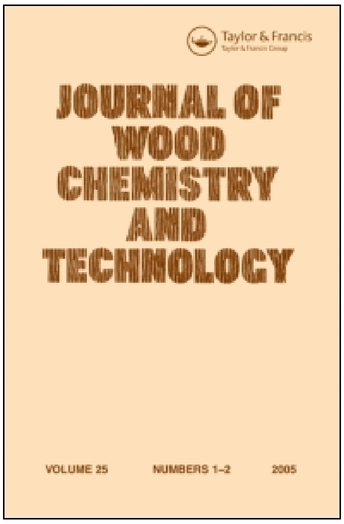

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Analysis of Solid Wood Surfaces by Diffuse Reflectance Infrared Fourier Transform (Drift) Spectroscopy

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ANALYSIS OF SOLID WOOD SURFACES BY DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM (DRIFT) SPECTROSCOPY

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ABSTRACT

Comparison of infrared spectra of wood taken by several methods indicated that the DRIFT spectrum of a dispersion of wood powder in KBr, expressed in Kubelka-Munk units, agreed best with the spectrum taken by transmission FTIR of solid wood sections; the DRIFT spectrum of solid wood, expressed in Kubelka-Munk units, was a close second, while the solid-wood DRIFT spectrum expressed in absorbance units differed most. The DRIFT spectrum of solid wood depended to a minor extent on the grain orientation and choice of late- vs early-wood. The spectrum depended strongly, however, on surface roughness with rougher surfaces producing more transmission-like spectra. Depth of penetration at 2242 cm^{-1} (90% loss in intensity of CN peak of polyacrylonitrile placed under wood sections) varied between 37 and 138 μm with an inverse linear relationship to wood density. DRIFT spectral analysis of chemically treated wood surfaces indicated an increase in carbonyl functional groups after chlorine or nitrogen dioxide treatment, followed by water extraction, and disappearance of aromatic nuclei after chlorine treatment. The DRIFT spectrum of heat-treated wood suggested formation of furan aromatic structures, while that of wood treated with oxygen radiofrequency plasma showed no discernible changes. The last result was most likely due to wood ablation predominantly by physical sputtering rather then chemical oxidation, coupled with the shallowness of plasma-induced effects compared with the depth of infrared light penetration.

INTRODUCTION

The number of methods available for chemical analysis of a solid wood surface is small in comparison with those applicable to the entire wood material. Of the methods available those based on infrared absorption (IR) are quite attractive - the instrumentation is relatively inexpensive and simple to use, and the amount of information potentially available is comparatively large. In particular, diffuse reflectance infrared Fourier transform (DRIFT) and internal reflection spectroscopy (IRS) have gained popularity in recent years. While diffuse reflectance IR spectroscopy was developed quite some time ago, the rather low signal-to-noise ratios obtained in dispersive instruments often precluded its use. It is the advent of efficient Fourier Transform Infrared Spectroscopy (FTIR) instrumentation that has removed this limitation, making DRIFT spectroscopy one of the methods of choice for surface analysis.

DRIFT analysis has been described in a number of articles [1-4] and diffuse-reflectance FTIR accessories of various optical geometries are commercially available. In DRIFT analysis, a beam of infrared light is focused on the surface of a sample and the diffusely reflected light collected by an integrating sphere and analyzed in the usual fashion. The result is a plot of light intensity vs wavenumber which is a function of the combined effects of absorption and reflection of the sample surface. While DRIFT spectra roughly correspond to conventional IR transmission spectra, substantial deviations are sometimes noted which include distortion of the bands, shifts of the maxima, and the appearance of spurious bands. In the case of powdered samples, these deviations can be minimized by analyzing the sample dispersed at a relatively low concentration in a nonabsorbing material of high reflectance such as KCl or KBr [2-4] and expressing the spectrum in Kubelka-Munk units [5,6] instead of in absorbance units:

$$F(R\infty) = \frac{(1 - R\infty)^2}{2(R\infty)} = \frac{2.303\ a\ c}{s}$$

where F(R∞) = the Kubelka-Munk function, R∞ = the ratio of the diffuse reflectance of the sample at "infinite depth" to that of the nonabsorbing matrix in which it is dispersed, a = absorptivity, c = concentration in moles per liter, and s = scattering coefficient. Even so, the spectra obtained are dependent upon a number of parameters including the particle size, packing density, and refractive index of the powders.

