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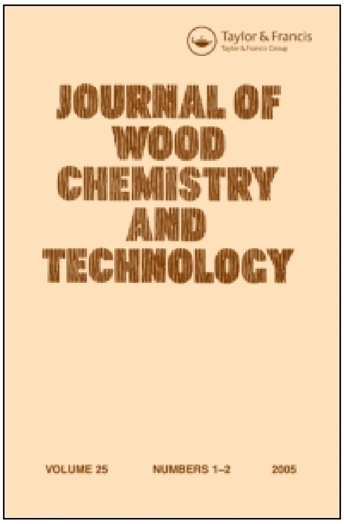

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ANALYSIS OF SOLID WOOD SURFACES BY INTERNAL REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR-IRS)

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ABSTRACT

The refractive index of white fir wood in the infrared region of the spectrum was determined by a measurement of the critical angle in FTIR-IRS to be 1.43. The depth of light penetration into wood (decrease in the original light intensity to 1/e) was calculated to be 0.13 - 2.15 μm depending upon the wavelength of light, angle of incidence, and the refractive index of the prism used. It was found that the signal-to-noise ratio in FTIR-IRS of wood could be greatly increased by either pressing the wood for 10 min. at 2,500 psi or sanding it against a flat surface with fine (600 grit) sandpaper. Microtoming alone was not satisfactory in producing a smooth surface and a high signal/noise ratio. The FTIR-IRS spectrum of oxygen plasma-treated wood indicated a substantial absorbance increase in the 1648 - 1633 cm^{-1} region due to formation of carbonyl groups.

INTRODUCTION

In our current work on the action of cold radiofrequency plasma upon the surface of solid wood we sought to apply infrared analysis to study chemical changes in the wood surface brought about by plasma treatment. In

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an earlier paper [1] we reported on the direct (neat) analysis of a wood surface by diffuse-reflectance Fourier transform infrared spectroscopy (DRIFT) and the factors influencing the resultant spectra. In the present paper we direct our attention to the other method for obtaining infrared spectra of a solid surface - internal reflection FTIR spectroscopy (FTIR-IRS) [2]. The theory and applications of the method have been summarized in a number of publications [3-5].

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In FTIR-IRS analysis a beam of IR light, introduced at a suitable angle, undergoes multiple total reflections as it passes through a prism of a transparent material (internal reflection element - IRE). If the reflecting faces of the IRE are in contact with an absorbing material, part of the light energy will be absorbed at the interface. The laws governing such absorption are primarily the same as those that govern the absorption of light in transmission and the two types of spectra are qualitatively quite similar. Significant quantitative differences arise, however, due to complications connected with the depth of penetration of infrared radiation into the sample and from difficulties in obtaining good contact between the IRE and a rigid sample surface. Investigation of the practical effects of these phenomena in the case of wood is the purpose of this study.

EXPERIMENTAL

Spectra were obtained on a Nicolet 20SX Fourier Transform Infrared Spectrophotometer, using 30 scans per spectrum, resolution 4 wave numbers, with a SpectraTech Model 300 Continuously Variable ATR (IRS) attachment (KRS-5 crystal). Samples were clamped against the crystal by tightening to 20 in-oz torque. For radiofrequency plasma generation a modified LTA-604 low-temperature asher (LFE Co.) operating at 13.56 MHz was used.

For study of compression, tangential 100 μm microtomed white fir wood sections were compressed with a Carver laboratory press between small 0.6 cm thick glass plates. Metal surfaces did not work as well and showed a noticeable flow at the pressure used. For study of surface roughness, 2-3 mm thick white fir samples were used. Sanding was done using commercial sandpaper against a flat surface.

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RESULTS AND DISCUSSION

Depth of Penetration

In FTIR-IRS, the depth of penetration of infrared light into a sample of wood can influence the spectrum in several ways. First, if the overall depth of penetration is much larger than the thickness of the surface layer of interest, the spectral information from the sample interior will mask that from the surface. Second, the increase in the depth of penetration with wavelength causes a proportional increase in the effective path length - and thus the absorbance - of the light. Finally, dispersive variations in the sample refractive index can alter the depth of penetration throughout the spectrum in a complex way and lead to spectral distortions.

