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CHARACTERIZATION OF COAL-DERIVED FLUIDS BY CAPILLARY COLUMN GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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SUMMARY

A coal-derived fluid has been analyzed by high-resolution gas chromatography-mass spectrometry with glass capillary columns, both before and after liquid chromatography on silica gel. The bulk of the sample consists of only a few types of compounds. Alkyl-substituted indanes and tetralins account for most of the constituents at the high-molecular-weight end of the mixture and cycloalkanes are the predominant substance type in the high-volatility range. Substituted aromatic hydrocarbons and alkanes, in particular *n*-alkanes, are distributed over the entire boiling point range. Oxygen- and nitrogen-containing substances are present in only small concentrations and cannot be analyzed directly without enrichment. A new method for the concentration of eluents resulting from liquid chromatography is introduced.

INTRODUCTION

The need for more and more energy with a concurrent decline in petroleum supplies has focused interests to fuels derived from coal, shale and tar sands. It can be expected that fuels derived from such sources will play a significant role in the future. Coal is the most abundant source of energy in the U.S.A. Many different technical approaches to convert coal into liquefied fuels have been experimented with, dating back to World War II. Within limits, some variables in the liquefaction process can be adjusted for a maximum yield of the desired products. Depending on the composition of the coal, varying proportions of undesirable byproducts also have to be dealt with. The composition of liquefied coal must be known in some detail to determine the reaction mechanisms underlying the conversion process. The necessary steps can then be undertaken to obtain the best product distribution.

Coal-derived fluids differ from petroleum products mainly in respect to the heterocyclic fraction. Nitrogen-containing compounds and oxygenated substances are relatively abundant in such fluids. In the U.S.A., there are presently only a few pilot plants in operation. Most technical operations are supported by the United States Energy Research and Development Administration and some of its agencies.

Many of the analytical procedures have been worked out at the Bartlesville Energy Research Center, and samples of coal fluids are available from this source for experimental purposes.

Chemical characterization of coal liquids have been performed only on a limited number of samples. Such analyses have usually been limited to relatively narrow boiling-point fractions, due to the complexity of the material. Some analytical data are also available on full-boiling-range liquids, but these are less detailed.

Coal fluids represent mixtures of extreme complexity and several analytical methods have been applied towards their characterization. In most cases, samples have been divided into several fractions by distillation. Adsorption chromatography, gel permeation chromatography or a combination of both has been extensively used for group type separations¹⁻⁷. Acid/base extraction or ion-exchange techniques often preceded chromatography and removal of certain groups of compounds by complexation or selective destruction has also been described^{8,9}. In most cases, several chromatographic steps had to be applied, making sample preparation rather time consuming. Spectroscopic methods, in particular NMR, have generally been applied to describe the overall compound distribution¹⁰. Mass spectroscopy¹¹⁻¹⁶ (MS) occupies a special position in the analytical scheme. Both low-resolution and high-resolution MS have been extensively applied, using matrices with sophisticated computer programs. This approach is especially useful for routine analysis, but has also been applied for the fraction containing heterocyclic and oxygenated compounds which are sometimes difficult to handle by chromatographic techniques. The cost of mass spectral instrumentation, however, is considerable.

Some of the first and most impressive applications of high-resolution gas chromatography (GC) with capillary columns have been in the field of petroleum chemistry where the technique is still extensively used. GC, however, has a limited scope in the overall characterization of coal-derived fluids. One of its major uses is for simulated boiling-point distributions^{17,18}. Short capillary columns are especially useful in that respect, since they easily cover a boiling-point range of several hundred degrees in a very short time with good accuracy and at minimal expenditure.

Capillary column GC can provide a detailed picture of individual components in a complex sample. In some cases, it may be desirable to identify such trace compounds for investigation of toxicological properties and to establish data which are related to health aspects. Although coal fluids have been fairly well characterized in respect to the chemical groups present, no detailed analysis of individual compounds by GC-MS has been done to this date. One purpose of this study was to obtain a picture of the distribution of major individual hydrocarbons. It was also of interest to determine to what extent the technique could serve as supplement or replacement for the mass spectral procedures in present use.

EXPERIMENTAL

Two Hewlett-Packard gas chromatographs, Models 5830 and 5720, with single flame ionization detector were used. Both instruments were modified to accept glass capillary columns. To protect the capillary columns from heavy materials, a short plug of approximately 10 mg of Tenax GC (Applied Science, State College, Pa., U.S.A.) held between two glass wool plugs, was inserted into the injector port glass

liner. The septum was partially insulated from the heat of the injector body by a disc of polyimide.

Thick-wall soft-glass tubing 1500 × 10 mm O.D. × 4 mm I.D. (Kimble Glass Co., Article No. 46475) was rinsed with several solvents, including detergents. The tubes were then carefully rinsed with water and dried in a flame. A Shimadzu glass drawing machine was slightly modified to accept this extra heavy tubing.