Unfortunately, the method of dispersing a powdered sample in KBr or similar compounds is inapplicable to surface analysis, unless it is possible to mechanically remove and pulverize the occasionally rather thin surface layer of the material to be analyzed.

A much simpler method consists of directly submitting the sample surface to DRIFT analysis. This of course raises the question of the extent to which the spectra so produced deviate from those obtained by transmission IR or KBr-dispersed DRIFT spectroscopy. Another important question is the effective depth of the surface layer giving rise to the spectrum.

Several papers have been published on the use of DRIFT for the study of the chemistry of lignocellulosics. Thus Schultz and Glasser studied lignin chemistry by DRIFT of lignin samples dispersed in KCl [7]. Schultz *et al.* [8], Berben *et al* [9], and Michell *et al.* [10] applied it to the study of wood pulps, exposing the neat material directly to infrared light. Apparently the only study involving solid wood is that of Ostmeyer *et al.* [11] who studied the chemical interactions of several preservatives with southern pine sapwood using direct (neat) DRIFT spectroscopy.

In our current research on the action of cold radio-frequency plasma on the surface of solid wood, we were naturally attracted to the very simple "direct" DRIFT technique. At the same time, in view of the lack of pertinent literature, we felt it necessary to first study the effects of various sample physical parameters on DRIFT spectra; the correspondence of the spectra with those obtained by transmission and other methods; and the thickness of the wood layer giving rise to the spectrum. The last is particularly critical since plasma interaction with wood could involve a rather thin surface layer which would contribute little to the DRIFT spectrum should the depth of infrared light penetration be much deeper.

In this paper we report the influence of (1) grain direction relative to the beam; (2) section orientation (radial vs. tangential surface); (3) early- vs late-wood; and (4) surface roughness, on the DRIFT spectrum of whole wood. We also examine the depth of penetration of infrared radiation into wood, the correspondence of DRIFT spectra expressed in absorbance and in Kubelka-Munk units with those obtained by transmission, as well as on the suitability of DRIFT spectroscopy for studying surface chemical changes brought about by plasma, chlorine, nitrogen dioxide, and thermal treatments of wood.

EXPERIMENTAL

IR spectra were obtained on a Nicolet 20SX Fourier Transform Infrared Spectrophotometer with a SpectraTech DRIFT attachment, using 30 scans. For radiofrequency plasma generation a modified LTA-604 low-temperature asher (LFE Co.) operating at 13.56 MHz was used. Potassium bromide was E. Merck IR grade; polyacrylonitrile was obtained from Scientific Polymer Products, Inc. as a fine, white powder. The wood samples were brought to equilibrium moisture content at ambient conditions prior to spectrum determination except for the study of wood surface roughness where they were dried overnight in vacuum and allowed to equilibrate for 1 hour in the purged sample compartment of the FTIR instrument. Wood surfaces of different roughness were produced by sanding with 80, 150, 220, 400 or 600 grit commercial sandpaper (160, 90, 60, 34, and 22.5 μm average abrasive particle diameter, respectively). Sanding was done gently to avoid excessive heat which could cause unwanted surface chemical transformations. All spectra were scaled so that the OH stretching band (about 3450 cm^{-1}) intensities were approximately equal.

The intensity of individual peaks was measured relative to a baseline drawn parallel to the abscissa through the point of minimum absorbance or Kubelka-Munk function, generally around 1850 cm^{-1}. The relative peak intensity was determined in relation to the 1510 cm^{-1} peak as suggested by Sarkanen *et al.* [12-14] and also because larger peaks are more subject to distortion in DRIFT spectroscopy [15, 16].

For measurement of the depth of penetration, polyacrylonitrile powder was placed in the measurement cup of the DRIFT attachment, a section of wood of appropriate thickness lightly pressed onto the surface and the spectrum run in the conventional fashion using 30 scans. Compressed white fir wood was prepared by pressing sections for 10 min. at 2500 psi and a platen temperature of 110°C.

RESULTS AND DISCUSSION

Comparison of FTIR Methods

The transmission spectrum of a 50 μm thick radial section of white fir wood (Abies concolor (Gord. & Glend.) Lindl.) plotted in absorbance units (A) was compared with: the DRIFT spectrum of powdered white fir earlywood dispersed in KBr, plotted in Kubelka-Munk units (B); the spectrum obtained directly from the unmodified wood surface, plotted in Kubelka-Munk units (C); and the spectrum obtained directly from the unmodified wood surface, plotted in absorbance units (D) (Fig.1). For (C) and (D) the surface was sanded with 150 grit commercial sandpaper. The KBr pellet transmission spectrum of white fir earlywood powder was also run. The spectrum was practically identical to spectrum (A) and was therefore omitted from the following comparisons.

