

# AROMATICITY DETERMINATION OF COAL, OIL SHALE AND THEIR DERIVATIVES BY X-RAY DIFFRACTION

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## INTRODUCTION

X-ray diffraction has been proven to be the most direct and non-destructive analytical method for the structural study of solid samples. The x-ray scattering pattern of coal at the medium and low angle regions reveals two unresolved peaks (1,2). The diffuse peak shifts more to the position of the most prominent graphite-peak (002) as the carbon content of coal increases. This suggests that coal contains small graphite ring clusters, which become more graphite-like as coalification proceeds. Suitable interpreted, the area and shape of the bands will provide insight into certain interesting structural features. By using a blend of low crystallinity polyethylene and carbon black, it demonstrated that aromaticity can be determined semiquantitatively by resolving the two peaks in the x-ray scattering pattern (3). The experimental results have led to the characterization of the structural parameter-- aromaticity in coal, oil shale and their derivatives.

## EXPERIMENTAL

### A. Instrumentation

The General Electric XRD-6 X-ray Diffractometer unit with copper as the x-ray target was used. The x-ray energy was set at 35 KV and 18 ma for each run. A scanning speed of  $4^\circ/\text{min}$  covering the range of  $2\theta$  from  $5^\circ$  to  $90^\circ$  was selected. All samples were ground to a 200 mesh size and pressed on a aluminum sample holder. The chart recorder was calibrated to read an exact count per second from the proportional counter.

To achieve monochromatic radiation from the copper source, a balance filter comprised of nickel (Ni) and cobalt (Co) at a thickness of 0.0068 mm and 0.0075 mm respectively, was used. The standard method employed running the experiment first using the Ni filter and then repeating the experiment using a Co filter so that a pass band could be made on the difference of data obtained from each of the runs. The exclusion of wavelengths outside the pass band can be considered practically complete.

### B. Procedure

The data from the recorder must be corrected for polarization effects, normalized to electron units, corrected for incoherent scattering, and examined for the effects of background radiation (4,5). In summary, a usable procedure for handling the data is the following:

1. Obtain data values from the differences between Ni and Co filter experiment.
2. Adjust data for polarization by dividing each intensity by  $(1 + \cos^2 2\theta)/2$ .
3. Adjust the data to electron units by normalizing the amplitudes in the region  $0.40 \leq \sin\theta/\lambda \leq 0.50$  is equal to the sum of the coherent and incoherent scattering expected in that range.
4. Subtract tabulated values of incoherent scatterings C.
5. Divide each value by the proper value of the independent coherent scattering E (Figure 1).

The data calculations above were performed by an IBM 360/44, and the results then plotted in analog form.

### C. Method

The interpretation of the x-ray diffraction results obtained from non-crystalline carbon compounds is based largely on the fact that one can put together some graphite and some paraffin or polyethylene and get an x-ray pattern that relates to

their composition (6). In the development of quantitative methods, some assumptions were involved; e.g. carbon atoms were regarded as either belonging to aromatic ring clusters or randomly distributed; and ring clusters were presumed to be perfect in their internal structure. There are also some problems in defining the two peaks in the range of  $\sin \theta / \lambda < 0.2$ , namely, the (002) peak and the gamma peak. This region of the x-ray spectrum has not been sufficiently investigated on a theoretical basis, and hence, the interpretation involves the superimposition of diffraction spectra from substances only supposedly understood.

#### 1. The (002) peak

The (002) band is attributed to the interplanar spacing of condensed aromatic rings. In natural graphite, the spacing corresponding to the (002) band is 3.35 Å, (Figure 2) which corresponds to  $\sin \theta / \lambda = 0.15$ . Different compounds will have different interplanar spacings as shown in Figure 3. The shifts observed in the (002) band in some compounds are shifts toward larger spacings and are attributed to actual changes in interatomic spacing or to the buckling of planes due to substitutions of heteroatoms.

Blayden et al. (7) studied carbonization products of various coals and their banded constituents as well as pure organic compounds. They contended that the asymmetry of the (002) peak was due to the gamma peak even if the gamma peak was absent at its position. Therefore, the peak was resolved into a symmetrical (002) band and a gamma band.

#### 2. The gamma band

The band centered around the spacing of 4.0-5.5 Å is observed in hot paraffin (Figure 4). It is attributed to the spacing between disordered aliphatic chains or alicyclic rings. There seems to be no published criterion for distinguishing between saturated rings and saturated chains based on the shape of the gamma band. The gamma band has been found to be symmetric (3). This becomes a very important point when one tries to separate the gamma band from the (002) aromatic band on the basis of arguments that defend this symmetry.

