

MICROSCOPIC INFRARED SPECTROSCOPY OF COALS

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Introduction

Most IR (infrared) spectroscopy of coal involves the use of finely crushed particles. Techniques in common use include incorporating the particles in potassium bromide disks (1) or slurring them in a hydrocarbon oil such as Nujol (2). Such particulate samples generally include a wide range of types of vitrinite and other macerals which are derived from different plants (such as trees, bushes, and grasses) and from various parts of each plant (such as trunks, stems, roots, leaves, etc). In addition, inorganic substances of various types and degrees of dispersion are generally mixed in. Because of their different derivations, the various organic plant remnants are likely to have different physicochemical characteristics; however, because of the intimate mixing of these subcomponents, which usually occurs on a microscopic scale, it is difficult to separately characterize the different maceral components. In particular, IR spectra obtained on pulverized coal samples give averaged information rather than being characteristic of any individual component in the coal. A few techniques have been utilized in the past to overcome this problem. These include the hand separation of macerals (3,4), sink-float techniques, and the recently developed method of centrifugal separation of very finely pulverized coal (5). These preparation techniques provide a mixture of material which is highly enriched in a selected maceral type. These maceral concentrates can then be analyzed by a variety of chemical procedures. The averaged properties of a maceral type can be characterized using these procedures, but they do not enable the IR analysis of individual microscope macerals.

The particulate samples of coal used for infrared analysis must be finely ground because of the high absorbance of the coal. The particles must be less than roughly 20 micrometers thick (depending on the rank) for substantial transmission of the IR radiation in the more absorbing regions of the spectrum. The small particles of coal cause considerable scattering to appear in the IR spectrum. Other complications are the differences in the thicknesses of the various particles of the sample, and the variations in thickness along each particle. For example, the thinner edges (with respect to the illuminating beam) of the particles will be more transparent than the central regions, so the volume of the particles may not be sampled uniformly. This can be a problem for a heterogeneous material such as coal. Thin section samples of coal having a relatively uniform thickness of 20 micrometers or less have been used occasionally in the past (6). However, the difficulties in preparing these thin section samples and problems of contamination with the adhesives used in the preparation of the sections (7) has limited their usage. Also, because the cross sectional area of the samples must be several square millimeters or more for analysis with most IR spectrometers, microscopic components of the thin sections can not be individually analyzed.

In this paper a technique for the IR spectroscopic analysis of individual microscopic components in coal is described. This method combines new procedures for preparing uncontaminated thin section specimens of coal with a sensitive IR microspectrophotometer which has recently become commercially available. Details of this new technique are discussed and some representative spectra are described.

Experimental

The coal used in this study was Illinois No. 6 which is a high volatile C bituminous coal. To prepare thin sections, a chunk of coal about 1.5 cm across was cut perpendicular to the bedding plan to produce a roughly flat surface. This surface was ground smooth on a 20 cm diameter wheel using 600 grit and then 8 micrometer silicon carbide on disks. The flat surface was cemented to a glass slide with a thermoplastic hydrocarbon-based adhesive (Paraplast, manufactured by the Lancer Company) which is soluble in hexane. A temperature of about 70°C was used in melting and applying the adhesive. The coal was exposed to this temperature for only about a minute before cooling was started. The coal on the slide was ground to a thickness of 15 micrometers using the abrasives described above. The sample was then soaked in hexane at room temperature until the thin specimen floated off of the slide. The sample came off as a number of small pieces of various sizes from less than a millimeter across to several millimeters long. Although no residual adhesive could be observed on the pieces of coal, to insure complete removal of the adhesive the samples were immersed in a large excess of fresh solvent for several days. Then the hexane was decanted off and the specimens were stored in nitrogen at room temperature until they were used.

The microscopic infrared spectrophometer used in this work (NanoSpec/20IR manufactured by Nanometrics Inc.) operates in transmission and contains reflecting lenses. Because of the reflecting optics, the visual and IR images of the sample correspond and the region of the sample being analyzed can readily be identified visually while it is in place in the IR microscope. This enables unambiguous correlation of visual microscopic characterization and IR analysis for the same area of the sample. The condenser and the objective of the microscope are both 15 power, 0.28 numerical aperture reflecting lenses. The part of the sample to be IR analyzed is optically delineated by an adjustable aperture at the image plane of the objective, so no masking is needed at the sample itself to define the analyzed area. The useful IR range of the instrument is from about 4000 to 700 cm^{-1} (2.5 to 14 micrometers). The IR monochromator is a variable interference filter. The resolution is only about 1% of the wave number value over the IR range; however, this should be adequate for many applications with coal because of the breadth of most of the absorbances. The IR source is a Nerst Glower and the detector is a liquid nitrogen cooled mercury cadmium telluride photodetector having high sensitivity. The operation of the spectrometer is computer-controlled and the data, which is stored digitally, can be automatically averaged and difference spectra can be obtained.

