

COMPARISON OF HYDROCARBON EXTRACTS FROM SEVEN COALS BY CAPILLARY GC AND GC/MS

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Coals have been shown to contain paraffinic hydrocarbons whose structures arise directly from biological precursors. The types of hydrocarbons usually considered in this group of biological markers include n-alkanes, acyclic isoprenoids, steranes and terpanes. The amounts of these materials that can be extracted from coal are small but even the characterization of these small amounts of alkanes can be very important in determining the origin and maturity of coals. A detailed understanding of the origin of coals and of the diagenesis and maturation of coals may someday be deduced by drawing upon the large body of available information on the relationships of biological markers to the geologic history of rocks, sediments, oil shales and petroleum. The subject has been reviewed (1,2). Some biological markers have also been detected in coal liquefaction products (3,4).

Seven coals were selected for analysis in this study. These seven coals have also been utilized for various liquefaction studies at the Grand Forks Energy Technology Center (GFETC). Their proximate and ultimate analyses are shown in Table 1.

The finely pulverized (-100 mesh) coals were sequentially extracted with chloroform (Soxhlet, 6 hr) and the ternary azeotrope chloroform: acetone: methanol, 47:30:23 (Soxhlet, 14 hr). Each extract was separated into a hexane-soluble and a hexane-insoluble portion. This report deals with the analysis of the hydrocarbons in the hexane-soluble portion (CHX) of the chloroform extract. This fraction contained the hydrocarbons of interest as biological markers. Extraction under these mild conditions gave the extraction yields shown in Table 2.

Capillary GC comparison of retention times with authentic standards and GC/MS were used to characterize the acyclic alkanes present in the CHX extracts. The extracts of Beulah 3 North Dakota lignite (B3), Wyodak Wyoming subbituminous coal (WY01), Highvale Alberta subbituminous coal (ALB1) and Powhatan Ohio bituminous coal (POW1) all contained homologous series of n-alkanes, Table 3. The low-rank coal CHX extracts for the limited members of the series present all gave Carbon Preference Indices, CPI's, (1), greater than one. The alkane distributions and the CPI values are shown in Figure 1. The observed n-alkane distributions were in agreement with the observation by Rigby et al. that increasing maturity of the coal was attended by a shift in maximum concentration to shorter chain length alkanes in extracts (5).

As has been previously reported, high temperature high pressure coal liquefaction as well as coal maturation lowers the odd/even carbon preference values to near 1.0 (3). This effect was also noted when the analyses of processed liquid products from the GFETC continuous processing liquefaction unit were compared with the CHX coal fractions extracted under mild conditions. CPI values of 1.0 were obtained for the processed liquids from B3 and WY01 low-rank coals compared with values of 1.8 for the fractions extracted under mild conditions. These coal extracts should contain alkanes that were present in the coal, whereas, the heat-altered, processed products also contain alkanes formed from cracking of waxes, other alkanes, and other aliphatic portions of the coal. In the case of the higher rank bituminous coal, POW1,

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TABLE 1
ANALYSIS OF COALS

	Reulah 3	Morwell	Big Brown 1	Big Brown 2	Wyodak	Highvale	Powhatan
	(ND) B3	(Australia) MOC	BB1 (TX)	BB2 (TX)	(Wyoming) WY01	(Alberta) ALB1	(Ohio) POW1
<u>Proximate Analysis</u>							
<u>As received:</u>							
Moisture	28.84	10.19	27.55	28.87	30.99	17.79	4.00
Volatile Matter	28.99	43.00	32.10	38.27	30.43	39.83	39.47
Fixed Carbon	30.76	43.63	30.72	19.53	32.96	32.01	46.71
Ash	11.70	3.19	9.63	13.33	5.62	10.37	9.81
<u>Ultimate Analysis</u>							
<u>Moisture-free:</u>							
Ash	16.44	3.55	13.29	18.74	8.15	12.61	10.22
<u>Moisture and ash-free</u>							
<u>(maf):</u>							
Carbon	69.49	70.64	73.15	74.00	73.74	74.41	79.01
Hydrogen	4.43	5.01	5.22	6.09	5.38	4.92	5.43
Nitrogen	0.99	0.46	1.40	1.22	1.22	0.95	1.29
Sulfur	2.81	0.33	1.30	1.21	0.53	0.20	3.92
Oxygen (by difference)	22.26	23.56	18.93	17.48	19.12	19.52	10.35

the CPI was the same, 0.9 both before and after processing indicating maturation of the coal.

