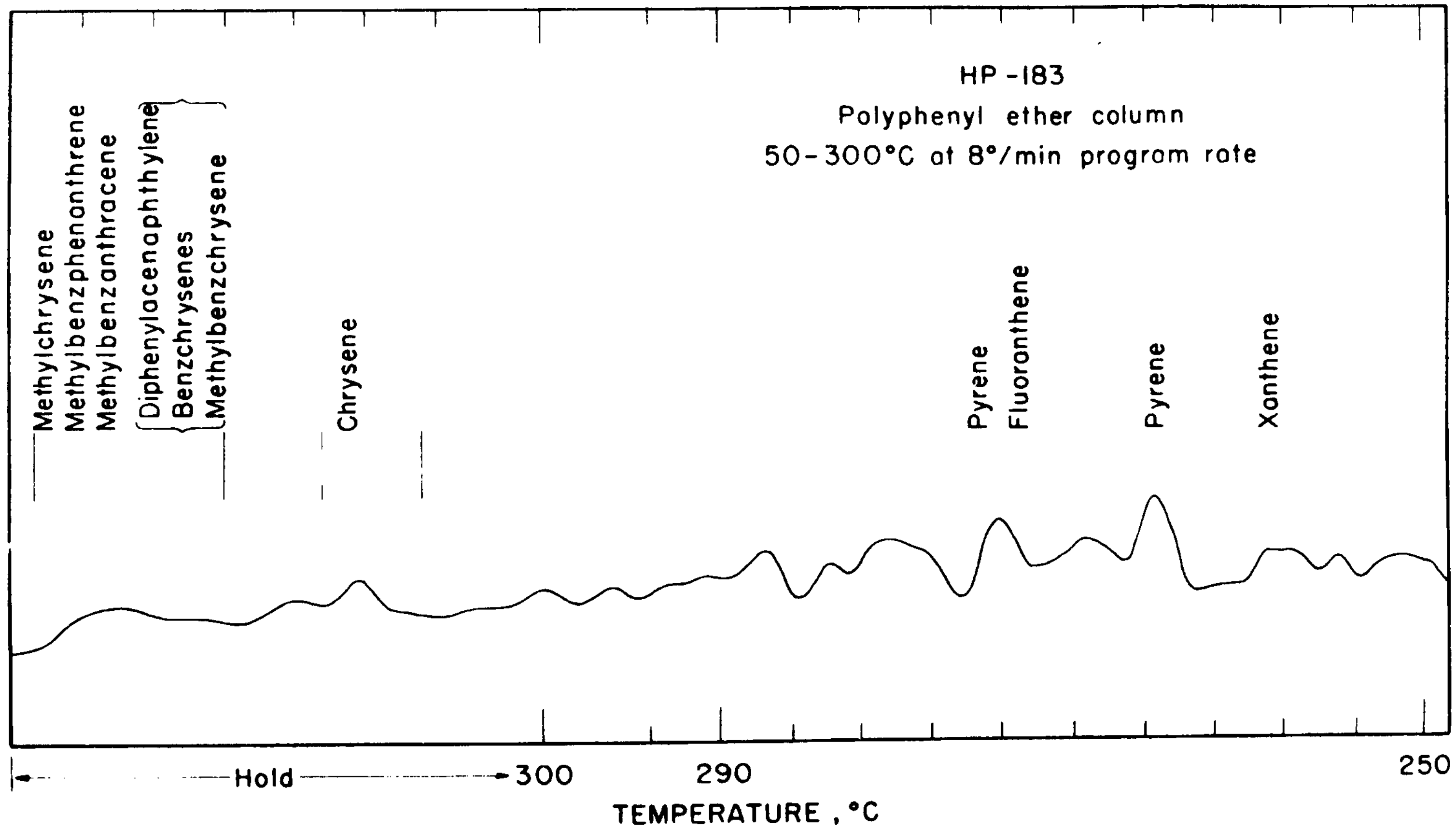

Fig. 7. – Analysis of gasifier tar HP-183 by combined gas chromatography–mass spectrometry. (250°–300°C).