Results

In this preliminary study, spectral characteristics of vitrinite and exinite macerals in Illinois No. 6 coal were examined to evaluate the utility of this new technique for microscopic IR analysis of coals. In Figure 1, a photomicrograph of a thin section specimen consisting of a megaspore (a form of liptinite) surrounded by relatively homogeneous vitrinite is shown. The thin section was placed on a barium fluoride disk on the stage of the IR microscope. The megaspore and a region of the vitrinite lying close to the megaspore on the same specimen were analyzed with the IR microscope. The analyzed regions are indicated by rectangles drawn on the photograph of the sample; they are each about 55 micrometers wide by 180 micrometers long. Spectra of the two regions were taken in air at room temperature; they are compared in Figure 2. The spectra are displaced vertically to avoid overlapping. The displayed spectra actually involve a reference scan which was taken without the sample present but with all other conditions the same. The subsequent sample spectra are automatically normalized with respect to the reference spectrum. Each of the two sample spectra in Figure 2 are 2 minute scans.

A number of differences between the liptinite and vitrinite spectra are apparent. Note that since the thicknesses of the liptinite and vitrinite regions are the same and since scattering is minimal, these spectra can be directly compared quantitatively on a per unit volume basis. Some of the more prominent of the differences are as follows. The broad hydroxyl peak around 3350 cm^{-1} is much deeper for the vitrinite. This probably is caused chiefly by a much larger number of phenols in the vitrinite, but it may also indicate more water absorbed on the vitrinite. Between 2800 and 2975 cm^{-1} the liptinite shows a much stronger absorption than the vitrinite. This indicates much more aliphatic hydrogen in $-\text{CH}$, $-\text{CH}_2$, AND $-\text{CH}_3$ groups in the liptinite. Also, at about 2850 cm^{-1} the liptinite shows a substantially larger peak than the vitrinite on the side of the larger absorption. At about 1600 cm^{-1} the vitrinite peak is much larger than the liptinite peak probably indicating much more aromatic character in the vitrinite. Conversely, the CH_2 , CH_3 peak around 1440 cm^{-1} is much more pronounced for the liptinite. The spectra clearly contrast the more aromatic and hydroxyl-containing structure of the vitrinite to the more aliphatic structure of the liptinite.

Mention should be made of some artifacts which appear in the spectra of Figure 2. At about 2350 cm^{-1} there is a peak caused by CO_2 in the air. (This peak could be eliminated, if desired, by sealing the region of the beam path and maintaining a nitrogen atmosphere). At about 2250 cm^{-1} and 1230 cm^{-1} are peaks caused by changes in the IR filters. Three filters are used to obtain the full spectrum, and small peaks occur where the second and third filters are brought into use. Another artifact is broad peaks seen around 2100 cm^{-1} in the liptinite spectrum, 1950 cm^{-1} in the vitrinite spectrum and in some other areas. These peaks are caused by interference fringes which arise from the IR radiation being internally reflected from the top and bottom surfaces of the sample. The fringes can be misleading if they are not correctly identified.

The applicability of this technique for "in situ" IR analysis during chemical treatments and the ability to perform kinetic measurements was tested by observing the effect of applying deuterated pyridine to a thin section of vitrinite and then allowing it to dry. An area 40×180 micrometers was analyzed. First a spectrum was taken of the untreated sample. Then the solvent was placed on the sample and repetitive scans were made to monitor changes in the IR spectrum as the deuterated pyridine evaporated. Figure 3 shows spectra of the untreated sample, the sample wet with pyridine, and the sample after drying for about 20 minutes. For the latter spectrum, peaks characteristic of deuterated pyridine are still prominent, such as those at about 950 and 820 cm^{-1} . Later scans showed no appreciable lessening of the peaks. The retention of some of the pyridine is consistent with the results of Collins *et. al.* (8).