The depth of penetration of electromagnetic radiation undergoing total internal reflection into the less optically dense of two materials in close contact is given by equation (1) [3-5]:

$$d_p = \frac{\lambda}{2\,\pi\, n_1 \surd[\sin^2\Theta - (n_2/n_1)^2]} \qquad (1)$$

where: d_p is the depth in μm at which the intensity of electromagnetic radiation drops to 1/e (36.8%) of its initial intensity. The variables influencing d_p include the wavelength of the light in vacuum (λ); the effective angle of incidence of the light beam (Θ); and the refractive indices of the IRE (n_1) and of the material investigated (wood in our case) (n_2), at the particular wavelength of the radiation. Since according to equation (1) d_p increases linearly with increasing wavelength, as mentioned earlier, the FTIR-IRS spectrum will differ from a transmission spectrum by exaggerated absorbance values at longer wavelengths. This problem can be simply remedied by multiplying the FTIR IRS absorbance values by λ/λ_o, (λ_o = shortest wavelength included in the spectrum) (Fig.1).

The last mentioned effect of dp on the FTIR-IRS spectrum - that due to variations in n_2 - is less easily accounted for. These variations in n_2 are closely connected with the absorption of electromagnetic radiation and are thus a function of the intensity of the individual bands. In theory, this leads to

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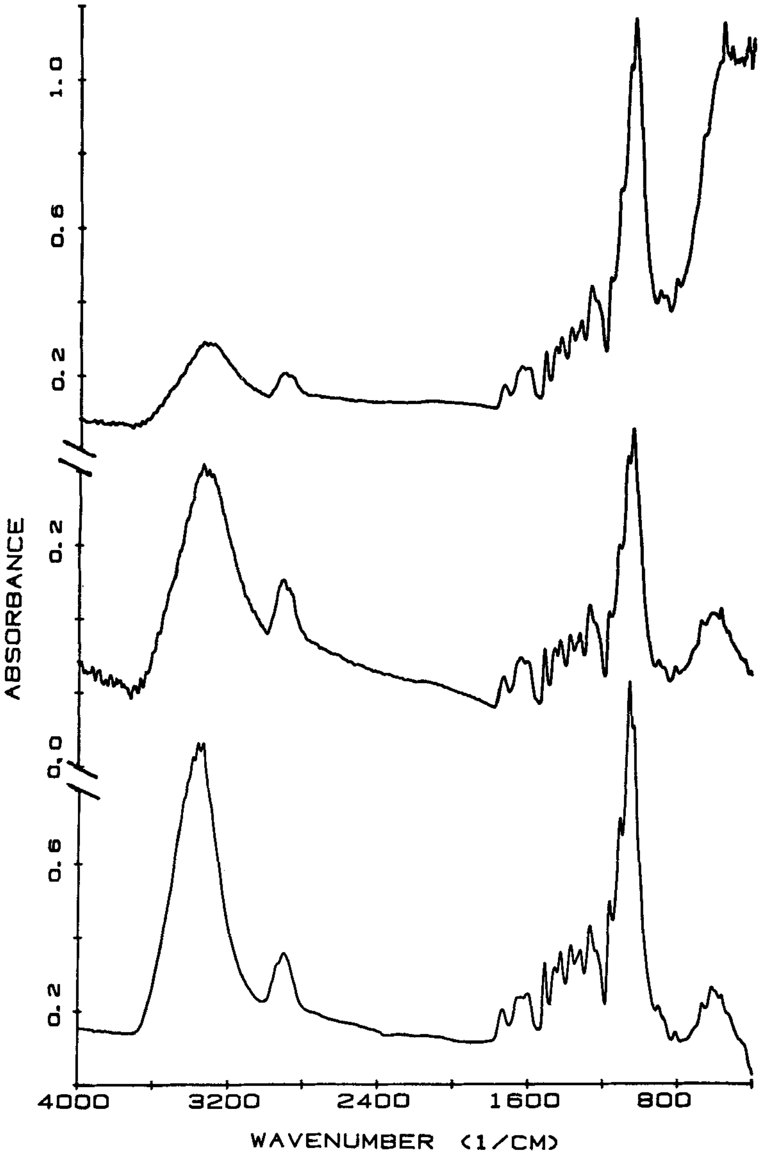

Figure 1. Infrared spectra of white fir wood. Top - FTIR-IRS spectrum, uncorrected; center - FTIR-IRS spectrum corrected for the depth of light penetration due to variation in wavelength; bottom - infrared spectrum obtained by transmission using 50 μm section of wood.

fluctuations in dp and distortions of the absorption bands throughout the infrared spectrum.

