

STRUCTURAL GROUP ANALYSIS OF ARGONNE PREMIUM
COALS BY FTIR SPECTROSCOPY

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INTRODUCTION

Infrared spectroscopy is a well-established method of coal characterization (1-12). Aspects of coal structure such as functional groups and hydrogen-bonding (11) and changes in structure during pyrolysis (6,7) and oxidation (4,5,9,10) have been described through infrared analysis and related to macromolecular processes. In particular, Painter *et. al.* (2), have proposed an FTIR procedure for a fairly exhaustive analysis of coal functional groups. Many of these suggestions are incorporated into the present study for the development of a functional group analysis data base for a set of standard coals.

EXPERIMENTAL

Eight Argonne premium coal samples were studied: Pennsylvania Upper Freeport, Wyodak, Illinois #6, Pittsburgh #8, Pocahontas #3, Utah Blind Canyon, West Virginia Stockton-Lewiston, and Beulah-Zap. Each ampoule of -100 mesh coal was mixed, opened, and the contents dried in a vacuum oven at 40°C for two hours. The dried samples were stored under vacuum until used. Diffuse reflectance infrared (DRIFT) spectra were obtained on neat dried samples with a Nicolet 60SXB FTIR with 500 scans at 4 cm⁻¹ resolution. KBr pellets were also prepared (about 0.3% coal by weight) and spectra collected with 128 scans at 4 cm⁻¹ resolution. Carbon, hydrogen and nitrogen analyses were performed with a LECO CHN-600 analyzer, and oxygen analyses were performed on a Carlo ERBA 1106 elemental analyzer. The low temperature ash of each coal was obtained with 0.5 g sample in an International Plasma Machine 1101B at 130 watts for several days. Another 0.5 g of each coal was acetylated by heating the coal at 100°C in a 2:1 mixture of pyridine and acetic anhydride for eight hours followed by filtering and vacuum drying.

RESULTS AND DISCUSSION

Each of the two sampling methods employed here, DRIFT and KBr pellets, have advantages and drawbacks in coal analysis. DRIFT suffers from a lower signal-to-noise ratio, but is very sensitive to some infrared bands which do not appear well in transmission spectra. Figure 1 compares the C-H stretching region of the Blind Canyon coal from DRIFT and KBr pellet spectra. Absorbance units are used rather than Kubelka-Munk units because the latter result in intensities too weak to resolve well. A weak band at 2732 cm⁻¹ is apparent in the DRIFT spectrum, but barely observed in the transmission spectrum. The relative intensities of the C-H bands also change, with the symmetric and asymmetric CH₃ modes enhanced in the DRIFT spectrum. DRIFT is especially useful because coal can be sampled without an interfering matrix, which is important in determinations of OH and water content. KBr pellets, on the other hand, offer the advantages of a high signal-to-noise ratio and better

control over sample concentration for quantitative work. The strengths of both methods have been exploited in this study.

A common method for determining relative aromatic and aliphatic hydrogen concentrations has been to compare the absorbances or integrated areas of the 3100-3000 and 3000-2800 cm^{-1} regions (2,7). Table 1 gives the results of using conversion factors obtained from model compounds to determine the relative amounts of aliphatic and aromatic hydrogen from the integrated areas of the CH regions. As expected, the ratio of aliphatic to aromatic hydrogen increases as the C/H ratio decreases. A pitfall in this procedure is the assumption of a single average conversion factor for all of the coals. Individual C-H groups have different extinction coefficients and variations in the composition of the aliphatic moiety would affect the average absorption coefficient. Inspection of the asymmetric CH stretch of these coals indicates that the ratio of CH_3 to CH_2 groups increases as the coal rank increases. Also, the second derivative and deconvoluted spectra show that the Beulah-Zap, Wyodak and Blind Canyon coals have very few CH_3 bands, while the other coals have a more diverse composition. In spite of this variation, a single conversion factor applied to all coals should result in a good approximation of the relative abundance of the aliphatic and aromatic hydrogens.

The out-of-plane aromatic CH region, 900-700 cm^{-1} , has three major bands in each of the coal spectra after subtraction of the low-temperature ash spectrum at 870-855 cm^{-1} , 816-812 cm^{-1} , and 754-748 cm^{-1} (Figure 2). These can be assigned to the bending modes of an isolated hydrogen, two adjacent hydrogens, and three or more adjacent hydrogens, respectively. From curve-fitting results, the coals with the highest C/H ratio, Pocahontas and Pennsylvania, have the largest contribution from the band due to lone hydrogen, along with the Illinois and Lewiston-Stockton coals, indicating a higher degree of substitution or cross-linking in these coals. The Wyodak, Blind Canyon and Beulah-Zap coals, with the lowest C/H ratios, have the largest contribution from the 815 cm^{-1} band and a much smaller contribution from the 870 cm^{-1} band, but also fewer aromatic hydrogens overall. This implies a less aromatic structure with less substitution and less cross-linking.