OV-101 and Dexsil 300 GC (Applied Science) served as stationary phases. The glass capillaries underwent different types of pretreatment before the final coating. Some columns were silanized in the gas phase¹⁹ followed by the deposition of a layer of Silanox 101²⁰ (Cabot Corp., Boston, Mass., U.S.A.). Others were coated with a thin layer of Carbowax 20M, heated to 275° overnight and then extracted with methylenechloride²¹. The columns were coated by either the mercury plug method²² or a modified static evaporation technique²³ in which the column is screwed into a hot oven. All these techniques yielded columns of approximately equal performance. We do not have a preference for any particular procedure for these nonpolar columns.

Group separations were performed on activated silica gel. Columns 300 × 10 mm O.D. were slurry packed with hexane Hexane and benzene (Burdick and Jackson Labs., Muskegon, Mich., U.S.A.) were used without further purification. A 50- μ l aliquot of the coal fluid (Syncrude from Western Kentucky Coal, obtained from Dr. J. E. Dooley) was transferred onto the head of the column with a syringe. 30-ml fractions were collected for each of these solvents. Further concentration was done by one of two methods: Blowing a gentle stream of purified nitrogen (charcoal cold trap) over the surface of the liquids, or by a modified microdistillation technique. In the latter, a 50-ml flask with a graduated tip at the bottom was used with a Snyder column. After the solvent had been reduced to 500 μ l an appropriate aliquot, usually between 10 and 50 μ l, was withdrawn and injected into a small tube, 80 × 4 mm O.D., filled with 20 mg of conditioned Tenax. The bulk of the solvent was blown off at ambient temperature for a few minutes with nitrogen, at a flow-rate of 40 ml/min. The adsorbent tube was placed directly into the injector port of the gas chromatograph for thermal elution of the trapped substances onto the glass capillary column. A small U trap at the beginning of the capillary, immersed in liquid nitrogen, provided the necessary sharp injection.

Identifications were performed on a LKB 9000 gas chromatograph-mass spectrometer combination. The glass capillary column was connected to the instrument via Vespel ferrules (Alltech, Arlington Heights, Ill., U.S.A.). The glass capillary 45 m × 0.35 mm I.D. was flow controlled at a rate of 3 ml/min. A single jet, held at 250°, served as interface. Spectra were taken at an ionization voltage of 70 eV and a trap current of 80 μ A. Scan time was 2 sec per decade. Spectra were largely deducted from standard tables²⁴. The boiling point distribution was determined by coinjection of a standard of *n*-alkanes.

RESULTS AND DISCUSSION

Several coal-derived fluids of various boiling-point ranges were run by GC with glass capillary columns coated with a nonselective high-temperature phase. A fluid, derived from Kentucky coal and prepared by the Char-Oil-Energy-Development

(COED) process, was chosen for our studies. The brownish viscous liquid was centrifuged, but failed to produce a noticeable amount of sediment.

Both acidic and basic substances are known to be present in the total fluid, and care has to be taken to select a glass capillary column with the proper acid/base behavior or to simultaneously employ two columns, one with a slightly acidic and the other with a slightly basic surface. Glass capillaries were tested for their behavior towards acidic and basic compounds. An acidic standard was prepared consisting of phenol, cresol isomers and *p*-ethylphenol. Another standard contained the basic compounds pyridine, aniline and *N,N*-dimethylaniline. Approximately 10 ng of each of these compounds, in a suitable solvent, were introduced into the column and all substances eluted, although some tailing was observed, especially with the phenols. Since both types of substances passed through the column at trace levels, it was decided not to prepare columns with basic or acid surfaces. Such surfaces are difficult to prepare reproducibly.

Proper surface deactivation for glass capillary columns is of prime importance for the analysis of mixtures as heterogeneous as coal fluids. Such samples contain large amounts of relatively nonvolatile substances. These heavy ends cause a deterioration of column performance with extensive use. It is therefore important to protect the column from such materials. The application of a short precolumn is a possibility. Passage of the desired substances onto the analytical column, however, must be verified, and the adsorbent also must be highly inert.

Two adsorbents, Carbo-pack BHT and Tenax GC, were tested for their suitability to serve as packing material for the precolumn. Plugs of approximately 1 cm length were introduced into the glass injector port lines. A standard consisting of *n*-alkanes in the range of C₅-C₄₀ was used to determine the boiling-point range for which the method is applicable at a given injector port temperature. The data are summarized in Table I. It can be seen that Carbo-pack BHT is rather active, whereas Tenax GC is more suitable for the purpose. Substances having boiling-points as high as pentacosane (b.p. 410°) can be desorbed at 320° without difficulty.

For MS applications, capillary columns must meet additional requirements.