Although mathematical correction of the FTIR-IRS spectrum for these distortions is not easily feasible, they can be practically minimized (Equation 1) by choosing larger Θ and smaller n_2/n_1 ratios, the former by simple adjustment and the latter by selecting a prism of high n_1, for example germanium ($n_1 = 4.01$).

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The infrared dispersion of n_2 has been calculated for a number of organic substances, including a few polymers, using the so-called Kramers-Kronig transformation [6-11]. While n_2 was reasonably constant in the non-absorbing spectral areas, in the areas of absorption it fluctuated above and below this value assuming a first derivative-like shape for each absorption band. At the same time the average values for n_2 for the absorbing regions were roughly the same as n_2 for the nonabsorbing regions of the spectrum. It follows that while it is possible to calculate d_p for all nonabsorbing regions of a spectrum using equation (1), the same d_p would only be an "average" d_p for the absorbing parts. Since a literature search indicated that the refractive index of wood is unknown for the infrared region, we used the relationship between the critical angle Θ_c and the refractive indices of wood and the IRE to estimate its magnitude [3,5] :

$$\Theta_c = \sin^{-1} n_2/n_1 \qquad (2)$$

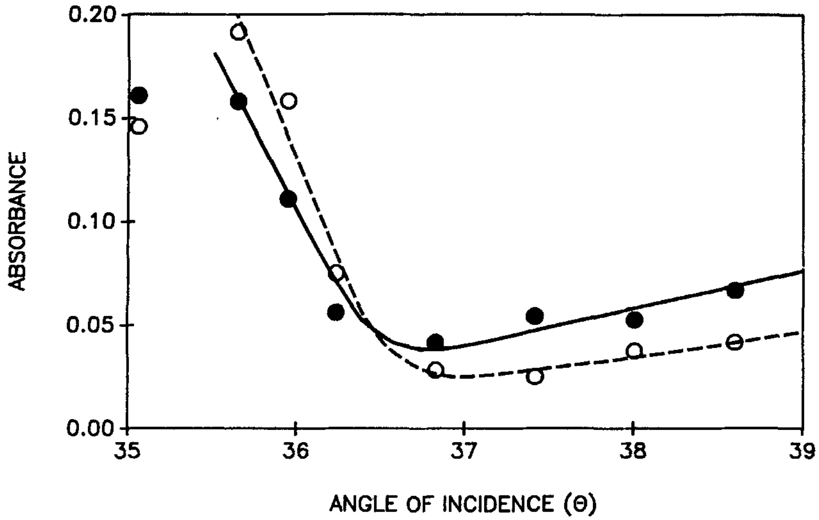

Figure 2. Plot of absorbance at 4000 (white circles) and 2000 cm^{-1} (filled circles) vs angle of incidence (ϴ) for white fir wood.

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Using the FTIR-IRS attachment we obtained a series of infrared spectra of wood (tangential section of white fir, precompressed at 2,500 psi) at angles of incidence varying from 35.1-38.6°. Plots of the absorbance at 4000 cm^{-1} and at 2000 cm^{-1} vs angles of incidence, and the spectra obtained at angles of 35.6° and 37.4°, are reproduced in Fig 2. At slightly below ϴ = 37° the absorbance begins to sharply increase as total internal reflection is lost, part of the light being transmitted into the wood. At about the same angle the spectrum changes from a typical FTIR-IRS (with short wave length bands suppressed), to a more DRIFT-like spectrum, most likely due to a part of the transmitted radiation being diffusely-reflected from the wood back into the IRE (Fig. 3).