Another facet of aromatic substitution may be the weak band at 2732 cm^{-1} which appears in all but the Wyodak and Beulah-Zap coals. Painter (2) has assigned this as an overtone of methyl groups attached directly to an aromatic ring. The increased intensity of this band as the aromaticity and CH_3 concentration increase supports this assignment. The integrated peak area of this band compared to the total aliphatic CH area can be converted into the percentage of aliphatic hydrogens in methyl groups attached to aromatic rings, using factors obtained from model compounds. The results for the six coals are given in Table 2. These results indicate that over half of the aliphatic hydrogens in the Pocahontas coal are in methyl groups attached to aromatic groups. This leaves few hydrogens which can form methylenic linkages. Blind Canyon coal, on the other hand, has very few hydrogens in this form. This is compatible with the observation that the Blind Canyon coal is less highly substituted.

The prominent band at 1600 cm^{-1} in the spectra of all coals has been attributed to an aromatic ring mode, highly conjugated carbonyls, electron transfer between aromatic planes, to a non-crystalline, non-aromatic graphite-like phase, or to combinations of these (12). Figure 3 shows the spectra of

the eight coals between 1700 and 1500 cm^{-1} after subtraction of the low-temperature ash spectrum. It can be seen that the shape and maxima of the bands shift for the different coals, suggesting a different underlying character. The most intense 1600 cm^{-1} band is found in the Beulah-Zap coal, with the intensity of this band in the other coals decreasing in the same order as the oxygen content decreases. Deconvolution, second derivative and curve-fitted spectra showed that the composition of this band varies. The Wyodak and Beulah-Zap coals have major bands at 1655 and 1562 cm^{-1} , usually assigned to conjugated carbonyls and carboxylate groups (2), but only weak features near 1600 cm^{-1} where the aromatic ring mode is expected. The Pocahontas and Pittsburgh coals, however, have their strongest contribution from a band at 1611 cm^{-1} .

In order to measure the phenolic and alcoholic content of the coals, acetylated derivatives were prepared. The subtracted spectra of the acetylated and initial coals were curve-fit between 1800 and 1500 cm^{-1} . Figure 4 shows the subtracted spectra for the Illinois, Pennsylvania, Wyodak and Pocahontas coals. The bands at 1770, 1740 and 1685 cm^{-1} have been assigned to acetylated phenolic, alkyl OH, and NH groups (2). Conversion factors were obtained from model compounds. Because of the inconsistency in the amine results, only the phenolic and alcoholic results are reported. Table 3 gives the relative abundance of phenolic and alkyl OH groups in the coals. Contrary to Painter's findings (2), this ratio is not very consistent, but increases significantly for the low rank coals. However, this discrepancy could be due to incomplete acetylation of less accessible OH groups.

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RPP/kate2/PF

Table 1. Relative Ratios of the Number of Aliphatic and Aromatic Hydrogens

	<u>Aliphatic Hydrogens/ Aromatic Hydrogens</u>	<u>C/H Ratio</u>
Pocahontas	1.1	20.03
Pennsylvania	2.75	16.54
Lewiston-Stockton	3.9	15.30
Pittsburgh No. 8	5.1	14.99
Illinois No. 6	7.4	14.23
Beulah-Zap	10.9	14.89
Blind Canyon	13.1	13.33
Wyodak	13.8	13.80

Table 2. Concentration of Aliphatic Hydrogens in ϕ -CH₃ Groups

	<u>%</u>
Pocahontas	56.4
Pennsylvania	42.9
Pittsburgh	26.4
Lewiston-Stockton	24.9
Illinois	14.7
Blind Canyon	12.9

Table 3. Ratio of Phenolic to Alkyl OH Groups in Coal

Pocahontas	3.3
Blind Canyon	3.7
Lewiston-Stockton	4.5
Pittsburgh	5.0
Pennsylvania	5.6
Beulah-Zap	9.1
Wyodak	10
Illinois	11