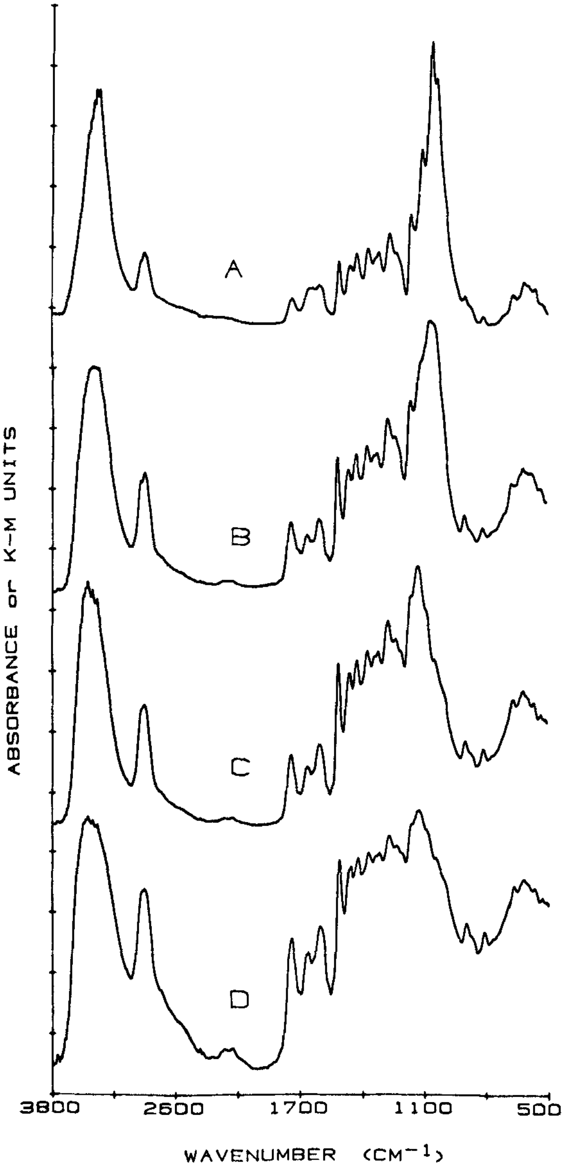

Figure 1. Infrared spectra of white fir wood obtained by: (A) transmission FTIR of a wood section, in absorbance units; (B) DRIFT of wood powder dispersed in KBr, in Kubelka- Munk units; (C) direct DRIFT spectrum of wood surface, in Kubelka-Munk units; and (D) direct DRIFT of wood surface, in absorbance units. Scale change at 2000 cm^{-1}.

TABLE 1

Sums of Peak Shifts, and Correlation Coefficients between Intensities, for the Eleven Major Peaks of Spectra A - D*).

	B	C	D
A	71 0.939	180 0.875	186 0.799
B		115 0.981	121 0.951
C			8 0.986

*) The sums of peak shifts (in cm^{-1}, first row) were obtained by summing the differences between the positions of the eleven most prominent peaks (listed below) of spectra B - D and those of the transmission spectrum A; correlation coefficients (second row) were calculated between the normalized intensities of the eleven most prominent peaks of spectrum A and those of spectra B - D. For all calculations the intensities and positions of the peaks at 3360, 2900, 1736, 1652, 1602, 1510, 1427, 1370, 1265, 1061, and 618 cm^{-1} were used. Peak intensities were normalized to that of the 1510 cm^{-1} peak.

All spectra were quite similar, with negligible differences in peak resolution, so that all major peaks could be qualitatively correlated between all four spectra. However, several peaks in spectra C and D (direct DRIFT method) showed small shifts towards shorter wavelength relative to the same peaks in the spectra A and B.