TABLE I

COMPARISON OF CARBOPACK BHT AND TENAX GC AS PRECOLUMN ADSORBENTS AT INJECTOR PORT TEMPERATURE OF 320°

<i>n</i> -Alkane	Recovery from precolumn (%)	
	Tenax GC	Carbo-pack BHT
C ₈	100	100
C ₁₀	100	100
C ₁₆	100	100
C ₁₈	100	94
C ₁₉	100	87
C ₂₂	78	15
C ₂₄	28	<5
C ₂₈	≈0	0
C ₃₂	0	0
C ₃₆	0	0
C ₃₈	0	0

Low bleeding at elevated temperature is of particular importance if the analysis of high-boiling substances is contemplated. A number of high-temperature stationary phases are commercially available. In some respect polar substrates such as the cyanosilicones are preferable since column deactivation becomes less critical. Resolutions are also often improved, since the elution of substances within a given boiling-point range is extended. Nonpolar phases, however, usually offer a wider temperature range and produce less bleeding at high temperature. We prefer OV-101 as stationary phase for high-temperature applications for these reasons. The phase can be used well beyond 200° at a very low background in the MS. Substances having boiling-points of above 350° can be eluted with ease.

Separation schemes for coal derived fluids are complex, and generally involve acid/base extraction and various combinations of liquid chromatography. It was planned to cut down on these sample preparation steps and take advantage of the extraordinary resolving power of an efficient glass capillary column. The selection of an essentially nonpolar stationary phase results in a separation according to the boiling-points of the sample components. Fig. 1 shows the total ion current monitor chromatogram of the coal fluid under study. Substances eluting after *n*-heneicosane have been omitted from the chart. Obviously, a considerable proportion of the components remains unresolved, especially at trace levels. About 280 mass spectral scans were taken during the run, but many substances eluted too fast to obtain adequate spectral scans. Overlap was still extensive in spite of the good separation power of the capillary. Investigation of the mass spectra revealed that most peaks were composed of several components.

Table II summarizes the identification of major components in the sample and gives an overview of the general nature of the most common substance types in the fluid. As expected, hydrocarbons, in particular homologues of substituted naphthenes, aromatics, indanes and naphthalenes make up the bulk of the sample. The mass spectra clearly indicate the substance type, but in cases where more than two hydrogen atoms have been substituted by alkyl groups, a large number of different patterns is possible. Since the mass spectra for such isomers are quite similar, GC retention data should be used if the identity of an individual compound needs to be established unequivocally.

There was no need for such detailed analysis, since the properties of interest of such homologues in a coal fluid are similar. Substitution patterns were only established in a few cases where standards are readily available. On well deactivated nonpolar columns, elution generally follows the boiling-points of the substances. Sometimes slight irregularities from this rule have been observed¹⁸. Caution must therefore be exercised if the order of elution is used as the basis for structural correlations.

Direct injection resulted in a very complicated chromatogram, and a way was sought to simplify the picture. A simple separation scheme involving silica gel column chromatography was applied to reduce some of the interferences. The sample was divided into polar and nonpolar fractions. Considerable overlap was observed, but the distribution ratio of a particular component in the fractions provided additional clues to its identity. Fig. 2 shows a total ion monitor chromatogram of a hexane fraction. The sample was prepared by successive injection of several charges of preconcentrated hexane eluent into an adsorbent tube containing Tenax, followed by frontal development of the solvent. The method is simple, fast and easily applicable