Tests were made to determine the minimum area of analysis which could be conveniently used with thin sections of coal in this technique. Figure 4 shows spectra of regions of a tiny roughly 30×30 micrometer piece of vitrinite. One spectrum was taken using a 21×21 micrometer analyzing area, and the other spectrum was taken using a 20×30 micrometer analyzing area. Four minutes were used for each scan. For this scan time, the smaller area gives quite a noisy spectrum, but the 20×30 micrometer spectrum is much better. By using a longer scanning time or by accumulating repetitive scans this spectrum could probably be made quite respectable. The spectral region having the greatest problem in the analysis of such very small areas is beyond 1000 cm^{-1} where the sensitivity of the spectrometer falls off. Subcomponents or macerals in the coal which are somewhat less than 25 micrometers across can probably be IR analyzed by using long data accumulation times. Preferably such small subcomponents should be physically separated from the surrounding material. Alternatively, the spectrum of a region including the subcomponent as well as some of the surrounding material could be subtracted (using an appropriate normalization factor) from a spectrum only of the surrounding

material in order to isolate the contribution of the subcomponent. Note, however, that for subcomponent sizes near the wavelength of the IR radiation the possibility of interference effects from the edges of the sample must be considered. Such effects ought to be made apparent by comparing spectra from subcomponents having different sizes or shapes.

Discussion

Infrared spectra of good quality have been obtained on uncontaminated individual microscopic macerals and microscopic subregions in coal. This development enables the infrared characterization of microscopic individual subcomponents of coals and other solid fossil fuels as opposed to obtaining statistically averaged data on complex mixtures. In addition, variations in functionalities over microscopic distances can be studied. The technique should also be applicable for the analysis of virtually any chemical process or chemical treatment of coal which causes changes in the IR spectrum and in which the area of interest is identifiable after the treatment. For example, the initial chemical functionality of an individual microscopic maceral or subregion can be determined with the microspectrometer; the maceral can be reacted; and the effect of the treatment on that same microscopic subregion can be determined.

In Figure 2 the IR spectrum of a subregion of vitrinite about 0.010 mm^2 in area is compared with the IR spectrum from an equal area which is within a single megaspore. The two regions of analysis are on the same piece of thin section and they are separated by only about 160 micrometers. The two minute scans of the 15 micrometer thick samples give excellent signal to noise. As described in the results section, these spectra clearly contrast the more aromatic and hydroxyl-containing structure of the vitrinite to the more aliphatic structure of the megaspore. The ability to analyze closely lying regions having identical preparation, equal areas being analyzed, and the same thickness, facilitates quantitative comparisons of the regions. Thus, while these data are generally consistent with the results of Bent and Brown (9) taken on maceral concentrates, the present technique enables a more direct quantitative comparison of the spectra.

The spectra in Figure 3 demonstrate the "in situ" treatment of an uncontaminated thin section of coal. One operational difficulty is the possibility of movement of the sample during treatment which would make analysis of the same microscopic region before and after treatment difficult. For example, application of a drop of solution to the coal is likely to cause movement. Movement can be avoided by securing the sample, but this may be difficult for small samples or it may affect the sample. Alternatively, if the region under analysis is carefully recorded, such as on a photograph, then during or after treatment the sample can be accurately repositioned on the stage.

Figure 4 demonstrates that isolated samples of coal less than 30 micrometers across can be satisfactorily IR analyzed and that delineated regions of a sample less than 25 micrometers across can be characterized by IR. Signal to noise levels which are improved over those shown in Figure 4 can be obtained by using longer data accumulation times. Alternatively, if better quality data is required only for some small regions of the spectrum, then those regions alone can be scanned to shorten the time needed to obtain an acceptable signal to noise level. The ability to analyze small regions of a coal sample is important even for a single maceral type such as vitrinite. For example, substantial variations occur in the structure (10,11) and swellability (12) of different microscopic areas of vitrinite from the same coal.

In the IR microscope the region of the sample being analyzed is delineated by a variable aperture at the image plane of the objective. Therefore, no spacial

restrictions are placed around or near the sample itself. Since the image of the sample has been substantially magnified at this image plane, it is relatively easy to accurately define even very small subregions of the sample for analysis with the aperature. However, the geometrical region delineated by the variable aperature which is observed visually is not nearly so well defined for the infrared radiation because of diffraction effects. The spacial uncertainty is proportional to the wavelength, so the resolution is considerably poorer near the long wavelength end of the IR range. The divergence or angular spread of the IR beam passing through the sample, which is determined by the numerical aperature, will further diminish the spacial specificity of the delineated area. This, of course, becomes more of a problem for thick samples. For analysis of a very small subregion in the coal, the most unambiguous way to avoid contributions from contiguous material is to physically remove the subcomponent from the surrounding material.