These peak shifts were evaluated by summing the absolute values of differences in position of the eleven most prominent peaks (Table 1). The DRIFT spectrum of wood powder in KBr (B) was least different from the one obtained by transmission (A), while spectra C and D exhibited greater shifts overall. Particularly large shifts to higher wave numbers were exhibited by the two most intense peaks (3360 cm^{-1} OH stretching and 1061 cm^{-1} C-O stretching, +92 and +63 cm^{-1}, respectively) of spectra C and D; appreciable deviation was also exhibited by the 3360 cm^{-1} peak of DRIFT spectrum B (OH stretching, +35 cm^{-1}). A shift to higher wavenumber for strongly absorbing bands in Kubelka-Munk plots has been discussed by Brimmer and Griffiths [15,16] and explained by the increase in Fresnel reflectance near absorption maxima. The same effect is also responsible for the marked intensity decrease of the strongly absorbing bands, which makes the less affected weaker bands (such as those in the 1500 - 1700 cm^{-1} region) appear to increase in relative intensity.

The difference in intensity of individual peaks from spectrum to spectrum was investigated by computing the correlation coefficients between the heights of the eleven most prominent peaks (normalized to the height of the 1510 cm^{-1} peak), for all pairs of spectra (Table 1). The best correlation was obtained between direct spectrum C in Kubelka-Munk units and direct spectrum D in absorbance units. Almost as close a correlation was obtained between powder-in-KBr spectrum B and spectrum C. The best correlation with transmission spectrum A was shown by spectrum B, closely followed by, spectrum C. The differences in relative height between the peaks of the transmission spectrum and the peaks of the other spectra were again greatest for the most intense peaks (3360 and 1061 cm^{-1}): expressed in percent of the height of the transmission spectrum peaks, the differences were 53.9 - 67.6%, and 55.5 - 73.2% for the above two peaks, respectively, vs an average of 20.4% (S.D. = 11.7%) for the other peaks in agreement with [15,16].

Influence of Surface Roughness

As mentioned earlier, the particle size strongly influences the DRIFT spectrum of powdered samples and must be kept constant to obtain reproducible results [2,17]. In solid wood surface analysis, the parameter comparable to particle size is surface roughness. To study its effect, we generated white fir surfaces of various roughness by simply sanding tangential sections with sandpaper of various grits. One result of increasing surface roughness was a 2.2 - 5.0 fold (mean 3.3, S.D. 0.91) increase in the Kubelka-Munk function, for the eleven most prominent peaks. Correlation coefficients for the Kubelka-Munk function and the average diameter of the abrasive particles of sandpaper were between +0.86 and +0.96 (average 0.92, S.D. 0.040).

As for the overall appearance of the spectra, the largest deviations from the solid wood transmission spectrum and the DRIFT wood powder-in-KBr spectrum (A and B) (Fig. 1) were seen in the spectra of the smoothest samples, particularly in the 600-grit sanded sample (Fig. 2); the differences were predominantly - but not exclusively - noted in the region below 1200 cm^{-1}. Our results were somewhat surprising in that prior work with powders has shown that finer, not coarser, particles yielded better resolved, more transmission-like DRIFT spectra [2,17]. The improvement in the whole-wood DRIFT spectrum with increasing roughness is probably related to a decrease in the Fresnel component of the reflected light [4].

Influence of Section Plane, Grain/Light-Beam Angle, and Early- versus Late-wood

DRIFT spectra (Fig. 3) of white fir were recorded using: tangential sections of early-wood (E), and late-wood (F), and radial sections (G), all with the grain oriented parallel to the light beam; and early-wood tangential sections with the grain oriented perpendicular to the light beam (H). In all cases, the surface was sanded to a uniform surface roughness with 150 grit sandpaper; spectra were plotted in Kubelka-Munk units. As can be seen, there is little difference between these spectra in the positions and relative intensities of the individual bands, with the exception of spectrum (H) in which a doublet at 1166 and 1124 cm^{-1} is present, while in spectra E - G the 1166 cm^{-1} peak appears only as a lower intensity shoulder. Interestingly