TABLE 2

SEQUENTIAL EXTRACTION OF COALS WITH CHCl_3 (SOXHLET), CHCl_3 :
ACETONE: METHANOL, 47:30:23, AZEOTROPE (SOXHLET) AND SEPARATION OF HEXANE
SOLUBLES (% MAF COAL, DUPLICATES WERE AVERAGED)

	Total CHCl_3 Soluble (Soxhlet)	Hexane Soluble Portion of CHCl_3 Extract	Total Azeotrope Soluble (Soxhlet)	Hexane Soluble Portion of Azeotrope Extract
B3	2.8	1.0	1.6	0.13
MOC ⁺	0.82	0.58	1.7	0.59
BB1	4.2	1.7	2.2	0.16
BB2	3.7	1.7	2.4	0.19
WY01	3.2	2.9	5.0	0.21
ALB1	0.58	0.35	1.8	0.28
POW1	0.70	0.51	5.8	1.1

⁺Values given from single extraction only.

The CHX extracts from B3 and POW1 were the only extracts of the seven that contained pristane. The bituminous coal, POW1, extract had more pristane than the B3 extract, Table 3. Phytane was not detected in any of the extracts, although both pristane and phytane were found in all of the coal liquefaction products from B3, BB1, WY01, and POW1. The ratio of pristane to phytane was about 5:1. It has been reported that the pristane content of the saturated hydrocarbon fraction from subbituminous coals of more than 76% C begins to increase (1). The increase in phytane concentration corresponds roughly to 83-85% C.

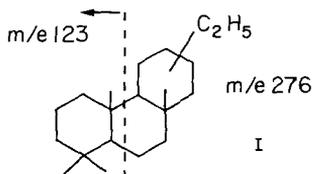
Some of the cyclic hydrocarbons found in the CHX coal extracts are shown in Table 4. They were tentatively identified by capillary GC/MS except for the naphthalenes, for which authentic standards were available. Selected ion scans were used to detect sesquiterpenes (m/e 206, 191), sesquiterpanes (m/e 208), alkanes (m/e 141), alkyl benzenes (m/e 191, 163), steranes (m/e 217), and tricyclic terpenoids (m/e 191, 163) as well as the m/e values for the parent ion of specific compounds. Figure 2 shows the results of one of these selected ion scans, m/e 206, from the CHX extract of WY01 along with a portion of the total ion chromatogram. The peaks shown in the m/e 206 trace between scan numbers 240 and 300 correspond to the sesquiterpenes listed in Table 4. All of these compounds showed M-15 peaks of various intensities (m/e 191), relatively intense M-29 peaks (m/e 177) and m/e 121 peaks. One compound, c, had a prominent even mass peak at 178. Six had more prominent M-43 (m/e 163) peaks than the others. The fragmentation patterns shown by these $\text{C}_{15}\text{H}_{26}$ sesquiterpenes resemble those reported by Richardson (6) for a series of $\text{C}_{15}\text{H}_{28}$ bicyclics identified in a crude oil. The sesquiterpene distribution for the CHX extracts of B3 and WY01 were distinctive and similar. The distribution for ALB1 gave smaller concentrations of sesquiterpenes, Table 4, but the mass spectra were identical for comparable ALB1, WY01, and B3 sesquiterpenes with the same GC retention times. POW1, MOC, BB1, and BB2 CHX extracts did not contain these compounds. No sesquiterpanes with (m/e 208) were detected in any of the CHX extracts. Gallegos (7) found a number of sesquiterpenes (m/e 206, 191) in pyrolysis products of six coals including Wyodak subbituminous coal and Noonan North Dakota lignite. Gallegos also detected cadalene (m/e 198, 183). Cadalene was present in the ALB1 extract and was probably a small component in the B3 extract. It was not found in the extracts of the other coals.

TABLE 3

ACYCLIC HYDROCARBONS FOUND IN EXTRACTS OF COALS AND THEIR
DISTILLABLE LIQUEFACTION PRODUCTS
(Capillary GC, Area Percent, FID)

