

CURRENT STATUS OF FTIR IN THE ANALYSIS OF COAL STRUCTURE

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INTRODUCTION

Infrared spectroscopy has been a basic "workhorse" technique for coal characterization since the pioneering work of Brown nearly 40 years ago (1). The optical and data handling advantages of FTIR have allowed various advances, such as the introduction of "hyphenated" techniques (GC-FTIR, IR-Microscopy, etc.) and novel sampling methods (diffuse reflection, photo-acoustic measurement, etc.), but most of the problems in coal structural analysis remain the same; the quantitative determination of various functional groups in coal and how the concentration of these groups varies with, for example, oxidation or liquefaction.

In a short article of this type justice cannot be done to the range and scope of work reported by various groups. Accordingly, we will concentrate our attention on just one problem, but a problem that is of central importance in the analysis of coal structure; the determination of the aliphatic and aromatic CH content of coal and coal derived material.

THE NATURE OF THE PROBLEM AND THE CURRENT STATE OF THE ART

Unlike nmr, band intensities in the infrared spectrum do not give a direct measure of the proportions of the functional groups giving rise to those bands. For spectra obtained in transmission the relationship depends on absorptivities or absorption coefficients through a Beers law relationship. Accordingly, it is the determination of these absorption coefficients for coal that is the central problem in applying FTIR to the analysis of coal structure. There are essentially three methods that in the past have been used to obtain these parameters;

- 1) calibration using model compounds
- 2) studies of solvent extracts, where calibration is provided by proton nmr measurements of the same samples.
- 3) equating band intensities to elemental hydrogen content and solving the simultaneous equations that can be written for a set of samples.

In one form or another all of these methods were used by the scientists who pioneered spectroscopic studies of coal (1-9), but most recent studies have used methods 2 and 3 to determine absorption coefficients. We will review this work first and in the following section indicate how some new work with polymeric models may contribute to solving various problems.

The seminal work on the application of FTIR to the quantitative measurement of the aromatic and aliphatic CH content of coals was performed by Solomon (10) and Solomon and co-workers (11-13). They employed the third calibration method listed above, setting up a set of simultaneous equations for a set of coals and coal derived materials, where the hydrogen contents determined by elemental analysis are equated to the OH and CH contents through equations involving band intensities and absorptivities. The principle problem with this approach is the ill-conditioned nature of the equations, which can result (depending on the sample set) in a range of almost equally valid solutions (14-16). In their most recent studies, Solomon and Carangelo (13) addressed this difficulty and obtained better defined solutions by broadening the range of their sample set. However, it is possible that the methodology used in this work introduces a systematic error, which we will discuss below.

In our studies we have employed a different methodology to that used by Solomon and co-workers. Our approach follows the general lines described in some older work (15), where absorption coefficients were determined by characterizing pyridine soluble coal extracts. The aromatic and aliphatic CH content of these materials can be established independently using proton nmr measurements. Naturally, if the extracts have a different average structure to the parent coal, then this procedure will not be of much use. This is only a problem with low rank coals, however. (See reference 17).

In early work (14) we studied only eleven samples. This is clearly inadequate if we are to accurately determine variations with rank, petrography, geological history, etc. Accordingly, in a recent study we characterized the extracts obtained from a very broad range of coals (17). The initial set of samples consists of 44 North American coals and 17 Polish coals. The use of such a large sample set has also allowed us to examine the effectiveness of various sample preparation

techniques (e.g., KBr pellets vs. diffuse reflectance) and methodologies. Space does not allow us to present the details of this work here, but our conclusion can be grouped into six separate areas;