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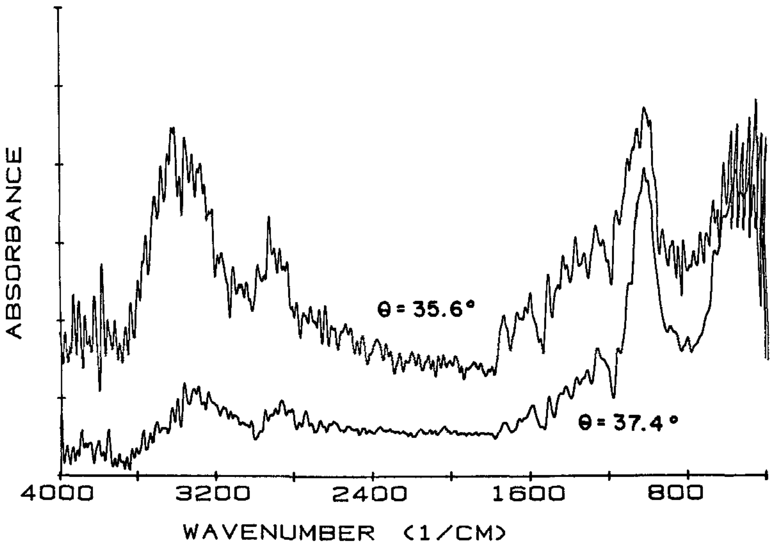

Figure 3. FTIR-IRS spectra obtained at Θ = 35.6° (below Θ_c) and Θ = 37.4° (above Θ_c). The spectra are rather noisy since near Θ_c the amount of light reaching the detector is very small.

From a value for the critical angle $\Theta_c = 36.9°$, obtained by interpolation, a refractive index of $n_2 = 1.43$ for the weak-to non-absorbing regions of the spectrum (4000 - 3700, and 2500 - 1800 cm^{-1}) was calculated; for strongly absorbing regions this would represent only the mean value as here n_2 exhibits wave-like fluctuations due to light absorption, as discussed earlier. Calculations of d_p for wood are given in Table 1 for KRS-5 and Germanium IREs, for wavenumbers of 4000, 2000, and 834 cm^{-1} (absorbance low to none), and for Θ = 45° and 60°.

TABLE 1

Depth of Penetration in μm of Infrared Radiation (Intensity Decrease to 1/e (36.8%)) in Wood for KRS-5 and Germanium IREs. [12,13].

Wavenumber	Wavelength	KRS-5 (n_1=2.38)		GERMANIUM (n_1=4.01)	
cm^{-1}	μm	θ=45°	θ=60°	θ=45°	θ=60°
4000	2.5	0.45	0.27	0.16	0.13
2000	5.0	0.90	0.54	0.32	0.25
834	12.0	2.15	1.29	0.78	0.60

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In our examination of the DRIFT method for obtaining infrared spectra of a wood surface [1] we concluded that the depth of penetration of infrared light (90% loss of intensity) varied between 20 and 160 μm depending upon wood density. Since in FTIR-IRS the amplitude of the electric field falls exponentially with the distance from the surface [3], the distance $d_p(f)$ at which light intensity drops to any chosen fraction (f) of the original intensity can be calculated by multiplying $d_p(1/e)$ in (1) by -ln f. For f=0.1 (90% loss of light intensity) and the data of Table 1, $d_p(O.1)$ is between 0.29 (Ge IRE, 60°) and 4.96 (KRS-5, 45°) μm., which is roughly 50 times less than with DRIFT. Thus it appears that from the standpoint of the depth of light penetration FTIR-IRS is more suited than DRIFT for the study of chemical changes taking place at the wood surface. Nevertheless, the d_p calculated for FTIR-IRS is still only slightly less then the thickness of the tracheids (1.5 - 7.0 μm) [14] and is several thousand times larger than a unit

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cell of cellulose (16.34 X 15.72 X 10.38 Å) [15]. FTIR-IRS is thus still ill-suited for investigation of chemical phenomena involving wood surface layers a few molecular diameters thick.

Contact between IRE and Wood

In order to maximize the signal-to-noise ratio of the internal reflectance spectrum, it is very important to ensure good contact between the material and the IRE. This is generally not a problem with liquids, powders, or pliable thin films, but it becomes much more difficult with a rigid substance like wood. A significant improvement in this direction was the introduction of FTIR-IRS attachments which allowed the application of pressure against the sample during the run. A number of additional methods have been proposed to further improve wood-IRE contact [13, 16, 17], of which the best is probably that of Michell [13] who used thin microtomed wood sections against a backing of double-sided adhesive tape.