	<u>Retention Time, min.</u>	<u>B3 Coal Extract</u>	<u>WY01 Coal Extract</u>	<u>ALB1 Coal Extract</u>	<u>POW1 Coal Extract</u>
<u>Isoprenoids:</u>					
pristane (2,6,10,14,tetramethyl- pentadecane)	168.9	0.15			1.35
<u>n-alkanes:</u>					
C-14					
C-15	125.8	0.82			
C-16					
C-17					
C-18					
C-19	194.1	0.74			0.49
C-20	205.0	0.99			0.41
C-21	215.6	1.38			0.26
C-22	223.9	1.22	1.04		0.46
C-23	232.7	0.69	0.73	1.38	0.31
C-24	241.2	0.67	0.33	0.43	0.46
C-25	249.2	1.89	0.82	1.85	0.34
C-26	256.9	1.55	0.57	0.37	0.29
C-27	264.5	2.92	0.99	0.92	0.33
C-28	271.6	0.42	0.31	0.31	0.25
C-29	278.5	0.76	0.98	0.77	0.25
C-30	285.1	0.57	0.52	0.2	0.25
C-31	290.2	0.29	0.56	0.59	0.10
C-32	296.1				0.02
C-33	300.1				0.03
C-34	304.3				0.001
C-35	308.7			0.19	0.03
C-36	312.0			0.09	0.004
C-37	316.6				0.01
C-38	320.4				0.006
C-39	324.0				0.008

Another compound which gave identical mass spectra in two of the extracts, WY01 and ALB1, appears to be one of the tricyclic alkanes, $m/e = 276$. An intense peak at m/e 247 corresponds to M-29. The mass spectrum was an excellent match with that presented by Philip, et al. (8) for which structure I was proposed. An intense peak at m/e 123 was noted and is probably due to the fragmentation shown.



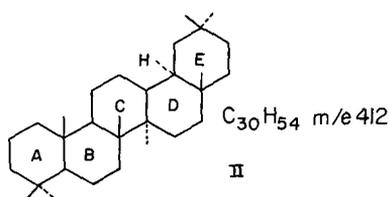
At a slightly longer retention time the component m/e 234 appears to be another tricyclic alkane, $C_{17}H_{30}$. Several similar tricyclic alkanes were reported by Jones et al. (4).

The spectrum of m/e 252, identical in WY01 and ALB1 extracts, corresponds to $C_{18}H_{36}$ but is not dodecylcyclohexane (9). There is a prominent M-15 peak at m/e 237 and relatively intense peaks at m/e 111 and 195. The peak at 111 could be assigned as a dimethyl-cyclohexyl fragment.

The compounds detected in the mass range 398-454 in B3, BB1, BB2, and POW extracts appear to be pentacyclic triterpanes since all have prominent m/e 149, 177, 191, and 205 peaks (10). When selected ion chromatograms are compared, WY01 extract shows no m/e 191 peaks for GC retention times in the pentacyclic triterpane region. The BB coal extracts, B3, ALB1 and POW1 all have numerous small peaks that are probably triterpenoids. Some of these gave appreciable GC FID responses and good mass spectra.

The spectrum of m/e 398 is identical for ALB1 and POW1 extracts. The compound is not adiantane since the m/e 191 is greater than 177, not of similar intensities (11). $C_{27} - C_{31}$ triterpanes, especially adiantane, C_{29} , have been found in bituminous coal extracts (12).

The pentacyclic component at m/e 412 resembles the spectrum of oleanane (II) or gammacerane. It is also similar to that of lupane (11,13) but lacks the M-43 (369) fragment indicative of any isopropyl sidechain. Therefore, ring E is probably 6-membered, not 5-membered as in lupane or the hopanes. Although the mass spectrum is a slightly better match to gammacerane, the short retention time probably rules out gammacerane but not oleanane.



The two different $C_{31}H_{54}$ pentacycles (m/e 426), one observed in BB2 extract and one in POW1 extract had no M-29, M-43 or M-57 fragments. The m/e 205 was small

ruling out structures like lupan-3-one (14). Other differences also eliminate friedelan-3-one and oleanan-3-one type of structure (14).

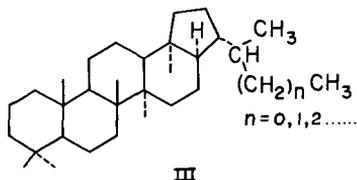
The m/e 440 pentacyclic representative found in BB1 and BB2 had an M-29 peak (411) and a prominent peak at 369. It could therefore be a homohopane. None of pentacyclic structures found in any of the extracts could correspond to the unaltered less stable $17\beta H$, $21\beta H$ hopane series because m/e 191 is much larger than the secondary fragment in all cases. The structure could be a $17\alpha H$, $21\beta H$ hopane which is common in geologically altered sediments of all kinds (III).