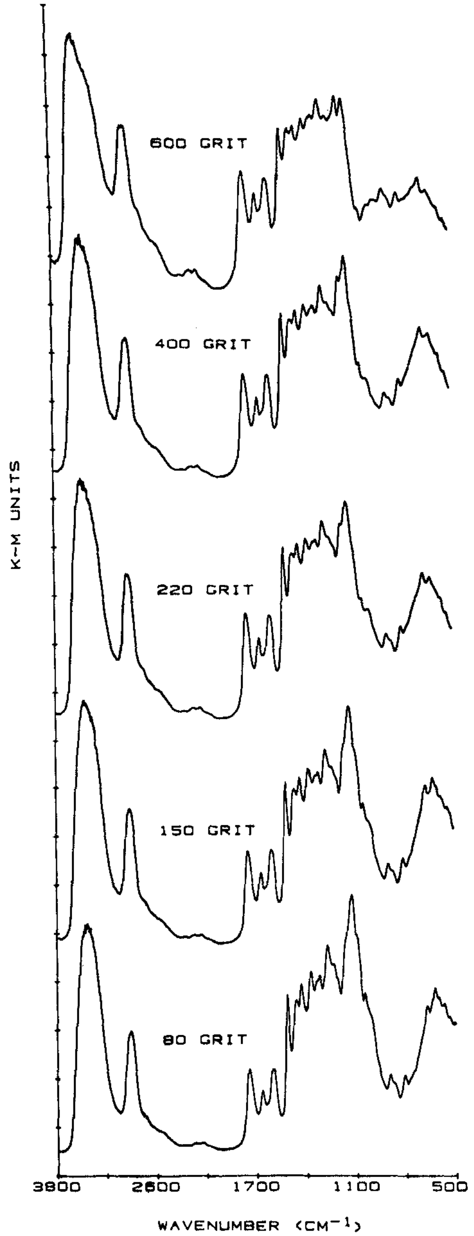

Figure 2. DRIFT spectra of white fir surfaces prepared with sandpaper of various grits. Spectra in Kubelka-Munk units with scales different for each spectrum. Wavenumber scale change at 2000 cm^{-1}.

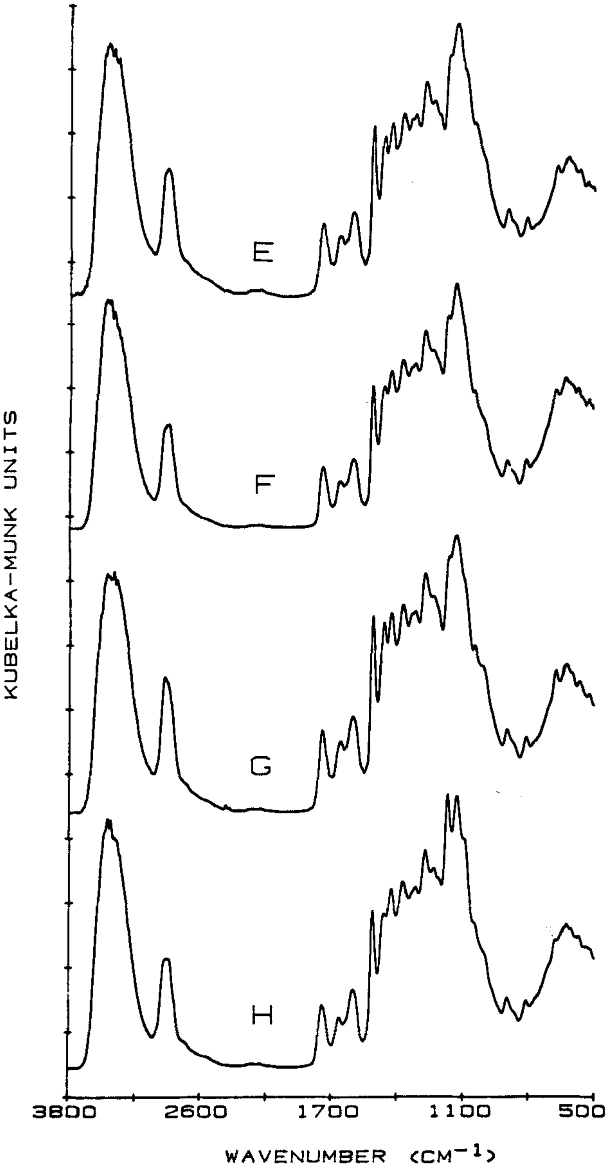

Figure 3. DRIFT spectra of sanded (150 grit) white fir wood surfaces: tangential section of early-wood (E), tangential section of late-wood (F), and radial section (G), all with grain oriented parallel to the light beam; and early-wood tangential section with grain oriented perpendicular to the light beam (H). All spectra in Kubelka-Munk units. Scale change at 2000 cm^{-1}.

enough, when the surface roughness was increased with 100 grit sandpaper, the doublet disappeared and the band became identical to that in spectra E - G.

Relatively small differences in correlation coefficients (R) were found between the normalized peak heights of spectra E - H and those of transmission spectrum A (for calculation method see Table 1). The highest (R = 0.875) was obtained with spectrum E, and the lowest (0.801) with the spectrum G, while spectra F and H exhibited intermediate R values (0.826 and 0.838, respectively). The correlation coefficients for spectra E - H *inter se* showed negligible differences and were very high (R = 0.982 - 0.996).