Aromaticity,  $f_a$ , is the fraction of the total carbon atoms in the sample present in aromatic rings (Figure 5). Implicit in the equation is the assumption that the area under the peaks is proportional to the concentration of each type of structure. The most convincing evidence for the usefulness of this computed aromaticity is from the experiment (6), in which a mixture of half polyethylene and half carbon black was to have an aromaticity of  $0.50 \pm 0.02$  (6).

### DATA ANALYSIS

The four coal samples in our study show a reasonable correlation with the coalification process (Sample source and their  $f_a$  values are shown in Table I). As carbon number increases with coal ranking, the  $f_a$  number also increases (Figures 6a and 6b). More samples will have to be acquired in order to make a more complete correlation. The two domestic oil-rich shales--the Green River Oil Shale (Eocene Shale, 60 million years ago) and Appalachian Black Shale (Ordovician Shale, 400 million years ago) show an increase in  $f_a$  number due to its degree of maturation acquired through geological aging. Because of high inorganic interference, for example iron fluorescence from pyrite, both samples must go thru a special treatment process in order to achieve a better form. Acid treatment (50:50 mixture HCl:HF) was used for Green River Oil Shale to remove the inorganic matrix, and  $\text{LiAlH}_4$  was used to remove the pyrite from the Appalachian Shale. Another oil shale under investigation is the Torbonite from Australia which is a marine deposit. Its formation age is approximately 250 million years (Permian). It is difficult to compare between lacustrine and coastal oil shale due to the different deposition environment which may be evolved. The next set of data were obtained from the two coal liquids process from FMC-CCED and Synthoil. For analytical reasons, asphaltene was separated from the coal liquid (8). To further fractionate the product, asphaltene was loaded on a  $\text{SiO}_2$  glass column, and eluted with ethyl ether and benzene respectively. Polar molecules or aromatic compounds are retained by the column better. The results of x-ray dif-

TABLE I. - Aromaticity of Coals, Shales, and Their Derivatives

Sample	Source	$f_a$
<u>Coal</u>		
Anthracite	Pennsylvanian	0.86
Low Volatile Bitumenous	West Virginian	0.83
High Volatile Bitumenous	Dorchester	
	Wise Co., Va.	0.64
Lignite	Montana	0.60
<u>Oil Shale</u>		
Torbanite	Coolaway Mtn., New So. Wales	0.12
Green River	Colorado, HF-HCl treated	0.15
Appalachian Black Shale	Plymouth, Ohio LiAlH <sub>4</sub> treated	0.50
<u>Coal Liquid Asphaltene</u>		
Synthoil (crude)*	U.S.B.M.	0.49
Benzene fraction**		0.43
Ethyl ether fraction**		0.36
COED (crude)*	FMC	0.45
Benzene fraction**		0.43
Ethyl ether fraction**		0.41
<u>Shale Oil Asphaltene</u>		
Synfuel***	Parahoe	0.46
Residual Oil****	Parahoe	0.49

\*The crude asphaltene is obtained by n-pentane precipitation, the residue dissolved in benzene, filtered, and freeze-dried.

\*\*Evaluated from SiO<sub>2</sub> column

\*\*\*Same as (\*), oil sample originated from DEI.

\*\*\*\*Have been through delayed coking process.

fraction analysis shows lower  $f_a$  number for the solvent eluted fraction. Finally, the shale oil asphaltene are listed. Notice that both crude and residual (after coking process) have much higher aromaticity values ( $f_a=0.5$ ) when compared to the original Green River Oil Shale having an  $f_a=0.1$ . The additional aromaticity naturally originates from the retorting operation.

#### DISCUSSION

Probably the most difficult separation is the resolution of the (002) and the gamma band. The high angle side of the broad peak is used as a guide to delineate the unresolved slopes of the (002) band, and the remaining intensity is attributed to the gamma band. However, in addition to the use of the high angle side as a guide, it is also necessary to determine a peak for the (002) band. This can be done completely at random, or through fixing a location for the peak. The (002) peak has been fixed as  $\sin\theta/\lambda = 0.140$  provided that there is no definite and clear break in the combination of (002) and gamma peaks at a different point. If aromaticities were determined randomly, the error would be approximately 20%. This points out the fact that aromaticities determined by x-ray may be relative and will vary according to the particular location chosen. Further errors may be involved when converting scattering from arbitrary into electron units. Increases in the spacing for the small stacks would give rise to an enhancement of the low angle side of the (002) band at the expense of the high angle side. Thus, the interlayer spacing cannot be regarded as constant. The discrepancy of determination of aromaticity may be attributed to a sim-