TABLE 4

OTHER HYDROCARBONS FOUND IN EXTRACTS OF COAL CAPILLARY
GC AND GC/MS, AREA %, FID

Miscellaneous:	Retention Time, Min.	m/e, Parent Ion	B3	MOC	Capillary GC, Area %			POM1	
					BB1	BB2	WY01		
naphthalene	47.9			0.32			0.18	0.12	1.2
2-methylnaphthalene	72.0			0.29			0.19	0.38	2.7
1-methylnaphthalene	75.6			0.04			0.09	0.13	2.0
C ₂ -naphthalene	95.3								0.68
cadalene	160.4	198	0.31						1.3
<u>Alicyclic terpenoids:</u>									
C ₁₅ H ₂₆	100.7	206							2.8
"	104.8	206							1.0
"	106.8	206	1.9					0.70	
"	108.9	206	1.12						3.3
"	111.2	206	0.24					0.17	
"	113.0	206						0.27	
"	114.9	206	2.3					1.9	
"	116.2	206	0.10					0.17	
C ₂₀ H ₃₆ tricyclic alkane	230.3	276						0.46	
"	233.4	252						0.50	
C ₁₇ H ₃₀ tricyclic alkene	236.4	234	1.2					0.50	0.10
"	272.5	Not Shown					0.66		
C ₂₉ H ₅₀	284.6	398						0.27	0.13
C ₃₀ H ₅₂	285.2	412							0.13
C ₃₁ H ₅₄	287.0	426					3.3		
C ₃₁ H ₅₄	295.8	426							0.03
C ₃₂ H ₅₆	312.0	440					3.0	1.1	
C ₃₃ H ₅₈	321.7	454	0.07				1.7	3.5	

The m/e 454 pentacyclic triterpene (BB1, BB2 extracts) is also unidentified.



A number of hydrocarbon fractions from liquefaction products produced at GFETC from the coals studied here were investigated using selected ion scans of the capillary GC/MS analyses. None of the hydrocarbon biological markers other than the acyclic alkanes already discussed were detected. There were no sesquiterpenes, sesquiterpanes, steranes, triterpanes or other cyclic terpenoids found.

CHX extracts of the seven coals were profiled using capillary GC. The best results were obtained using a J. & W. DB5 60 N fused silica capillary column with H₂ carrier and flame ionization detector. Temperature programming from 50° to 125°C at 0.5°C/min, from 125° to 250°C at 1.0°C/min and from 250° to 350°C at 1.5°C/min, then an isothermal plateau at 350°C was used.

There were some striking similarities and differences between profiles for the coal CHX extracts. The profiles for CHX extracts of MOC, BB1 and BB2 were very similar. They show no detectable alkanes and very few peaks until 230 min when the maximum temperature was reached. Between 230 min. and 320 min. a large group of peaks form a dense envelope.

The capillary GC profiles for B3 and WY01 extracts are also strikingly similar, with nearly every major GC peak having a counterpart in each chromatogram. ALB1 extract shows some similarity to the WY01 trace but differs, the POW1 extract profile is also different. All of the GC profiles for B3, WY01, ALB1 and POW1 CHX extracts have continuous baseline resolved peak distributions from about 50 to 350 minutes with various recognizable patterns. From duplicate extractions of the same coal and by comparing BB1 and BB2 extracts, it may be seen that the profiling of the hydrocarbon extracts is reproducible and may be used to identify and group coals.

Each of the CHX extracts also contained some oxygen compounds. The elemental analyses showed 5-6% oxygen present. Although the characterization of these compounds is not complete, it may be noted that all of the extracts contained some 60-70 carbon nonvolatile waxes (long chain fatty acid esters). The presence of these esters was demonstrated by methanol/BF₃ transesterification followed by capillary GC and 200 MHz ¹H NMR analyses.

SUMMARY

The chloroform extraction of seven coals yielded extracts that gave unique capillary GC profiles. Several groups of hydrocarbon biological markers were detected in the coal extracts by mass spectrometry using selected ion scans. n-Alkanes, pristane, sesquiterpenes, several tricyclic alkanes and pentacyclic triterpanes with molecular weights from 398 to 454 were detected. The coal extract profiles fell into four groups: 1) BB1, BB2 (Texas lignites) and MOC (Australian lignite); 2) B3 (North Dakota lignite) and WY01 (Wyoming, subbituminous); 3) ALB1 (Alberta, Canadian subbituminous), and 4) POW1 (Ohio, bituminous). Profiles were characteristic and reproducible for each coal.