The 15 micrometer thickness for the Illinois No. 6 coal is quite satisfactory since the percent transmissions of a number of the larger peaks are below 40 percent, but without saturation. Also, at this thickness the thin sections can be conveniently manipulated without fracturing. Using the described grinding technique for preparation, samples containing any maceral types and even substantial amounts of mineral matter can be prepared. A wide range of coals (with the possible exception of very low or very high ranks) can be handled by these techniques.

The interference peaks which occur in the spectra of Figure 2 can be misleading when trying to interpret the spectra. These fringes occur when some of the IR radiation reflects from the top and bottom surface of the sample and then interferes with the unreflected beam. The fringes are particularly a problem where the top and bottom surfaces are nearly parallel and where the thickness of the sample is comparable to the wavelengths of the radiation such as for the thin section specimens used in the technique described here. However, the intensity of the interfering beam is not large since it is reflected twice and it passes through the sample three times instead of once. Thus, as seen in Figure 2, the fringes are most prominent in the spectral regions having low absorbance. The fringes can be partially compensated for by determining their position and intensity in a low absorbance region and then calculating and subtracting out their contribution to other parts of the spectrum where their presence is less obvious. Alternatively, tilting the sample, or using samples of different thicknesses and of higher adsorbance can be used to identify the effects of the fringes on a spectrum so that they can be compensated for.

Summary and Conclusions

Microscopic macerals and subregions in coal have been characterized by infrared spectroscopy using a new technique. Individual macerals or subregions of the coal as small as 25 micrometers across can be analyzed. The technique utilizes new procedures for preparing uncontaminated thin sections of coal in combination with a recently available microscopic IR spectrometer.

Because the thin section specimens are not contaminated with adhesives or embedding materials, and because the samples are readily accessible on the stage of the IR microscope, this technique is well suited for "in situ" treatments of the coal. Alternatively, since the 15 micrometer thick specimens of coal can ordinarily be handled and transported without damage (if proper care is taken), an untreated sample can be initially analyzed, then it can be removed from the instrument for chemical or thermal treatment, and finally, the same specimen can be returned to the microspectrometer for determination of the changes in the IR spectrum. The analysis of the same spectrum before and after treatment is highly desirable for micro-heterogeneous substances such as coal.

The microscopic IR spectroscopy technique described here differs from and complements prior IR work on maceral concentrates in being able to spatially delineate an individual subcomponent being IR analyzed and to characterize it visually in the context of its surroundings.

Preliminary IR measurements on microscopic subregions of individual macerals of homogeneous-appearing vitrinite and of megaspores in Illinois No. 6 coal clearly demonstrate quantitative as well as qualitative chemical differences between these macerals. This work demonstrates that good quality IR spectra of microscopic subregions of coal can be obtained.

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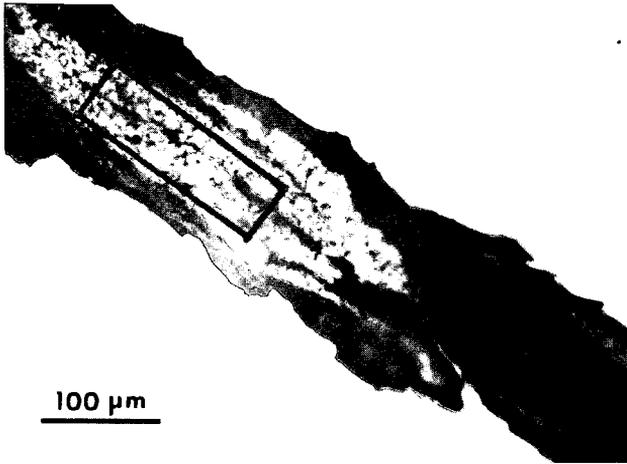


Fig. 1. Thin Section Sample of Illinois No. 6 Coal Containing Regions of Vitrinite and Liptinite