To optimize the FTIR-IRS spectra, we investigated the possibility of improving wood-IRE contact by pre-pressing the sections against a hard, flat surface or finely sanding the specimens. To evaluate the degree of wood-IRE contact we used the absorbance at 1,025 cm^{-1} (strongest band in the wood spectrum).

The influence of pressing time on the absorbance of the 1,025 cm^{-1} band of white fir at a constant pressure of 2,500 psi and a temperature of

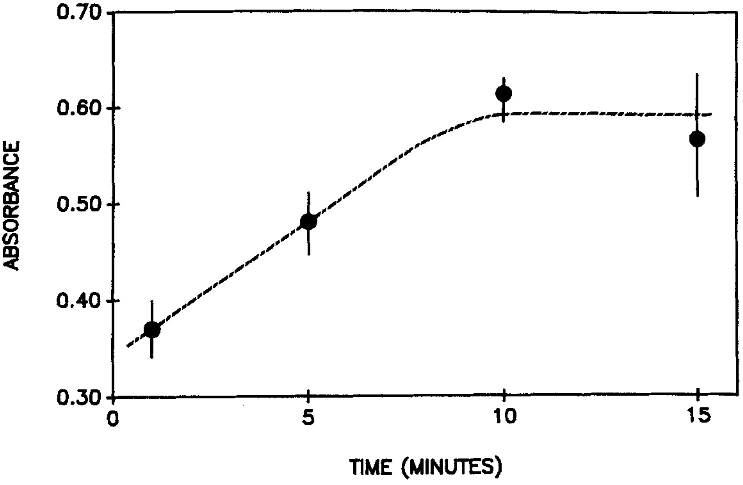

Figure 4. Influence of time of sample pressing (2500 psi) on the absorbance value of the 1,025 cm^{-1} band.

50°C is summarized in Fig. 4. Under these conditions a time of 10 min. was sufficient to reach the maximal value. It is likely, however, that the time might vary with the hardness of the wood and would be less at higher pressures and temperatures.

We expected that an increase in temperature of the press plates would increase the absorbance due to softening of hemicelluloses and lignin. However, the observed absorbance increase between samples pressed at 20-90°C and 91-130°C (P=2,500 psi, t=10 min.) was only 2.5% and was statistically insignificant.

Applied pressure, in contrast, exerted a very strong influence on the absorbance values (Fig. 5). Somewhat higher absorbance values were reached

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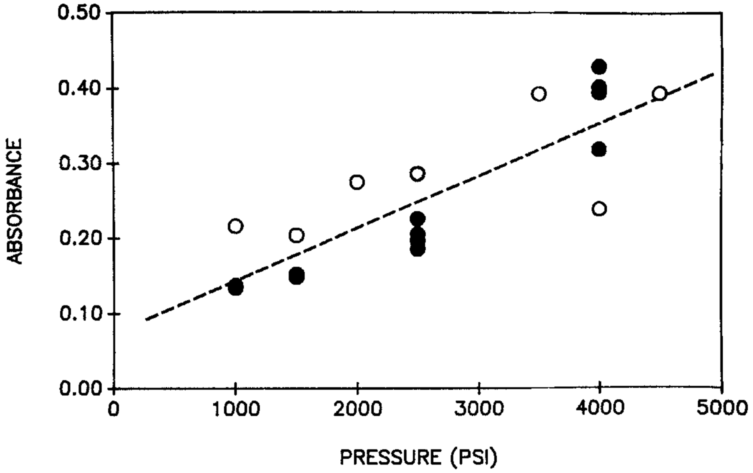

Figure 5. Influence of pressure (10 min) on the FTIR-IRS absorbance of the 1,025 cm^{-1} band of white fir wood. White circles - T = 90-110°C; black circles - T = 20-70°C.

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when higher press temperatures were used but the effect was again not very pronounced.

The influence of surface roughness was investigated by sanding the sample surface with commercial paper of various grits and measuring the absorbance. The sandpaper grit used exerted a strong influence on absorbance, the values increasing from about A=0.1 (grit 100) to about A=0.6 (grit 600) (Fig.6). Interestingly enough, wood surfaces prepared by microtoming showed absorbance values equivalent to the roughest surfaces. Subjecting samples sanded with 600 grit paper to pressing at 2,500 psi (10 min, 20°C) did not further increase the absorbance.