Depth of Penetration of Infrared Light

As was mentioned earlier, knowledge of the depth of penetration of infrared light in DRIFT of whole wood samples is critical for meaningful analysis of their surface. If chemical changes being studied involve only a very thin upper layer of wood, deep light penetration would produce spectra which are influenced largely by the chemistry of the bulk of unchanged wood, making it difficult or even impossible to detect surface changes. Furthermore, variations in the depth of light penetration due to varying wood characteristics could affect comparisons between individual samples.

The depth of penetration of infrared light in wood was estimated by determining the height (in Kubelka-Munk units) of the 2242 cm $^{-1}$ band (CN stretching) of polyacrylonitrile powder covered with wood sections of various thicknesses. The results thus represent changes in the Kubelka-Munk intensity of the CN band due to screening by the wood.

At the wavenumber of the CN band both cellulose and lignin absorb negligibly so that the loss of light intensity as it penetrates the wood should be due mainly to factors other than absorption, such as Fresnel reflectance, refraction, and diffraction. Since the refractive index of the medium (in this case wood) depends upon its absorptivity and influences the above factors, the depth of penetration of light measured by this technique will be strictly valid only for the area near the wavenumber used and should be considered only as a rough estimate for other regions of the DRIFT spectrum.

Plots of the Kubelka-Munk CN peak height versus wood section thickness are given in Fig. 4 for balsawood (Ochroma lagopus Sw.), and Pacific yew (Taxus brevifolia Nutt.), densities 0.148 and 0.676 g/ml, respectively. Similar plots for uncompressed and compressed white fir wood (densities 0.445 and 1.150 g/ml, respectively) are given in Fig. 5.

In all cases the intensity of the CN peak decreased approximately exponentially with wood thickness. The rate of decrease depended, however, upon the wood density. Thus the overlay thickness causing a 90% CN peak intensity loss varied linearly from about 138 μm for Balsawood to about 37 μm for compressed white fir (Fig. 6). This relationship is most likely due to the increased concentration of inhomogeneous anatomical elements in denser woods giving rise to increased Fresnel reflectance, refraction and diffraction. The phenomenon could be important in, for example, the surface analysis of samples containing both early- and late-wood, where the depth of penetration would be less with the denser late-wood.

Recently, McKenzie *et al.* [18] and Culler *et al.* [19] reported that in DRIFT spectroscopy the depth of penetration of infrared radiation in neat polymers can be reduced to 1.5 μm by using an overlayer of finely-powdered KBr or similar materials. They allowed, however for "the possibility that the bands observed in the DRIFT spectra .... are due not to chemical differences in the surface carbonyl groups but to band distortions and splittings due to refractive index complications."

When we applied this technique to the surface of untreated and oxygen radiofrequency plasma-treated wood, we obtained low-intensity, poorly resolved spectra whose differences from spectra obtained without KBr could not be clearly attributed to a reduction in the depth of penetration.

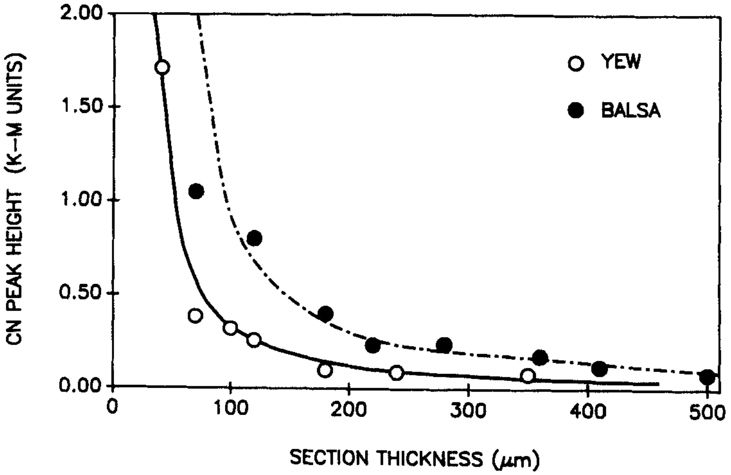

Figure 4. Intensity of polyacrylonitrile CN stretching band (2242 cm^{-1}) as a function of the thickness of balsawood and Pacific yew wood overlays.