RPP/kate2/PF

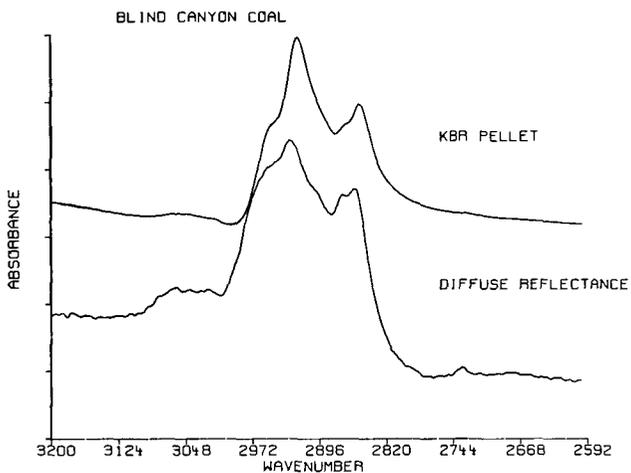


Figure 1. Comparison of KBr pellet and diffuse reflectance spectra of Blind Canyon coal.

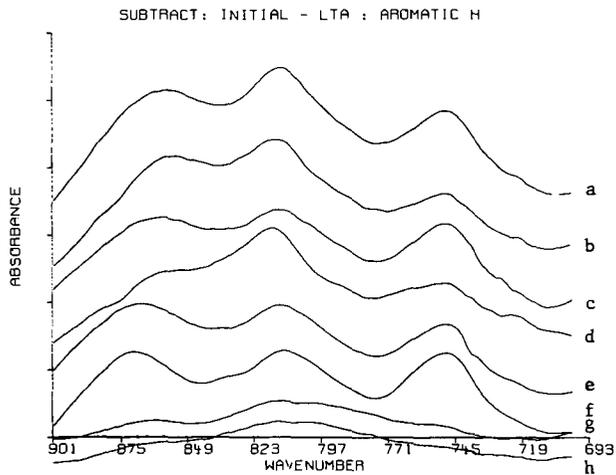


Figure 2. Aromatic hydrogen out-of-plane bending modes (a = Pittsburgh, b = Illinois, c = Lewiston-Stockton, d = Blind Canyon, e = Pennsylvania, f = Pocahontas, g = Wyodak, h = Beulah-Zap).

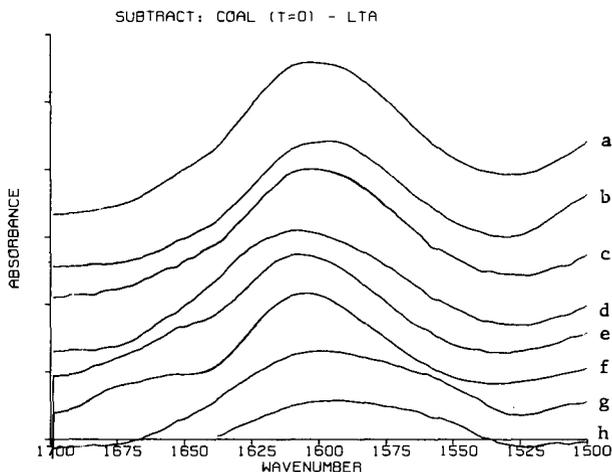


Figure 3. Comparison of 1600 cm^{-1} band for the different coals (a = Pittsburgh, b = Illinois, c = Lewiston-Stockton, d = Blind Canyon, e = Pennsylvania, f = Pocahontas, g = Wyodak, h = Beulah-Zap).

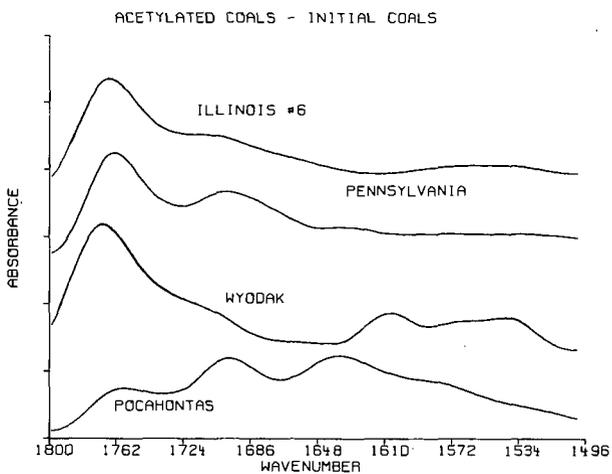


Figure 4. Spectra of Acetylated OH and NH groups for Illinois, Pennsylvania, Wyodak and Pocahontas coals.