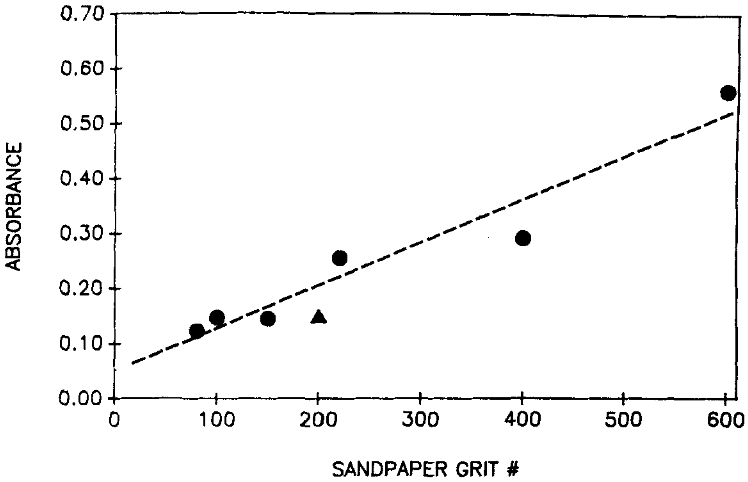

Figure 6. Influence of sandpaper grit on the absorbance of the FTIR-IRS 1,025 cm^{-1} band of white fir wood. Triangle - microtomed surface.

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It can be concluded that microtoming does not represent an optimal method for preparation of wood surfaces for FTIR-IRS. Pressing the surface against glass or, in cases where the experiment allows removal of material from the surface, fine-sanding (e.g. 600 grit paper) produces a surface giving an IR spectrum with a high signal-to-noise ratio.

FTIR IRS Spectrum of the Radiofrequency Plasma Treated Wood

In our earlier report we mentioned the failure of DRIFT to detect oxidative changes on the surface of white fir wood following treatment with oxygen radiofrequency plasma despite the fact that such changes (increase in carbonyl groups) has been demonstrated by ESCA analysis [1]. This was

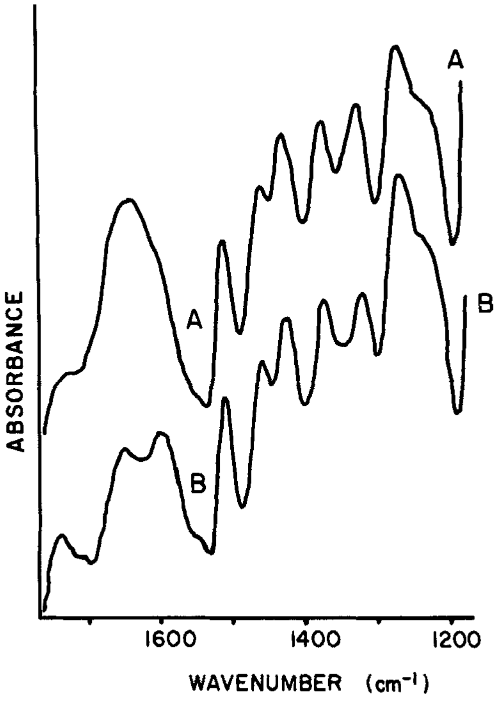

Figure 7. FTIR-IRS Spectrum (1200 - 1760 cm^{-1}) of the surface of white fir wood (A) treated with radiofrequency plasma (30 min, 300 W) and (B) not treated.

explained by the relatively large depth of penetration of IR light which resulted in the bulk of the spectral information coming from the deeper, unaffected wood regions, thus masking the surface changes. Since the depth of penetration in FTIR-IRS is about 50 times less than that of DRIFT it was of interest to see whether the oxidative surface changes brought about by plasma could be detected by FTIR-IRS.

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Fig. 7 clearly demonstrates a strong increase in carbonyl absorption at 1,648 - 1,633 cm^{-1} following plasma treatment. The position of the band suggests the formation of acid or keto carbonyls which are hydrogen bonded to neighboring hydroxyl groups.

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