

ATR-PYROLYSIS SPECTRA OF COAL

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Infrared spectra of coal have been prepared, historically, as might be expected, by the usual techniques. Each of these has something to recommend it and each has some disadvantage. Both mulls and alkali halide discs have exhibited excessive scattering and have provided good spectra only after long periods of grinding, often under selected solvents.

But even after a sample was prepared and its spectrum recorded, the interpretation was complicated by the presence of a large amount of carbon which contributes nothing. In fact, the presence of a large amount of highly absorbing carbon detracts from the spectrum by imposing attenuation requirements on the reference beam. In addition, the organic components have reacted with alkali halide discs and in some cases spurious water bands have been reported.

The combination of ATR and pyrolysis offers a new approach to the study of coal samples by infrared spectrophotometry. In this study a Barnes PY-2 Pyrolyzer and a Barnes ATR-4 unit were used in conjunction with a Perkin-Elmer 257 Spectrophotometer. The use of this combination of techniques simplifies sample preparation but imposes certain precautions which must be observed in interpretation.

Experimental

Two charges of 250mg each were used to prepare each spectrum. One charge was deposited on each side of an ATR-4 KRS-5 (thallous bromide-iodide crystal). After appropriate experimentation, a time of 90 seconds and 900°C was used for each charge. All of the samples were pyrolyzed in a vacuum of 0.1mm or less. Pyrolysis in a vacuum is necessary in order to eliminate open flame combustion and to minimize possible end group reactions.

Results

Six coals of varying rank were studied. These were obtained from Dr. R. A. Friedel, the symposium chairman. They are described in Table I.

TABLE I

COAL	SOURCE AREA	PERCENTAGE C
Anthracite	Reading, Pennsylvania	92.5%
Bituminous	Pocahontas, West Virginia	91.0%
Low volatile		
Bituminous	Wyoming County, West Virginia	89.0%
Medium volatile		
Bituminous	Waltonville, Illinois	79.2%
High volatile B		
Bituminous	Bruceton, Pennsylvania	83.1%
High volatile A		
Sub-bituminous	Sweetwater County, Wyoming	73.7%

One of the results of this study which was somewhat surprising is that the same time-temperature conditions could be applied to produce spectra of approximately equivalent appearance for all six of the samples studied.

Fig. 1 shows the ATR spectrum of the pyrolyzate of sub-bituminous coal. The spectrum shows the presence of phenols in large amounts. The -OH band centered at about 3225 cm^{-1} . There are shoulders on both sides of the absorption peak indicating the presence of other species of -OH or perhaps -NH.

In Fig 2, which is the pyrolyzate of high volatile A bituminous, shows clearer separation of bands in the -OH stretch region. The carbonyl region is substantially unchanged and the phenyl frequencies in the $650\text{ to }850\text{ cm}^{-1}$ region have become more complex. The spectrum continues to show the presence of phenols.

The pyrolyzate of high volatile B bituminous shown in Fig. 3 shows that the amount of volatile -OH has decreased in quantity and in complexity. The phenyl frequency region from $650\text{ to }850\text{ cm}^{-1}$ has become somewhat less complicated. The carbonyl region is also changed and shows fewer bands. This indicates that the very volatile components found in very low rank coals are present in decreased amounts.

The spectrum of medium volatile bituminous shown in Fig. 4 shows a pattern in the carbonyl region and in the $1400\text{ to }1500\text{ cm}^{-1}$ region. The -OH stretch region remains about the same. The phenyl frequencies from $650\text{ to }850\text{ cm}^{-1}$ have again become more complex. The appearance of the band at 1420 cm^{-1} may be taken to mean that there has been an increase in the aliphatic substitution of the phenyl systems.

Low volatile bituminous which has almost the same carbon content as the pyrolyzate shown in Fig. 5. The spectrum is not as intense probably because there are not as many volatiles present. The band at $1200\text{ to }1300\text{ cm}^{-1}$ has almost disappeared. The $650\text{ to }850\text{ cm}^{-1}$ region has become quite complex.