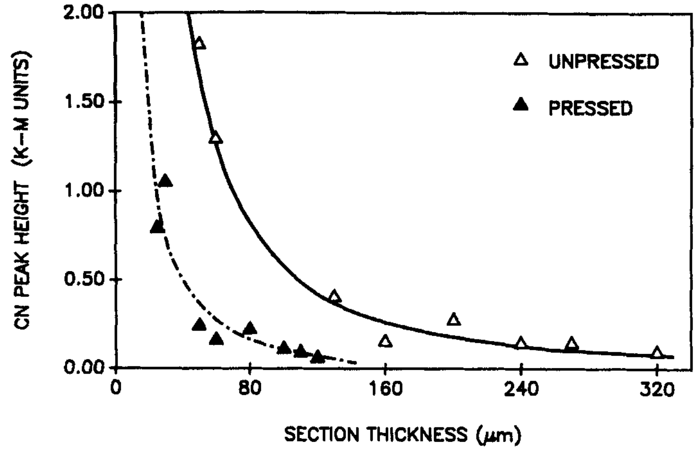

Figure 5. Intensity of polyacrylonitrile CN stretching band (2242 cm^{-1}) as a function of the thickness of uncompressed and compressed white fir overlays.

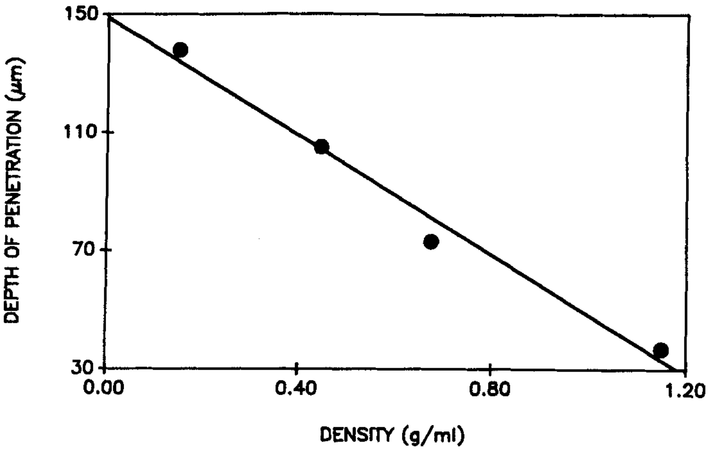

Figure 6. Wood thickness required to reduce to 10% of its original value intensity of the CN stretching band of polyacrylonitrile as a function of wood density.

Application to Surface Analysis

Samples of white fir early-wood were subjected to (1) treatment with O_2 radiofrequency plasma, (2) treatment with Cl_2 gas, (3) treatment with NO_2 gas, and (4) thermal degradation of the surface; then the DRIFT spectra (Fig. 7) were compared with that of the untreated surface.

No differences could be observed in the spectrum of the sample treated with radiofrequency plasma (O_2 atmosphere, 300 W, 30 min.). This could be due to two effects - (1) Oxidative changes could be limited to an extremely thin layer at the wood surface, in which case the chemical changes would be masked by the chemistry of the unchanged bulk of the wood; and (2) predominant removal of the wood substance by physical sputtering, with negligible oxidative changes [20]. That sputtering is not solely responsible for wood removal has been recently demonstrated by experiments with ESCA which indicate that O_2 plasma treatment results in some oxidative changes on the surface [21].