1. Our first set of conclusions deals with sampling and curve resolving methodology. First, because relatively small amounts of material are required for analysis (1-2 mg), variations due to the inhomogeneous nature of coal are important. It is therefore necessary to average the results of a number of KBr pellets (≥ 5) in order to obtain consistent results. Second, in applying curve resolving methods to the stretching region of the spectrum, allowance must be made for the different band shapes of the aromatic and aliphatic modes. Ignoring this factor leads predominantly to errors in the determination of the areas of the aromatic modes, the much more intense aliphatic modes are barely affected.
2. The absorption coefficients determined for the stretching modes vary not only with rank, the values for bituminous coals being distinctly different to those obtained for lignites and sub-bituminous coals, but also with the origin of the coal. We believe this is a particularly important result and to illustrate the type of data we obtained we have reproduced in figure 1 values of the ratio's of the intensities of the aromatic and phthalic CH stretching modes plotted against the ratio of aromatic to aliphatic CH content of the coal extracts determined by proton nmr. When the bituminous coals in our sample set are considered together then there is clearly a band of values, but when separated according to origin (U.S. Interior and Eastern Province Coals, U.S. Rocky mountain coals and Polish coals), good straight line correlations are obtained. The slopes of the lines are different, however, which translates into a difference in the ratio of the absorption coefficients (aromatic CH/aliphatic CH). Because the lines are straight it is reasonable to conclude that these absorption coefficients, which represent an average over the functional groups present, do not vary *within* each sample set. Variations in the relative proportion of such groups, and hence the average absorption coefficient, appear to be more significant between bituminous samples of different origin. [Also, an equivalent plot obtained for lignites and sub-bituminous coals has a very different slope to those shown in figure 1].
3. We have also demonstrated (see reference 17) that the use of the aromatic out-of-plane region of the spectrum ($900-700\text{ cm}^{-1}$) must introduce a systematic error due to the presence of aliphatic rocking modes. This error depends on the absorption coefficient of such vibrations relative to the aromatic out-of-plane modes, but its size remains unknown at this point. This is important in that even though we have successfully obtained absorption coefficients for the stretching modes (see figure 1), the measurement of the area of the aromatic CH band is particularly prone to error because of its weak intensity. Measurements based on the out-of-plane modes are much easier to make and alleviate many problems associated with curve resolving the stretching modes. We will return to this point in the following section as we believe there is a set of experiments that can be performed that will allow us to assess the extent of any error in using the area of the bands between 900 and 700 cm^{-1} . Preliminary experiments indicate that any error may be extremely small.
4. Similarities in the spectra and other considerations lead us to conclude that absorption coefficients for the pyridine extracts of bituminous coals can be applied to their parent material. This is not so for lignite and sub-bituminous coals, however, as the extracts are far more aliphatic than their parent material and appear to have very different absorption coefficients. A different procedure will have to be devised in order to determine absorption coefficients for these coals.
5. We have also characterized all of our samples using diffuse reflectance sampling methods. This technique is much easier to use and superficially less demanding than the preparation of KBr pellets and if we could establish appropriate procedures it would allow FTIR to be applied to coal characterization in a much more routine fashion. Unfortunately, the plots of the ratio of the intensities of the aromatic to aliphatic CH stretching modes show considerably more scatter than the equivalent plots for KBr pellets. The diffuse reflectance results are shown in figure 2. In part, this scatter may reflect a fundamental problem in the diffuse reflectance technique, in that weaker modes appear to be selectively enhanced in intensity (relative to absorption measurements) and this, in turn, depends on things such as packing (in the sampling cup) that are not easily controlled or reproducible.
6. Finally, how consistent are the results that have been obtained using different methodologies? The older work (compare refs 10-12 and 14-16) displayed some distinct differences, but there has been a remarkable convergence of values of the absorption coefficients obtained in more recent studies. Solomon and Carangelo(13) reported values for the absorption coefficients of the aliphatic CH stretching mode, a_{al}^{st} , and out-of-plane bending modes, a_{ar}^{op} of 744 and 684, respectively, for a Pittsburgh seam coal. These values are in remarkably good agreement with those reported in our work (17) for US bituminous coals from the Eastern and Interior Provinces (764 and 665, respectively, ref. 17). This agreement is truly extraordinary, considering the different methodologies employed in these studies. Clearly, as far as the stretching modes and the $900-700\text{ cm}^{-1}$ region of the spectrum are concerned, the procedures used to prepare KBr pellets, measure band areas, etc. must be producing equivalent results. Furthermore, the absorption coefficients determined for extracts by calibration with proton nmr.

are apparently also in agreement with the results of the procedure applied to whole coals and char, indicating an equivalence in structure. There remains the question of the extent of the error that is introduced by the rocking modes that also appear in the 900-700 cm^{-1} region of the spectrum, and this is where some new work sheds some light.

PHENOLIC RESINS AS MODELS FOR COAL

In order to determine the extent of any contribution of CH_2 aliphatic rocking modes to the bands between 900 and 700 cm^{-1} we have embarked on a study of various phenolic resins. Essentially, our plan is to prepare resins where the phenolic rings are protonated and the methylene linkages are deuterated (i.e., - CD_2 -) and resins where this labeling is reversed. We have synthesized the first models and it appears from preliminary spectra that methylene vibrations contribute negligibly to the 900 - 700 cm^{-1} region of the spectrum. This work will be completed in the next two months and a more complete discussion presented at the conference. The synthesis of these resins has also opened up what might become a new and intriguing area of study involving the near infrared region of the spectrum, and we will conclude this paper with a brief discussion of these initial results.

The near infrared region (~9000 - 4000 cm^{-1}) of the spectrum of coals (and many other materials) has not been studied in great detail, but appears to be very sensitive to aromatic and aliphatic CH content (because these modes are overtones and combinations and are a result of a breakdown of quantum mechanical selection rules, they usually involve vibrations of protons, which are "light" and therefore more likely to be anharmonic). A comparison of the spectrum of an all-protonated and CD_2 linked resin is shown in figure 3. Coal has a similar spectrum, but with additional bands probably due to CH_3 species as illustrated in figure 4. It is particularly interesting that the modes between about 6300 cm^{-1} and 5500 cm^{-1} have a band near 6000 cm^{-1} which can be assigned to an overtone of aromatic CH stretching vibrations, that is much more intense than the aliphatic modes near 5700 cm^{-1} , reversing the intensity ratio of the fundamentals. This may prove to be very useful in quantitative work.