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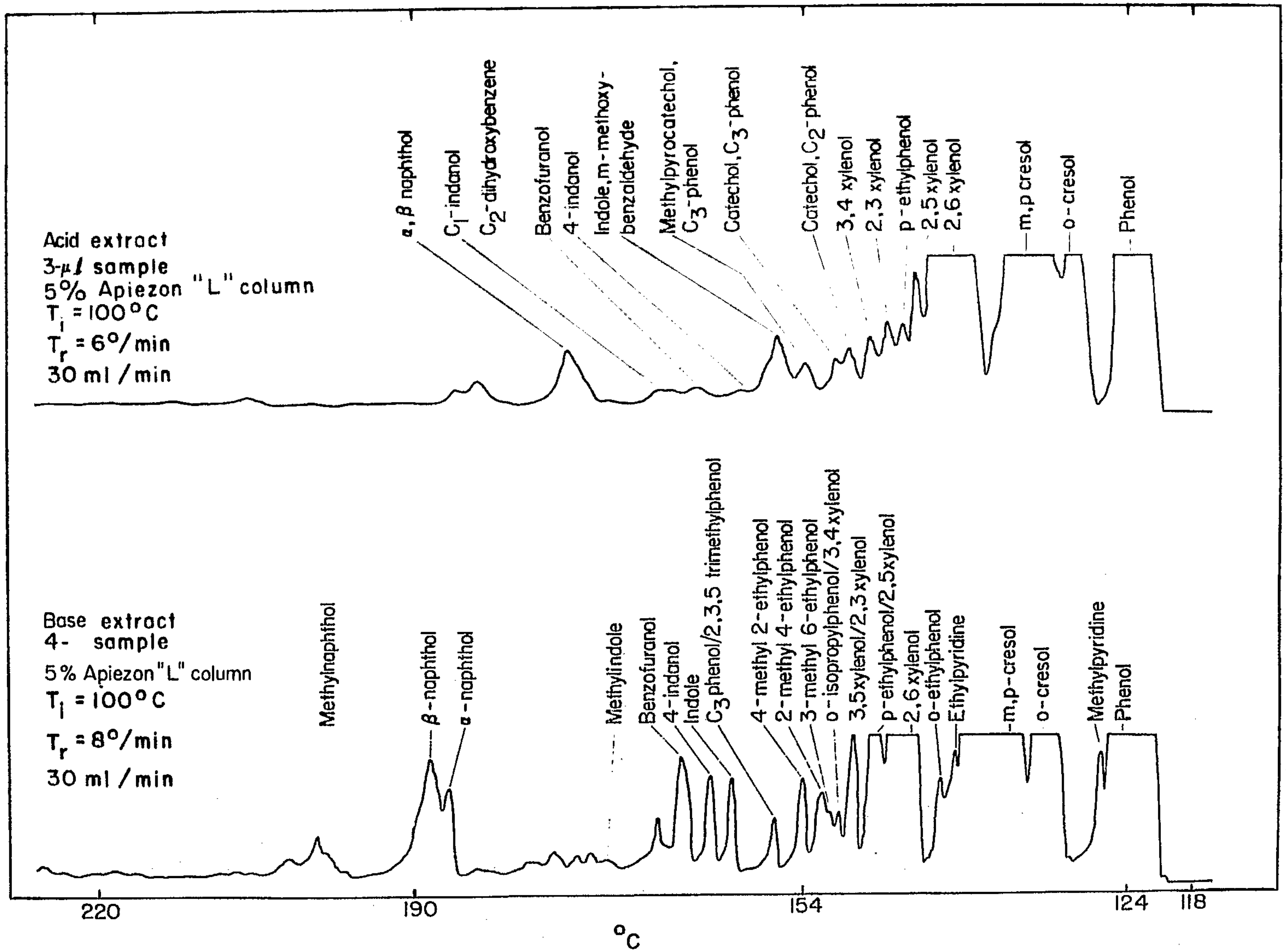

Fig. 8. Contaminants in product water from coal gasification: gas chromatography-mass spectrometry data.

Table 8.--Mass Spectrometric Analyses of the Benzene-Soluble Tar, Volume-Percent.

Structural Type (includes alkyl derivatives)	Illinois No. 6 Coal[a]
Benzenes	2.1
Indenes	8.6[b]
Indans	1.9
Naphthalenes	11.6
Fluorenes	9.6
Acenaphthenes	13.5
3-ring aromatics	13.8
Phenylnaphthalenes	9.8
4-ring peri-condensed	7.2
4-ring cata-condensed	4.0
Phenols	2.8
Naphthols	b/
Indanols	0.9
Acenaphthenols	---
Phenanthrols	2.7
Dibenzofurans	6.3
Dibenzothiophenes	3.5
Benzonaphthothiophenes	1.7
N-heterocyclics[c]	(10.8)
Average Molecular Weight	212

a/ Spectra indicate traces of 5-ring aromatics.
b/ Includes any naphthol present (not resolved in these spectra).
c/ Data on N-free basis since isotope corrections were estimated.

Table 9.--Trace elements in condensate from an Illinois No. 6 coal gasification test.

	Weight, Percent
Ppm:	
Calcium	4
Iron	3
Magnesium	2
Aluminum	0.8
Ppb:	
Selenium	360
Potassium	160
Barium	130
Phosphorus	90
Zinc	60
Manganese	40
Germanium	40
Arsenic	30
Nickel	30
Strontium	30
Tin	20
Copper	20
Columbium	6
Chromium	6
Vanadium	3
Cobalt	2

the most complex and perhaps the most difficult to screen for hazardous compounds. A high-resolution mass spectrometry technique has been devised at PERC and is currently being applied to many types of samples (11). In providing formulas for the various components in the oil product, samples can be surveyed for a wide range of contaminants and hazardous components. This is in contrast to conventional methods now being devised for the precise determination of a few individual hazardous components. The basis of the high-resolution technique is very simple. A list of several hundred hazardous components can be included in the computer program and, as a final step in the tabulation of data, these formulas can be matched against formulas of components detected in the sample. In this screening process literally hundreds of components can be eliminated and the analytical effort can be concentrated on compounds for which formulas were detected. This screening process simply serves as a guide, as again, the particular isomeric form cannot be determined. Application of this technique to organic material derived from airborne particulates is illustrated in Table 10.