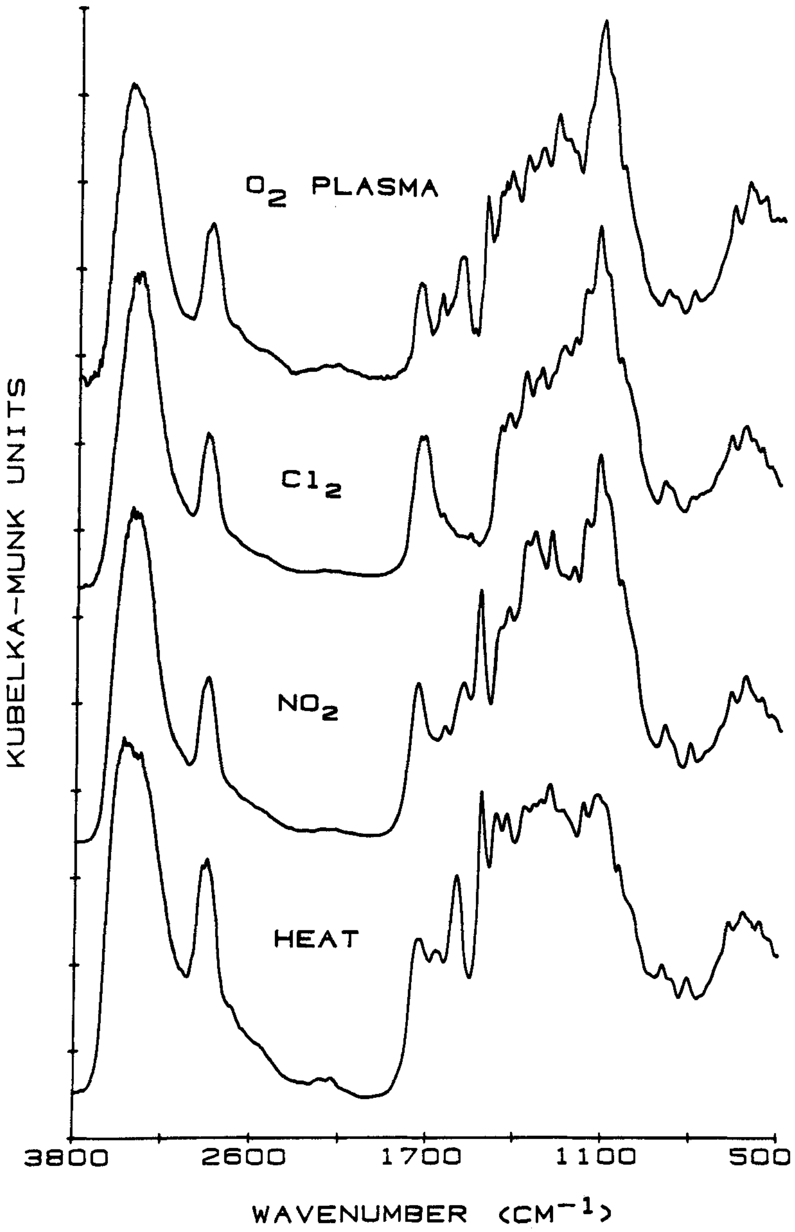

Figure 7. DRIFT spectra of white fir wood (150 grit sanded) after treatment with oxygen radiofrequency plasma, chlorine gas, nitrogen dioxide gas, and a heated metal plate. Spectra in Kubelka-Munk units. Scale change at 2000 cm^{-1}.

Treatment of wood with chlorine gas for 60 min., followed by water extraction, doubled the intensity of the carbonyl 1736 cm^{-1} stretching band, and also shifted it to 1719 cm^{-1}. In addition, bands at 1602 and 1511 cm^{-1} (aromatic skeletal vibrations) either disappeared or decreased drastically. Surprisingly, no bands assignable to carbon-chlorine stretching (around 800 cm^{-1}) could be identified. The observed changes are consistent with processes known to take place when wood is chlorinated in the analysis of holocellulose. This process involves degradation of lignin by chlorinating and opening the benzenoid rings, and by splitting and oxidation of sidechains, all of which leads to formation of a great variety of products, many of them carrying carbonyl groups [22].

Treatment of wood samples with nitrogen dioxide for 60 min., followed by water extraction, resulted in less drastic changes in the spectrum. The largest change was the doubling in intensity of the carbonyl band at 1736 cm^{-1}, most likely due to oxidative formation of carbonyl groups.

Thermal degradation of the wood surface using a metal plate heated to just below red heat gave a DRIFT spectrum quite similar to that of a very smooth (600 grit sanded) wood surface. It appears that contact with the heated metal effectively polished the wood surface. The aromatic band at 1602 cm^{-1} did shift to 1595 cm^{-1} and also increased in intensity by about 40% compared to the untreated wood spectrum. These changes are possibly due to formation of aromatic furan structures from carbohydrates.

CONCLUSIONS

Direct DRIFT spectroscopy of wood surfaces represents an excellent method for studying their chemistry if the inherent depth of penetration of infrared light (90% intensity loss at 37 - 138 μm, wood density dependent) is appropriate to the problem at hand. It appears advantageous to express the results in Kubelka-Munk units. In order to obtain consistent results the surfaces must be of the same - preferably high - roughness; grain orientation and late- vs early-wood appear to be of secondary importance, particularly if the sample surfaces are sufficiently rough.

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