plifying assumption involved in the above method that carbon atoms in coals or coal derivatives are either in the aromatic ring clusters or otherwise distributed randomly. It appears that arrangements of organometallics and non-hydrocarbons will lead to the production of a diffuse x-ray interference pattern which may affect the curves. This is a very important consideration since it is extremely difficult to remove the last traces of iron (in pyrite or organic form) from coal or oil shale samples. The fluorescent radiation that is produced forms a considerable proportion of the total x-ray scattering. In some cases, like the Black Appalachian Shale which has a high iron content, the spectrum is masked completely. This is the reason for the treatment of Appalachian Shale samples with  $\text{LiAlH}_4$  as a method for the removal of pyrite.

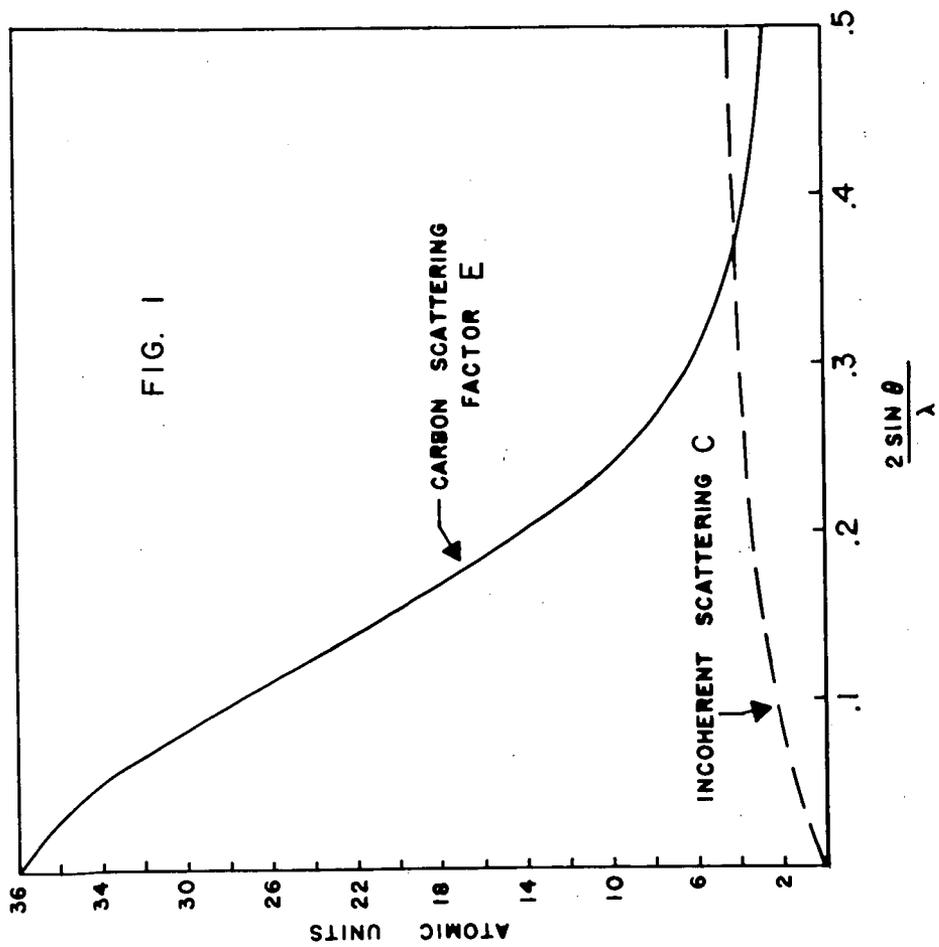
A better understanding of the structure of coal and oil shale and the development of more valid quantitative methods of interpretation of x-ray scattering patterns are more or less interdependent. Investigation of the structure of these materials by other physical and chemical methods (IR, UV,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , ESR, chemical oxidation, etc.) will also provide additional information which would improve the techniques and interpretation of amorphous scattering.

