

SPECTROSCOPIC STUDIES OF COAL PYRIDINE EXTRACTS

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This study is part of a larger program aimed at developing an FTIR methodology for the quantitative determination of the aliphatic and aromatic CH content of coals. Although a number of infrared studies of these quantities have appeared, there remains significant differences in the values reported by different groups, reviewed in reference 1. A recent publication by Solomon and Carangelo (2) is not included in this review and is a significant addition to the literature. The origin of these discrepancies is largely due to the difficulty in determining adsorptivities or absorption coefficients, those quantities that relate the intensity of an infrared band to the concentration of functional groups giving rise to that particular absorption. There are essentially three ways of doing this:

- a) calibrate using model compounds;
- b) equate the hydrogen content (from elemental analysis) to the sum of the functional group contributions;
- c) calibrate using soluble coal extracts.

The first is obviously unsatisfactory, not least because it begs the question "what is the structure of coal and hence what is an appropriate model compound." The second method was pioneered, in its application to FTIR studies, by Peter Solomon and his group (2-5), but is equivalent to a procedure described by von Tschamler and deRuijter more than 25 years ago (6). The hydrogen content of the coal is equated to the sum of the contributions from various functional groups

$$H_T = H_{OH} + H_{ar} + H_{al}$$

where the total hydrogen content H_T is measured by elemental analysis and H_{OH} is determined by FTIR or other measurements. [COOH groups should also be measured in low rank coals]. Then;

$$[H_T - H_{OH}] = E_{ar}I_{ar} + E_{al}I_{al}$$

where E_{ar} and E_{al} are "conversion factors" (an inverse function of the absorption coefficients) and I_{ar} and I_{al} are the intensities of appropriate infrared bands. If a set of coals of roughly the same character (rank) are studied, we can assume E_{ar} and E_{al} are constants for that set and, from the experimentally measured values of H_T , H_{OH} , I_{ar} and I_{al} , solve as a set of simultaneous equations for E_{ar} and E_{al} . As we have found in previous studies, however, this set of simultaneous equations is classically ill-conditioned (reviewed in detail in reference 1). In other words, even small experimental errors in a limited sample set results in the calculation of a range of almost equally valid solutions. In their recent study Solomon and Carangelo (2) employ the same method, seeking to improve the accuracy of their calculations by including data from coal chars, and conclude that there is also a variation in absorption coefficients with rank. They are no doubt right, but the problems with this methodology have not been overcome. Furthermore, in forming chars certain types of alkyl groups are preferentially cleaved and lost as volatiles while the remainder of the coal molecule undergoes a degree of reorganization that depends upon the conditions of char formation. This could also lead to some variation in absorption coefficients.

The final method listed relies on the fact that the aromatic and aliphatic CH content of soluble material can be directly determined by proton nmr, thus allowing the absorption coefficients of infrared

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bands of the same sample to be unambiguously calibrated. Of course, if the extract is significantly different in structure to the parent coal, thus having different absorption coefficients, these values would not be transferable. This is indeed the case for those coals where there is a high proportion of extractable long chain alkanes. Fortunately, the CH stretching vibrations of paraffin-like materials are characteristically sharp and readily recognizable and the correspondence in the spectra of most extracts and their parent coals demonstrates a similarity in structure. Clearly, in order to determine the range of absorption coefficients associated with coal structure of varying degrees of aliphatic character by this method it is necessary that we obtain and study a wide range of samples. This serves to define the range of inevitable experimental error.

Accordingly, at this point we see no substitute for a slow, meticulous, brute-force approach to data collection and analysis. During the past 3 years we have obtained the pyridine extracts of more than thirty-five U.S. coals and seventeen Polish coals. In this brief communication space does not permit a full description of the characteristics of these samples and the details of our analytical procedures; these will be presented elsewhere, but the FTIR methodology is similar to that described previously (1). Here we will simply present an overview of our results.

The data from proton nmr studies of the coal extracts, together with elemental analysis and a knowledge of the OH content (from FTIR studies of acetylated samples), allows the aromatic and aliphatic hydrogen contents of the coals to be determined. Preliminary results are shown in figure 1. Although there is some scatter, to be expected from materials as heterogeneous as coal, the data is fairly closely grouped and clearly shows the expected trend of decreasing aliphatic CH content and increasing aromatic CH content with rank (% carbon content of parent coal).

In principle, this data can now be applied to a determination of the absorption coefficients of infrared bands assigned to aromatic and aliphatic CH groups. In practice, errors play a major role in determining the accuracy of this procedure. Figure 2 shows a plot of the ratio of the intensities of the aromatic and aliphatic CH stretching modes, determined as band areas (from samples prepared as KBr pellets) by curve-resolving procedures described elsewhere (1). There is some scatter in the results that is not simply a matter of the natural variability of aromatic and aliphatic CH content in coals from different sources. Obviously, a plot of the ratio of the intensities of the infrared bands should follow the ratio determined by proton nmr. This relationship need not be linear, if absorption coefficients vary with rank, but should at least be systematic. Figure 3 shows that although a consistent trend can be obtained and a reasonable average value of the ratio of absorptivities determined, the effect of cumulative errors in the data is such that it is not possible to determine any variation with rank with any degree of certainty. The precision in this data can only be improved by averaging the results of additional spectroscopic analysis of these samples, a time consuming process which we are presently in the process of performing.