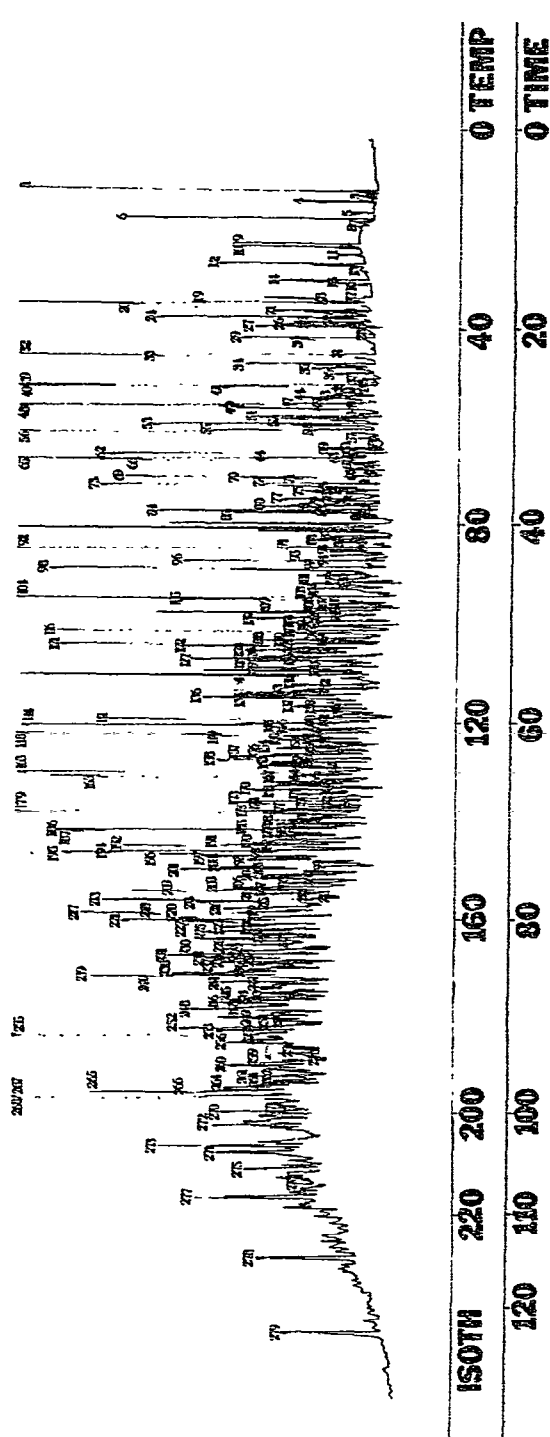


Fig. 1. Total ion current monitor chromatogram of a coal fluid derived from Western Kentucky coal. Conditions: glass capillary column, 45 m \times 0.35 mm I.D. coated with OV-101; carrier gas (helium) flow-rate: 3.0 ml/min; temperature program: 0° (10 min), 0–220° at 2°/min. For identification of peaks see Table II.

TABLE II
 IDENTIFICATION OF MAJOR COMPOUNDS IN A COAL-DERIVED FLUID

Peak No.	Compound	Peak No.	Compound
1	Ethane	80	<i>o</i> -Xylene
3	Chloromethane	82	C ₉ H ₁₈
4	C ₄ H ₁₀	84, 85	Methylethylcyclohexane
6	Pentane	87	Isopropylbenzene
7	Dichloromethane	88	Propylcyclohexane
9	2-Pentene	90, 91	Methylethylcyclohexane
10	2-Methylpentane	92, 93	Propylcyclohexane
11	3-Methylpentane	95, 96	<i>n</i> -Propylbenzene
12	<i>n</i> -Hexane	97	1-Methyl-3-ethylbenzene
14	Methylcyclopentane	98	1-Methyl-4-ethylbenzene + <i>trans</i> -hexahydroindan
15	C ₇ H ₁₄	99	1,3,5-Trimethylbenzene + methylnonane
17	C ₇ H ₁₄	100	1-Methyl-2-ethylbenzene
18	Benzene	101	1-Methyl-2-ethylbenzene
19, 20	Cyclohexane	102	C ₁₀ H ₂₀ + C ₄ -alkylcyclohexane
21	Dimethylpentane	103	1,2,4-Trimethylbenzene
23	Cyclohexene	104	<i>cis</i> -Hexahydroindan
24	C ₇ H ₁₆	105	C ₄ -Alkylcyclohexane
25	C ₇ H ₁₄	106	C ₁₀ H ₂₂
27	Dimethylcyclopentane	107	C ₃ -Alkylcyclohexane
28	C ₅ H ₁₆	108, 109	C ₁₀ H ₂₂ + C ₄ -alkylcyclohexane
29	C ₇ H ₁₆	110	C ₁₀ H ₂₀
31	Dimethylpentane	111	C ₁₀ H ₁₈
32	Dimethylpentene	112	1,2,3-Trimethylbenzene + C ₁₀ H ₁₈
34	3-Ethyl-1-pentene	113	C ₁₀ H ₁₈ + C ₄ -alkylbenzene
35	3-Ethyl-2-pentene	115	Indan
36	C ₇ -Alkylcyclopentane	117	<i>sec</i> -Butylcyclohexane
37	C ₈ H ₁₈	118	<i>n</i> -Butylcyclohexane
38	Methylhexadiene + C ₈ H ₁₈	119	C ₄ -Alkylcyclohexane
39-41	Toluene	120	C ₁₀ H ₁₈
43	Methylhexadiene	121	C ₄ -Alkylbenzene
44	2,5-Dimethylhexane	122	C ₄ -Alkylbenzene
45	C ₈ H ₁₈	124, 125	C ₄ -Alkylbenzene
46	C ₈ H ₁₈	126	C ₄ -Alkylcyclohexene + C ₁₀ H ₁₈
48-50	Dimethylcyclohexane	127	<i>trans</i> -Decahydronaphthalene
51, 52	Methylethylcyclopentene	128	C ₄ -Alkylbenzene + C ₁₀ H ₁₈
53	Dimethylcyclohexane	129	<i>cis</i> -Decahydronaphthalene
54	Dimethylcyclohexane	130	C ₄ -Alkylbenzene
56	Dimethylcyclohexane	131	C ₁₁ H ₂₄
59	Methylethylcyclopentane	134	C ₅ -Alkylbenzene
60	Dimethylcyclohexene	135	C ₁₀ H ₁₈ + C ₁₁ H ₂₂
64-66	C ₃ -Alkylcyclopentane	136	Methyldecane + <i>nor</i> -undecane
67	C ₈ H ₁₆	137	Methyldecahydronaphthalene
68	C ₃ -Alkylcyclopentane	138	Dimethylindan
69	Ethylbenzene	140	Ethylstyrene + C ₅ -alkylbenzene + 5-methylindan
71	Trimethylcyclohexane	141	Methyldecahydronaphthalene
72	<i>p</i> -Xylene	142	C ₂ -Alkylindan + C ₅ -alkylbenzene
73	<i>m</i> -Xylene	143	C ₅ -Alkylbenzene
74	C ₈ H ₁₄	144	5-Methylindan
75	Ethylcyclohexene		
77	Methyloctene		
78, 79	Trimethylcyclohexane		