The spectrum of the pyrolyzate of anthracite is shown in Fig. 6. This spectrum is not related to the others. It is, in fact, simply a spectrum of tar. The same spectrum has been observed from asphalts used to black top roads and driveways. The only difference is in the size of the charge used to produce the spectrum. A charge of about 25mg of asphalt will produce the spectrum of about the same intensity as a 250mg charge of anthracite.

The spectra in this study show that a combination of ATR and pyrolysis offer a new approach to the study of coal spectra. The major benefit of the technique lies in the fact that it speeds up sample preparation.

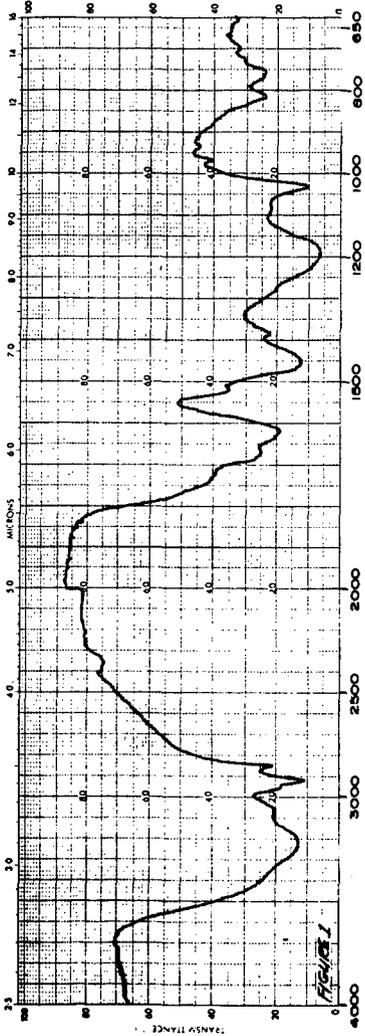


Figure 1.

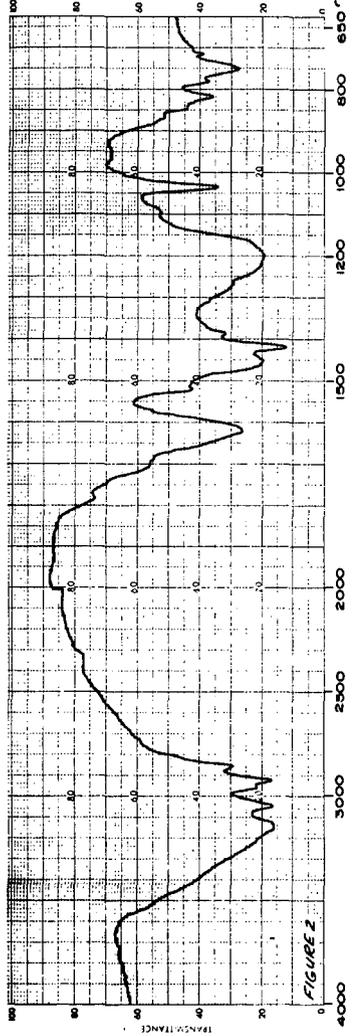


Figure 2.

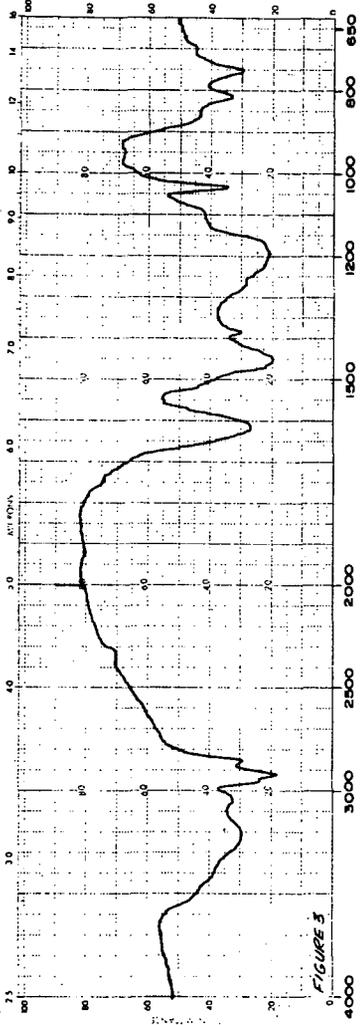


Figure 3.