#### ACKNOWLEDGEMENTS

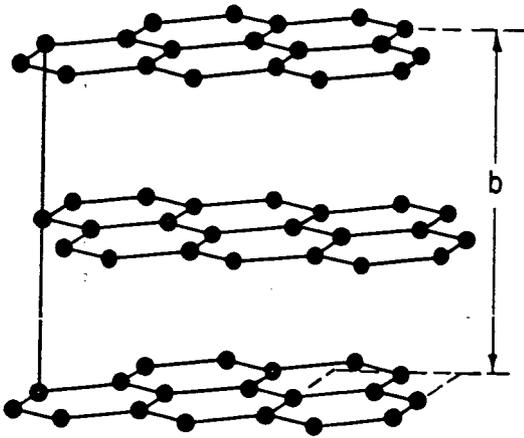
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GRAPHITE



Hexagonal Unit Cell

$$a = 2.46 \text{ \AA}$$

$$b = 6.70 \text{ \AA}$$

$$d_{002} = b/2$$

$$a/\sqrt{3} = r$$

$$d_{100} = \frac{\sqrt{3}}{2} a = \frac{3}{2} r = 2.1 \text{ \AA}$$

$$d_{110} = \frac{\sqrt{3}}{2} r = 1.2 \text{ \AA}$$

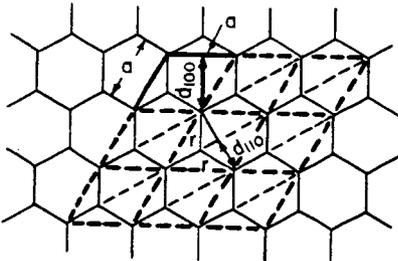


FIG. 2

### INTERLAYER DISTANCES

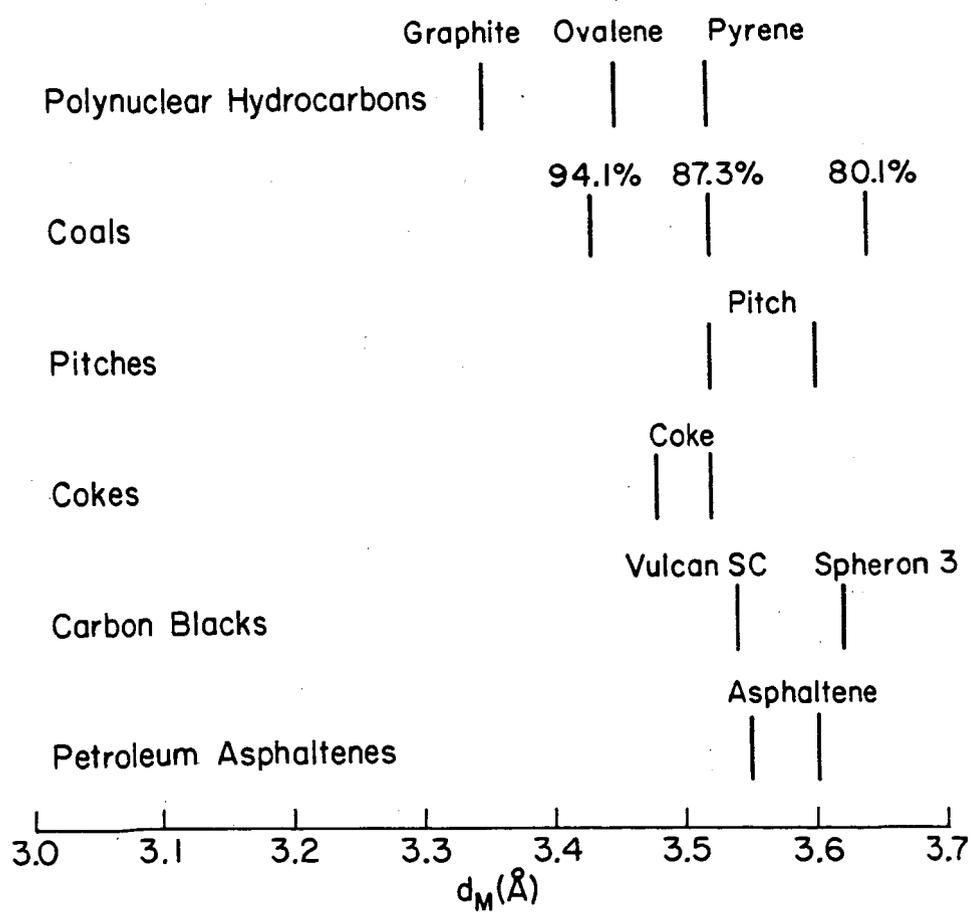
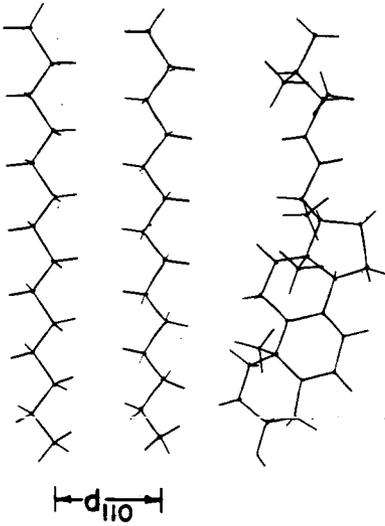