(Continued on p. 220)

TABLE II (continued)

Peak No.	Compound	Peak No.	Compound
145	4-Methylindan	200	C ₂ -Alkyltetrahydronaphthalene + methylcyclohexylhexane
147	C ₅ -Alkylbenzene	201	C ₂ -Alkyltetrahydronaphthalene
148	Tetrahydronaphthalene	204	C ₂ -Alkyltetrahydronaphthalene
150	C ₅ -Alkylbenzene + methyl-decahydronaphthalene	205	C ₂ -Alkyltetrahydronaphthalene
151	C ₅ -Alkylbenzene	206	C ₂ -Tetrahydronaphthalene
153	C ₅ -Alkylbenzene	208	C ₁₃ H ₁₈
154	Naphthalene	210	C ₁₃ H ₁₈
155, 156	C ₂ -Alkylindan	212	C ₁₃ H ₁₈
157	C ₂ -Alkylindan	213	C ₂ -Alkyl-naphthalene + C ₃ -alkylindan + C ₁₃ H ₂₈
158	C ₂ -Alkylindan	214	C ₃ -Alkylindan
159	C ₂ -Alkylindan	215	C ₂ -Alkyl-naphthalene + C ₁₃ H ₁₈
160	C ₂ -Alkylindan	216, 217	C ₂ -Alkyl-naphthalene + C ₁₃ H ₁₈
161	4,1-Dimethylindan	218	C ₁₃ H ₁₈
162	C ₅ -Alkylbenzene	219	C ₂ -Alkyl-naphthalene
163	<i>n</i> -Dodecane	220	C ₂ -Alkyl-naphthalene
164, 165	Methyltetrahydronaphthalene	221	C ₂ -Alkyl-naphthalene + C ₁₃ H ₁₈
166	C ₃ -Alkylindan	222	C ₁₃ H ₁₈
167	C ₅ -Alkylbenzene	223	C ₁₃ H ₁₈
168	C ₆ -Alkylbenzene + C ₁₃ H ₂₈	224	C ₁₃ H ₁₈
169	Methyltetrahydronaphthalene	225	C ₃ -Alkyl-naphthalene
170, 171	C ₃ -Alkylindan	226	C ₁₃ H ₁₈
172	C ₃ -Alkylindan	229	C ₃ -Alkyl-1,2-dihydronaphthalene
173	C ₂ -Alkylindan	230	C ₁₄ H ₂₀ + C ₁₅ H ₃₂
174, 175	C ₆ -Alkylbenzene	231	Diphenylmethane
177	C ₃ -Alkylindan	232	C ₁₃ H ₁₈
178, 179	Methyltetrahydronaphthalene + C ₁₇ H ₂₄	235	C ₁₄ H ₂₀
181	C ₃ -Alkylindan	237	C ₃ -Alkyl-naphthalene
182	C ₃ -Alkylindan	238	<i>n</i> -Pentadecane
183	C ₃ -Alkylindan	240	C ₁₄ H ₂₀
184	C ₁₃ H ₂₈	241	C ₁₄ H ₂₀
185	C ₃ -Alkylindan	243	C ₃ -Alkyl-naphthalene
186	Methyltetrahydronaphthalene + C ₃ -alkylindan	247	C ₃ -Alkyl-naphthalene
187	2-Methylnaphthalene	249	Fluorene
188	C ₃ -Alkylindan	255	Hexadecane
189	C ₂ -Alkyltetrahydronaphthalene	260	C ₁₇ H ₃₆
190	1-Methylnaphthalene	262	Octahydrophenanthrene
191	<i>n</i> -Tridecane	263, 264	Methylfluorene
193	Cyclohexylcyclohexane	265	<i>n</i> -Heptadecane
194, 195	Dimethyltetrahydronaphthalene	268	C ₁₈ H ₃₈
196	Ethyltetrahydronaphthalene + C ₇ -alkylbenzene	269	Methoxyfluorene
197	C ₃ -Alkylindan	273	<i>n</i> -Octadecane
198	C ₃ -Alkylindan	274	Dimethylfluorene
199	C ₃ -Alkylindan	277	<i>n</i> -Nonadecane
		278	<i>n</i> -Eicosane
		279	<i>n</i> -Heneicosane

for any dilute sample which requires additional concentration by solvent removal. The procedure is especially useful for the concentration of relatively small sample volumes (*i.e.*, between 10–100 μ l).