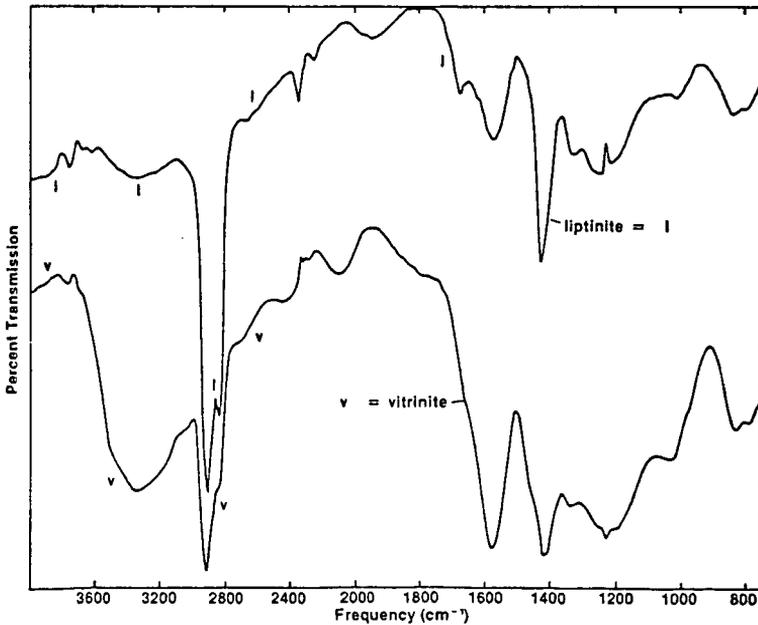


Fig. 2. IR Spectra of Microscopic Regions of Vitrinite and Liptinite in the Same Thin Section Sample of Illinois No. 6 Coal

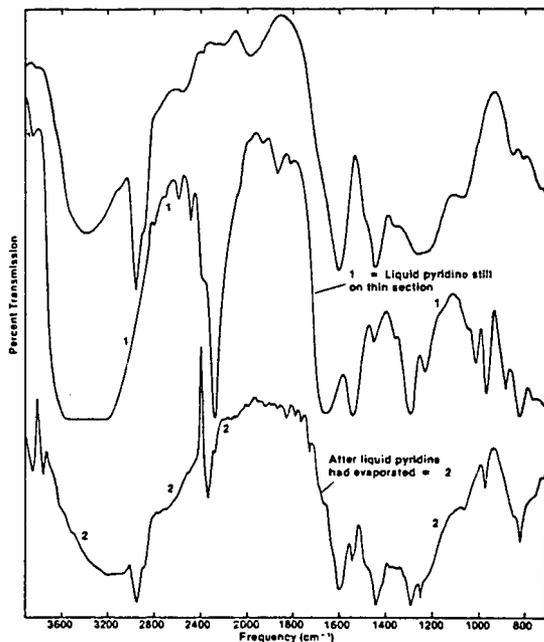


Fig. 3. IR Spectra of a Microscopic Region of Vitrinite in a Thin Section of Illinois No. 6 Coal Top ----- Untreated Sample
 Middle -- Liquid Deuterated Pyridine on the Sample
 Bottom -- After Pyridine has Evaporated

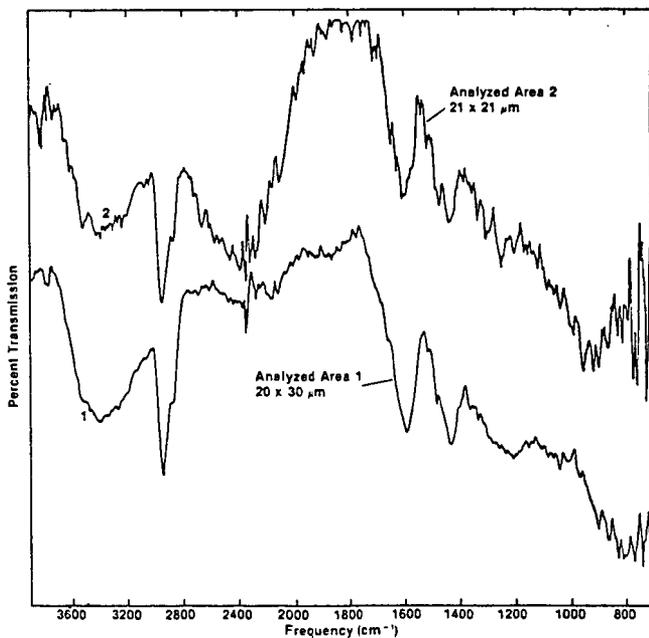


Fig. 4. IR Spectra of a Thin Section Sample of Illinois No. 6 Coal having an Area of $30\mu\text{m} \times 30\mu\text{m}$
 Top ----- Delineated Area is $21\mu\text{m} \times 21\mu\text{m}$
 Bottom -- Delineated Area is $20\mu\text{m} \times 30\mu\text{m}$