FIG. 3

PARAFFIN



Othorhombic Unit Cell

$$a = 7.40 \text{ \AA}$$

$$b = 4.93 \text{ \AA}$$

$$d_{200} = a/2$$

$$d_{020} = b/2$$

$$d_{110} = \frac{\sqrt{a^2 + b^2}}{2} \sin(2 \tan^{-1} \frac{b}{a})$$

$$= 4.1 \text{ \AA}$$

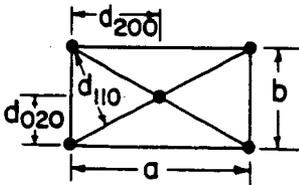


FIG. 4

AROMATICITY,  $f_a$

$$f_a = \frac{C_A}{C} = \frac{C_A}{C_A + C_S}$$
$$= \frac{A_{002}}{A_{002} + A_\gamma}$$

$C_i$  = No. of  $i$ th Type Carbon  
Atoms per Structural Unit

$i$  = A, Aromatic

$i$  = S, Saturated

$A_i$  = Integrated Intensities

Under the  $i$ th Type Bands

$i$  = 002, Bands at  $2\theta = 26^\circ$

$i$  =  $\gamma$ , Bands at  $2\theta = 18^\circ$

FIG. 5

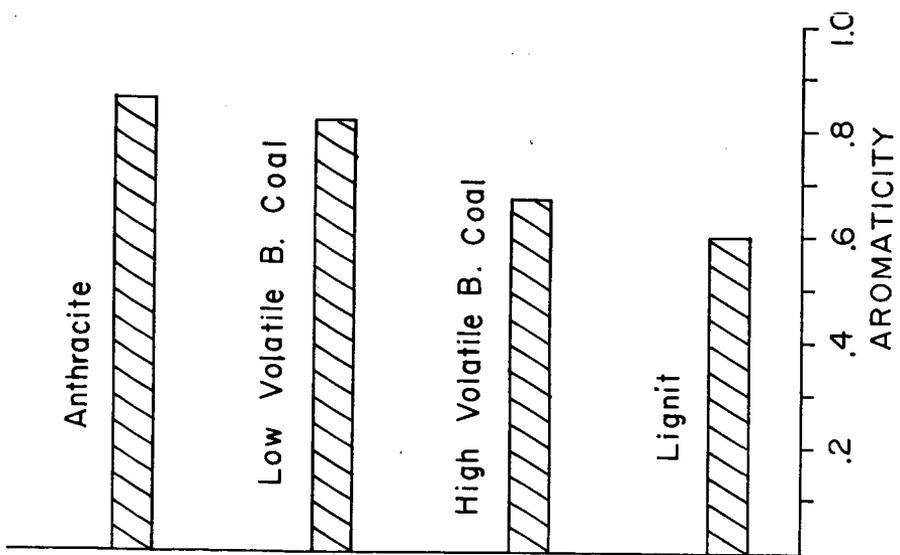


FIG. 6a

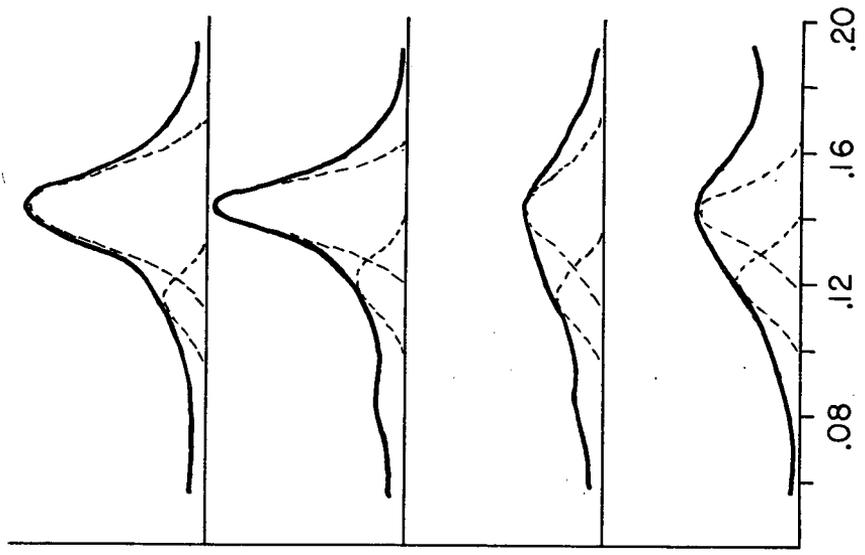


FIG. 6b