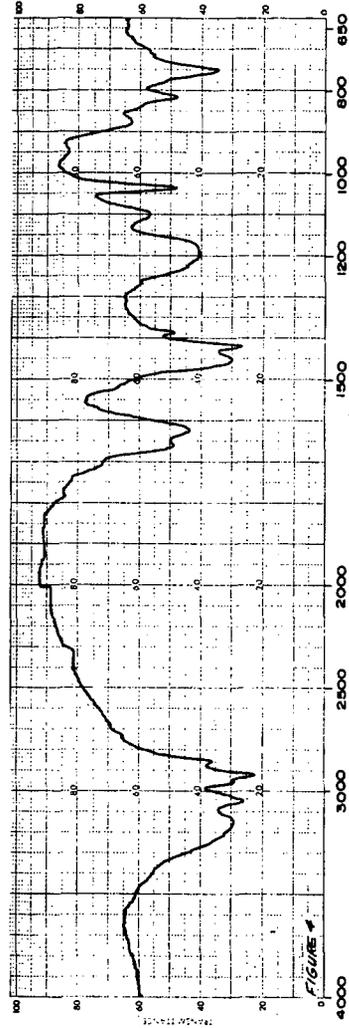


Figure 4.

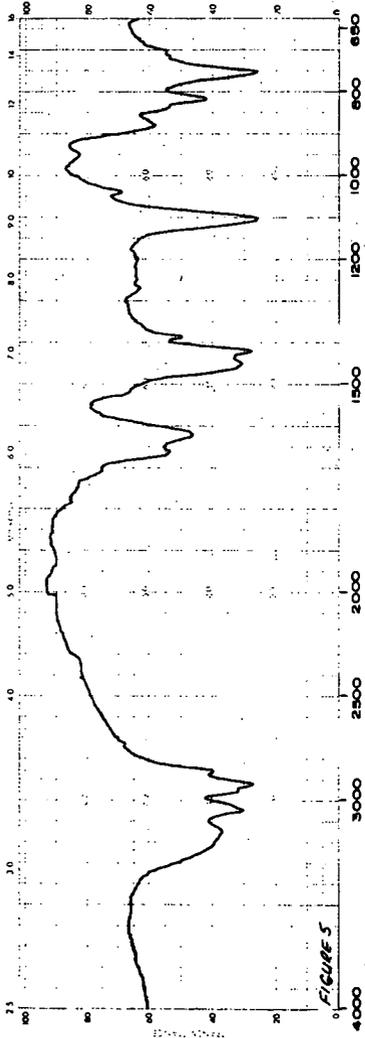


Figure 5.

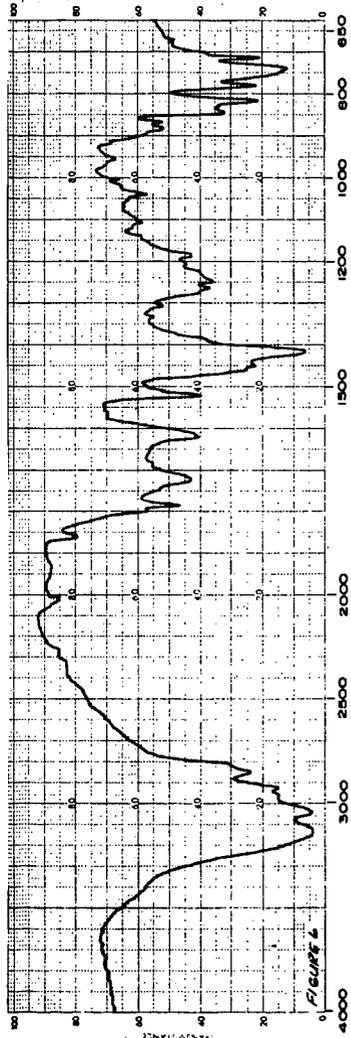


Figure 6.