Finally, we are also analyzing the same samples by diffuse reflectance measurements, so that the two FTIR methodologies can be directly compared. A plot of the ratio of intensities of the aromatic to aliphatic CH stretching modes against the ratio of the aromatic to aliphatic CH content determined by proton nmr is shown in Figure 4. The ratio of the values of the absorption coefficients is somewhat different to that determined from KBr pellets, but again errors, particularly in some of the high rank (larger H_{ar}/H_{al} ratio) coals necessitates additional work. Again a reasonable average value can be determined, but the subtleties of variation with rank are beyond detection given the present precision of the data.

Acknowledgment

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References

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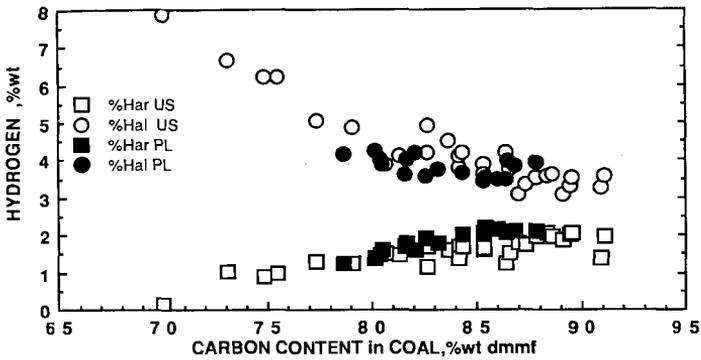


Figure 1. Plot of the aliphatic and aromatic hydrogen content of a set of U.S. and Polish (PL coals), determined by proton nmr.

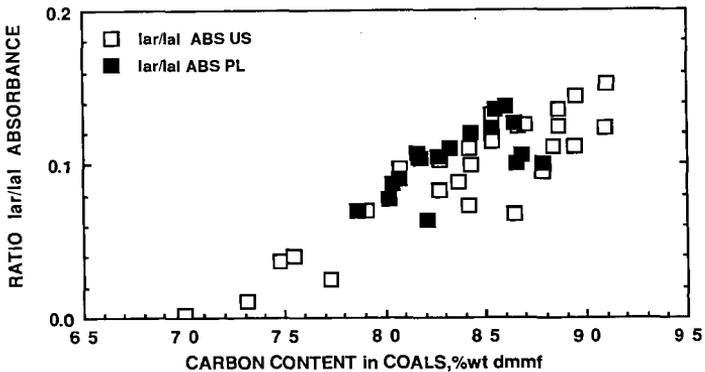


Figure 2. Plot of the ratio of the infrared band areas of the aromatic and aliphatic CH stretching modes for the set of extracts.

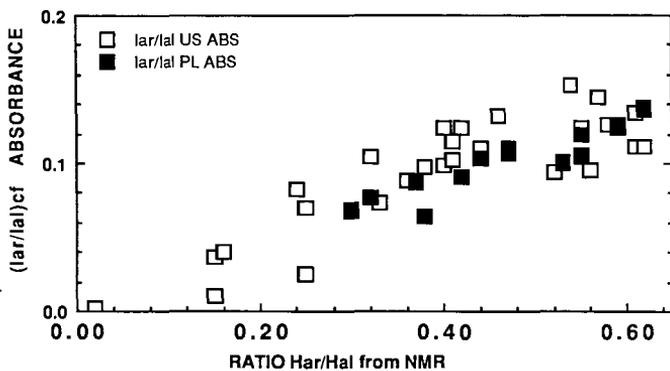


Figure 3. Plot of the ratio of the band areas of the aromatic and aliphatic infrared stretching modes vs the ratio H_{ar}/H_{al} determined by proton nmr.

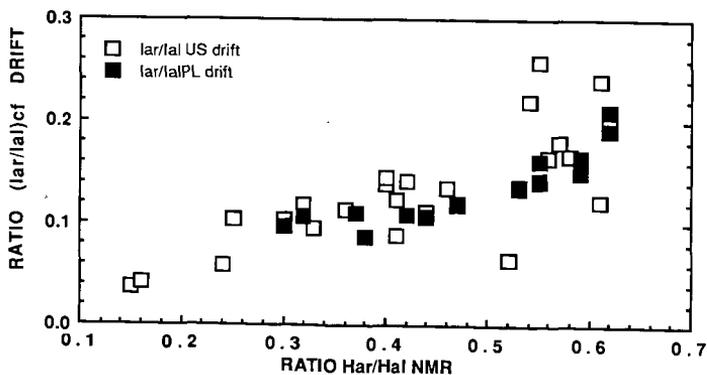


Figure 4. Plot of the ratio of the aliphatic to aromatic CH stretching modes determined by DRIFT to the ratio H_{ar}/H_{al} determined by proton nmr.