Fig. 3 shows a chromatogram of a sample which was concentrated by con-

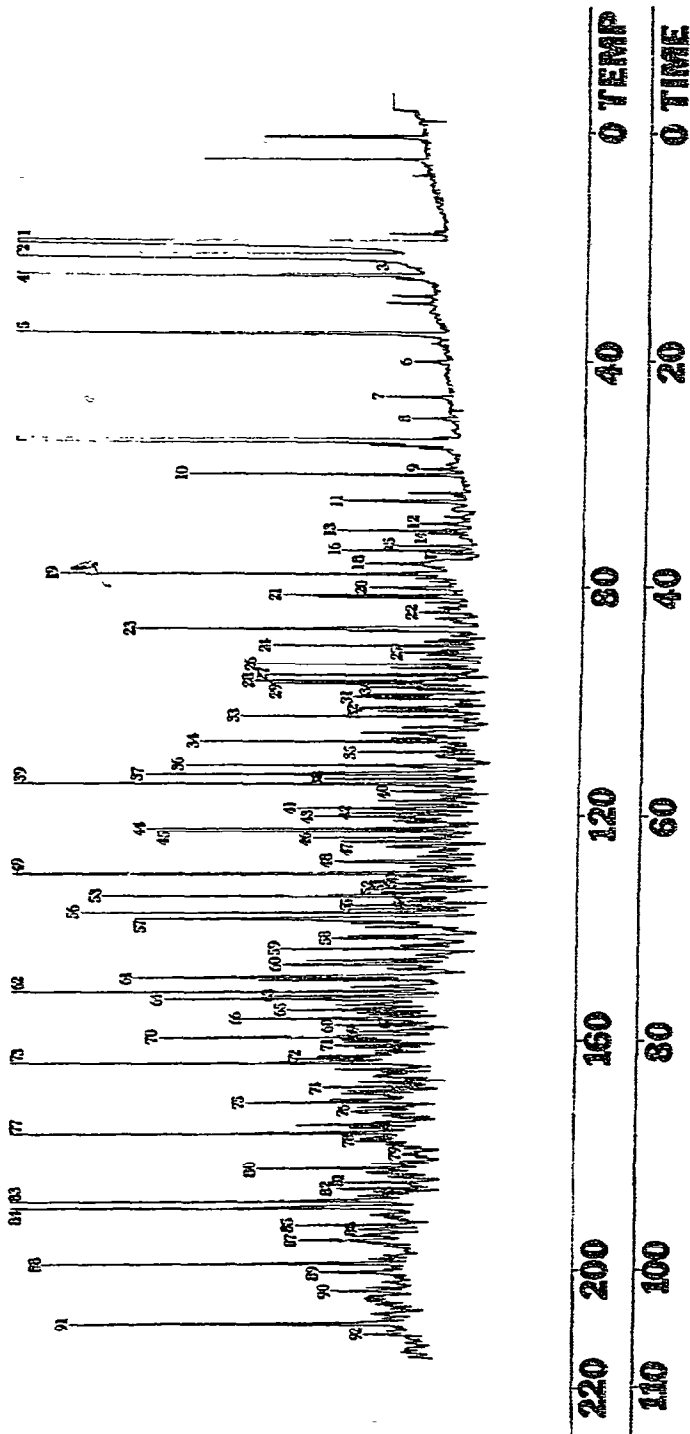


Fig. 2. Total ion current monitor chromatogram of a hexane fraction concentrated by frontal development on Tenax GC. Conditions: glass capillary column, 45 m x 0.35 mm I.D. coated with OV-101; carrier gas (helium) flow-rate: 3.0 ml/min; temperature program: 0° (10 min), 0-220° at 2°/min. For identification of peaks see Table III.