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REFERENCES

1. Bartle, K.D., Jones, D.W., Pakdel, H. "Analytical Methods for Coal and Coal Products," Academic Press, New York, San Francisco, London, 1978; Part II, 209-262.
2. Bartle, K.D., Jones, D.W., Pakdel, H. "Coal and Coal Products: Analytical Characterization Techniques," American Chem. Society Symp. Ser., American Chemical Society, Washington, D.C., Volume 205, 1982, 27-45.
3. White, C.M., Shultz, J.L., Sharkey, A.G., Jr. Nature, 1977, 268, 620-622.
4. Jones, D.W., Pakdel, H., and Bartle, K.D. Fuel, 1982, 61, 44-52.
5. Rigby, D., Batts, B.D., and Smith, J.W. Org. Geochem., 1981, 3, 29-36.
6. Richardson, J.S. and Miller, D.E. Anal. Chem., 1982, 54, 765-768.
7. Gallegos, E.J. J. Chromatog. Sci., 1981, 19, 156-160.
8. Philip, R.P., Gilbert, T.D., and Friedrich, J. Geochim Cosmochim Acta, 1981, 45, 1173-1180.
9. Rubinstein, I. and Strausz, O.P. Geochim. Cosmochim Acta, 1979, 1387-1392.
10. Kimble, B.J., Maxwell, J.R., Philip, R.P., Eglinton, G., Albrecht, P., Ensminger, A., Arpino, P., and Ourisson, G. Geochim. Cosmochim. Acta, 1974, 38, 1165-1181.
11. Henderson, W., Wollrab, V., Eglinton, G. Advan. Org. Geochem., Proc. Int. Meet., 4th, 1968, (1969), 181-207.
12. Allan, J., Bjorory, M., Douglas, A.G. Advan. Org. Geochem., Proc. Inst. Meet., 7th, 1975, (1977), 633-654.
13. Ekweozor, C.M., Okogun, J.I., Ekong, D.E.U., and Maxwell, J.R. Chem. Geol. 1979, 27, 11-28.
14. Budzikiewicz, H., Wilson, J.M., Djerassi, C.D. J. Am. Chem. Soc., 1963, 85, 3688-3699.
15. Ensminger, A., Van Dorsselaer, A., Spyckerelle, Ch., Albrecht, P., Ourisson, G. Adv. Org. Geochem., Proc. Int. Meet., 6th, 1974, (1976), 245-260.

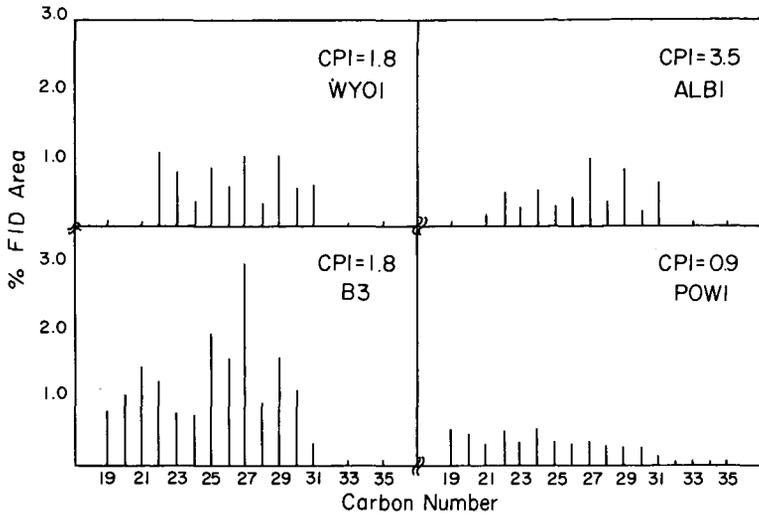


FIGURE 1. Alkane distribution in coal extracts.

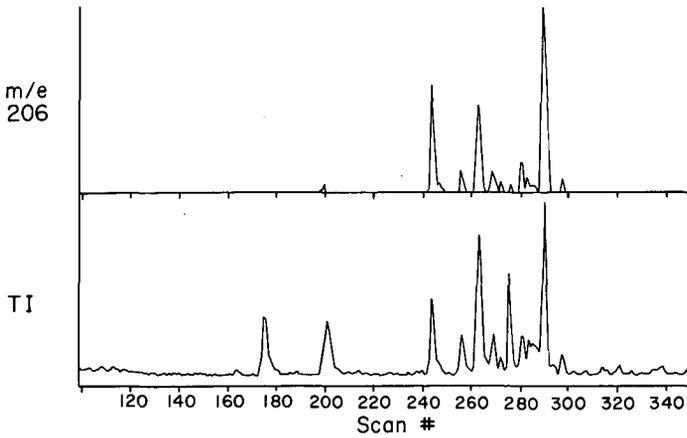


FIGURE 2. m/e 206 selected ion scan for sesquiterpenes and total ion current chromatogram, WY01 CHX extract.