Analytical Needs of Future

The above summary indicates the extensive role that mass spectrometry is now playing in the analysis of coal hydrogenation and coal gasification products. Many of the techniques required can be carried over from established methods for the analysis of petroleum products. Major deficiencies in the above analytical scheme, where mass spectrometry could play a major role in the future, include (1) devising a routine technique for the analysis of the product oil to evaluate operating parameters and (2) expanding research to devise techniques for evaluating environmental concerns.

ACKNOWLEDGMENTS

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Table 10.--Screening for possible carcinogenic compounds in airborne particulates.

Possible Compound	Molecular Weight a/	Formula	Pomona, Calif.	St. Louis, Missouri	New York City	Pittsburgh, Pa.	Fresno, Calif.
Acetylaminofluorene	223.0997	$C_{15}H_{13}NO$	— b/	—	—	x c/	—
Aminodiphenyl	169.0891	$C_{12}H_{11}N$	—	—	—	—	—
Benzidine	184.1000	$C_{12}H_{12}N_2$	—	—	—	—	—
Dichlorobenzidine	252.0221	$C_{12}H_{10}N_2Cl_2$	—	—	—	—	—
Dimethylaminoazobenzene	225.1266	$C_{14}H_{15}N_3$	—	—	—	—	—
Naphthylamine	143.0735	$C_{10}H_9N$	x	—	x	—	x
Nitrodiphenyl	199.0633	$C_{12}H_9NO_2$	—	—	—	—	—
Nitrosodimethylamine	74.0480	$C_2H_6N_2O$	—	—	—	—	—
Propiolactone	72.0211	$C_3H_4O_2$	x	x	x	—	—

a/ Precise mass
b/ Formula not detected.
c/ (x) indicates formula detected.

REFERENCES

1. Aczel, Thomas, J. Q. Foster, J. H. Karchmer. Characterization of Coal Liquefaction Products by High Resolution-Low Voltage Mass Spectrometry. Am. Chem. Soc., Fuel Div., 157th Meeting, Minneapolis, Minn., 1969.

2. Clerc, R. J., A. Hood, and M. J. O'Neil. Anal. Chem., v. 27, 1955, 868.

3. Forney, A. J., Progress Report on SNG Technology. Pipeline Industry, v. 37, no. 4., Sept. 1972. pp. 27-29.

4. Forney, Albert J., William P. Haynes, Stanley J. Gasior, Glenn Johnson and Joseph P. Strakey, Jr. Analysis of Tars, Chars, Gases, and Water, Found in the Effluents from the SYNTHANE Process. BuMines TPR 76, January 1974. 9 pp.

5. Hastings, S. H. Analysis of the Aromatic Fraction of Virgin Gas Oil by Mass Spectrometry, Anal. Chem., 28, 1956, 1243.

6. Kessler, T., A. G. Sharkey, Jr., and R. A. Friedel. Spark-Source Mass Spectrometry Investigation of Coal Particles and Coal-Ash. BuMines TPR 42, Sept. 1971. 15 pp.

7. Kessler, T., A. G. Sharkey, Jr., and R. A. Friedel. Analysis of Trace Elements in Coal by Spark-Source Mass Spectrometry. BuMines RI 7714, 1973. 8 pp.

8. Schmidt, C. E., A. G. Sharkey, Jr., and R. A. Friedel. Mass Spectrometric Analysis of Product Water from Coal Gasification. BuMines TPR 86, December 1974. 7 pp.

9. Sharkey, A. G., Jr., J. L. Shultz, and R. A. Friedel. Advances in Coal Spectrometry. Mass Spectrometry. BuMines Rept. of Inv. 6318, 1963. 32 pp.

10. Shultz, J. L., R. A. Friedel, and A. G. Sharkey, Jr. Mass Spectrometric Analyses of Coal Tar Distillates and Residues. Bu Mines Rept. of Inv. 7000, 1967. 14 pp.

11. Shultz, J. L., A. G. Sharkey, Jr., B. Nathanson, and R. A. Friedel. Mass Spectral Studies of Airborne Particulates and Possible Pollution Sources, Biomed. Mass Spec., v. 1, 1974. pp. 137-141.

12. Swansiger, J. T., F. E. Dickson, and A. T. Best. Liquid Coal Compositional Analysis by Mass Spectrometry. Anal. Chem., v. 46, 1972. pp. 730-734.

13. Yavorsky, Paul M., Sayeed Akhtar, and Sam Friedman. Process Development: Fixed Bed Catalysis of Coal to Fuel Oil. Presented at 65th Annual AIChE Meeting, November 26-30, 1972, New York.

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