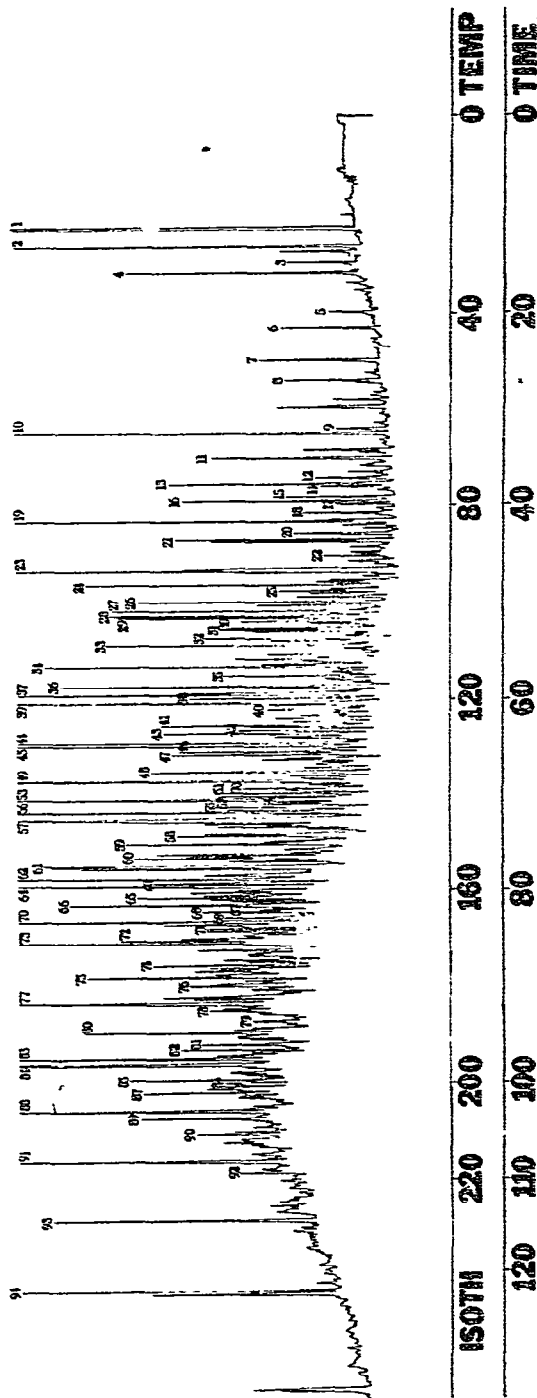


Fig. 3. Total ion current monitor chromatogram of a hexane fraction, concentrated by sweeping the solvent surface with nitrogen at room temperature. Conditions as in Fig. 2.

ventional methods. The surface of the hexane eluent was swept at room temperature with a stream of purified nitrogen. Both chromatograms also indicate good reproducibility between the two methods. Table III lists substances identified in this fraction.

Analysis was also performed on polar fractions. A multitude of substituted

TABLE III
IDENTIFICATION OF MAJOR COMPOUNDS IN THE HEXANE FRACTION

Peak No.	Compound	Peak No.	Compound
1	C ₆ H ₁₄	43	4,7-Dimethylindan
2	<i>n</i> -Hexane	44	<i>n</i> -Dodecane
3	Benzene	45	Methyltetrahydronaphthalene
4	Cyclohexane	46	C ₃ -Alkylbenzene + C ₃ -alkylindan
5	C ₇ H ₁₆	47	C ₆ -Alkylbenzene + C ₁₃ H ₂₈
6	2,3-Dimethylpentane	48	C ₂ -Alkylindan
7	Toluene	49	C ₃ -Alkylindan + C ₁₇ H ₂₄
8	C ₂ -Alkylcyclohexane	50	C ₃ -Alkylindan
9	Methylcyclohexane	51	C ₃ -Alkylindan
10	C ₃ -Alkyl- <i>n</i> -pentane	52	C ₁₃ H ₂₈
11	<i>m</i> -Xylene + <i>p</i> -xylene	53	2-Methylnaphthalene + C ₃ -alkylindan
12	<i>o</i> -Xylene		
13	C ₉ H ₁₆	54	C ₃ -Alkylindan
14	1-Methyl-1-ethylcyclohexane	55	C ₂ -Alkyltetrahydronaphthalene
15	Dimethylheptane	56	C ₁₄ H ₃₀
16	C ₉ H ₁₈	57	C ₂ -Alkyltetrahydronaphthalene
17	Isopropylbenzene	58	C ₂ -Alkyltetrahydronaphthalene
18	C ₃ -Alkylcyclohexane	59	C ₂ -Alkyltetrahydronaphthalene
19	Propylcyclohexane	60	C ₃ -Alkyltetrahydronaphthalene
20	<i>n</i> -Propylbenzene	61	C ₂ -Alkylindan
21	1,4-Ethylbenzene	62	C ₂ -Alkylindan + C ₁₃ H ₁₈
22	1-Methyl-2-ethylbenzene	63	C ₂ -Alkylindan
23	C ₄ -Alkylcyclohexane	64	C ₁₃ H ₁₈
24	C ₁₀ H ₂₂ + C ₁₀ H ₂₀	65	C ₁₃ H ₁₈
25	C ₁₀ H ₁₈	66	C ₃ -Alkyltetrahydronaphthalene
26	C ₁₀ H ₂₀	67	C ₁₄ H ₂₀
27	Butylcyclohexane	68	C ₁₃ H ₁₈
28	C ₄ -Alkylbenzene	69	C ₃ -Alkyldihydronaphthalene
29	C ₄ -Alkylbenzene	70	Diphenylmethane
30	Decyne + C ₉ -alkylcyclohexane	71	C ₁₄ H ₂₀
31	C ₄ -Alkylbenzene	72	<i>n</i> -Pentadecane
32	Decahydronaphthalene	73	C ₁₄ H ₂₀
33	C ₁₁ H ₂₂	74	C ₃ -Alkylindan
34	Methyldecahydronaphthalene	75	C ₁₇ H ₃₆
35	Methyldecahydronaphthalene	76	Fluorene
36	Methyldecahydronaphthalene + C ₁₁ H ₂₄	77	<i>n</i> -Hexadecane
37	5-Methylindan	80	C ₁₇ H ₃₆
38	4-Methylindan	84	C ₁₈ H ₃₈
39	Tetralin	88	<i>n</i> -Octadecane
40	C ₅ -Alkylbenzene + methyldecahydronaphthalene	89	Dimethylfluorene
41	C ₂ -Alkylindan	91	<i>n</i> -Heptadecane
42	C ₂ -Alkylindan	93	<i>n</i> -Octadecane
		94	<i>n</i> -Nonadecane