CONCLUSIONS

The development of FTIR techniques for the quantitative determination of the functional groups present in coal has advanced considerably in the past few years. There has been particular progress in the measurement of aliphatic and aromatic CH content, with a pleasing convergence in the values of the absorption coefficients obtained by different groups using different methodologies. It appears that the use of phenolic resins as models should enable us to "sort out" the remaining problems and also allow band assignments in the near IR region of the spectrum, thus opening up a new means of analysis.

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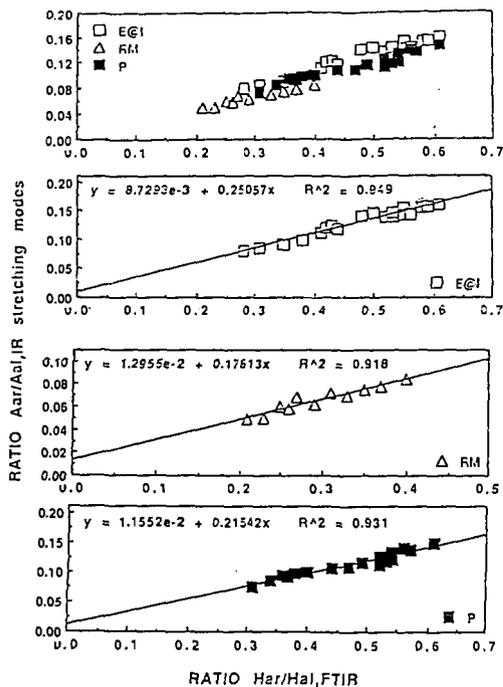


Figure 1. Plots of the ratio of the areas of the aromatic to aliphatic CH stretching modes of KBr pellets of coal to aliphatic hydrogen determined by proton nmr.

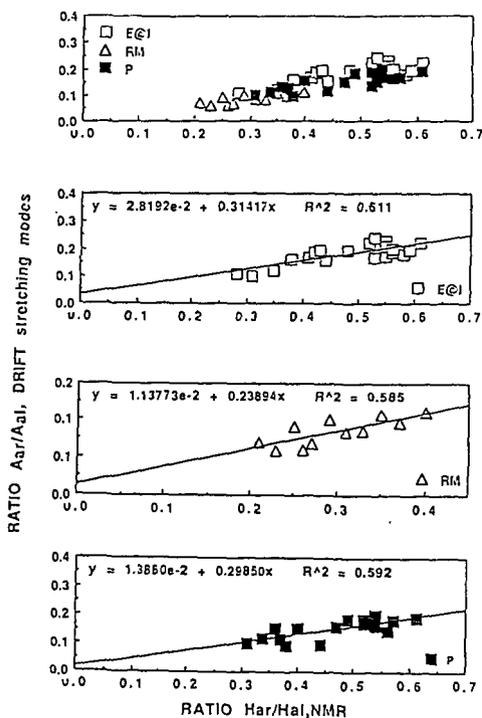


Figure 2. The same plots as Figure 1, but with the spectra of the extracts obtained by diffuse reflectance.

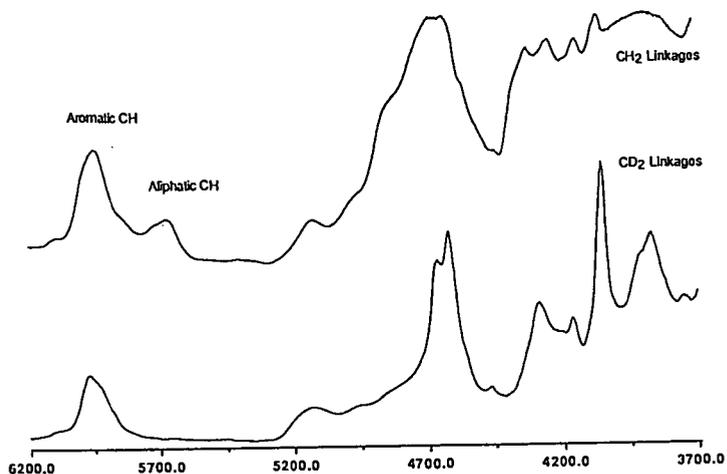


Figure 3. Near infrared spectrum of phenolic resins where the aromatic group are connected by CH₂ linkages (top) and CD₂ linkages (bottom).

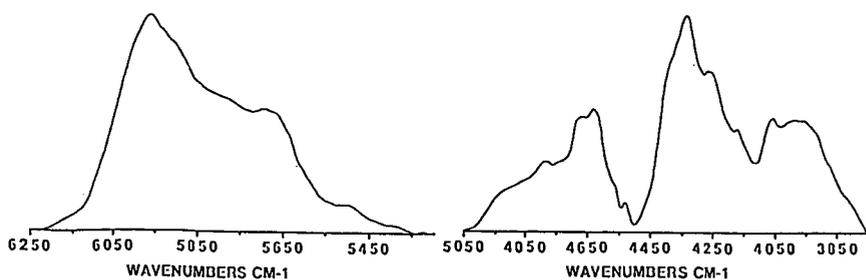


Figure 4. Near infrared spectrum of a coal extract.