phenols ranging up to C₅ were observed. Only traces of nitrogen-containing compounds were detected. The analysis of the polar fraction will be the subject of a separate communication.

Several coal fluids from different sources were compared by GC. As expected, large differences exist and the correlation among samples from different sources is very poor. High-resolution GC does provide a good picture of the general composition of such fluids and is a valuable aid in their characterization. The complexity of the samples, however, is beyond the present level of instrumental capability. Group separations by liquid chromatography, although time consuming, do provide the necessary simplification which makes a detailed analysis much easier.

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REFERENCES

- 1 J. E. Dooley, G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh and C. J. Thompson, *Technical Publication BERC/RI-75/7*, U.S. Energy Research Development Administration 1975.
- 2 G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh, S. A. Holmes and J. E. Dooley, *Technical Publication BERC/RI-75/12*, U.S. Energy Research and Development Administration, 1975.
- 3 P. W. Woodward, G. P. Sturm, Jr., J. W. Vogh, S. A. Holmes and J. E. Dooley, *Technical Publication BERC/RI-76/2*, U.S. Energy Research and Development Administration 1975.
- 4 H. M. Tenney and F. E. Sturgis, *Anal. Chem.*, 26 (1954) 946.
- 5 H. R. Coleman, C. J. Thompson, R. L. Hopkins and H. T. Rall, *J. Chromatogr.*, 20 (1965) 240.
- 6 D. E. Hirsch, R. L. Hopkins, H. J. Coleman, F. O. Cotton and C. J. Thompson, *Anal. Chem.*, 44 (1972) 915.
- 7 C. D. Thompson, J. E. Dooley, J. W. Vogh and D. E. Hirsch, *Hydrocarbon Process.*, 53 (1974) 93.
- 8 H. J. Coleman, J. E. Dooley, D. E. Hirsch and C. J. Thomson, *Anal. Chem.*, 45 (1973) 1724.
- 9 L. P. Jackson, C. S. Allbright and H. B. Jensen, *Anal. Chem.*, 46 (1974) 604.
- 10 D. R. Clutter, L. Petrakis, R. L. Stenger and R. K. Jensen, *Anal. Chem.*, 44 (1972) 1395.
- 11 J. T. Swansinger, F. E. Dickson and H. T. Best, *Anal. Chem.*, 46 (1973) 730.
- 12 H. Pichler and A. Herlan, *Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem.*, 26 (1973) 401.
- 13 J. L. Schulz, T. Kessler, R. A. Friedel and A. G. Sharkey, *Fuel*, 51 (1972) 242.
- 14 T. Aczel, D. E. Allan, J. H. Harding and E. A. Knipp, *Anal. Chem.*, 42 (1970) 341.
- 15 A. W. Peters and J. G. Bendoraitis, *Anal. Chem.*, 48 (1976) 968.
- 16 J. T. Swansinger, F. E. Dickson and H. T. Best, *Anal. Chem.*, 46 (1974) 730.
- 17 T. H. Gow, I. M. Whittenmore and R. E. Jentoff, *Anal. Chem.*, 42 (1960) 1394.
- 18 B. W. Jackson, R. W. Judges and J. L. Powell, *J. Chromatogr. Sci.*, 14 (1976) 49.
- 19 M. Novotný and K. D. Bartle, *Chromatographia*, 3 (1970) 272.
- 20 A. L. German, C. D. Pfaffenberger, J. P. Thenot, M. G. Horning and E. C. Horning, *Anal. Chem.*, 45 (1973) 930.
- 21 L. Blomberg, *J. Chromatogr.*, 115 (1975) 365.
- 22 G. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 99 (1974) 63.
- 23 E. L. Ilkova and E. A. Mistryukov, *J. Chromatogr. Sci.*, 9 (1971) 569.
- 24 *Eight Peak Index of Mass Spectral Data*, Mass Spectrometry Data Centre, Aldermaston, 2nd ed., 1970.