

# NOTE ON A TECHNIQUE FOR OBTAINING INFRARED SPECTRA OF TREATED WOOD SURFACES

*Anthony J. Michell*

Principal Research Scientist  
CSIRO Division of Forestry and Forest Products  
Private Bag 10, Clayton, 3168  
Australia

(Received May 1987)

## ABSTRACT

This note describes a simple technique for obtaining good quality frustrated multiple internal reflectance (FMIR) infrared spectra of treated wood surfaces. The effect on *Pinus radiata* wood treated with 30 percent aqueous hydrogen peroxide is shown as an example.

*Keywords:* Frustrated multiple internal reflectance, infrared spectra, wood surfaces.

## INTRODUCTION

Much of the useful information about wood and about changes in its chemistry resulting from various treatments can be obtained from its infrared spectrum (Marchessault 1962; Harrington et al. 1964). To overcome problems arising from scattering when absorption by milled wood is used, Tschamler et al. (1953) suggested the use of thin wood sections, and Harrington et al. (1964) extended this technique to the use of a sandwich of up to five thin wood sections in pressed potassium chloride, noting that the quality of the spectra could be greatly improved. Such techniques, however, give information about the bulk of wood rather than its surface. The surface of wood and its modification are now of considerable interest in relation to wood's activation for bonding (Jenkin 1976; Zavarin 1984) and its degradation by agents such as ultraviolet light (Hon and Chang 1984).

One means of measuring directly the infrared spectrum of a wood surface is by using the frustrated multiple internal reflectance (FMIR) technique (Hse and Bryant 1966; O'Brien and Hartman 1969). This technique requires a sample to be placed in intimate contact with a flat surface of a prism of a material having a higher refractive index. When infrared radiation passes through the crystal in such a way that it undergoes multiple reflections, it enters the surface of the contacting sample where some of the radiation is absorbed and the remainder reflected. Clearly the degree of contact between the sample and the prism is critical. The difficulty with wood samples is that their surfaces are naturally neither smooth nor conformable.

This note describes a simple technique for obtaining good quality FMIR spectra of wood surfaces.

## EXPERIMENTAL

Sections 15  $\mu\text{m}$  thick were cut from the tangential surfaces of water-saturated *Pinus radiata* wood. Details of the sandwich technique used with these sections have been given previously (Harrington et al. 1964). An area of 50  $\times$  20 mm for the FMIR spectra was obtained by joining a number of 100  $\mu\text{m}$  sections on double-sided adhesive tape (Bear 13A ex Norton) and excess tape was trimmed off. Two

samples prepared in this manner were then fixed, to a given pressure set with a torque wrench, against the faces of a KRS-5 prism in a RIIC TR25 FMIR unit.

The treated sections were first wet with 0.1 M FeSO<sub>4</sub> and then dried between polyester cloths and blotters and then in an oven between microscope slides. The dried sections were then wet with 30% (aq) H<sub>2</sub>O<sub>2</sub>, flattened between the slides and heated in an oven at 105 C for 40 min.

The spectra were obtained by using a Mattson Alpha Centauri Fourier Transform Infrared Spectrophotometer equipped with a water-cooled source, with a computer-controlled iris and a DTGS detector. They were at a resolution of 4 cm<sup>-1</sup> and were averages of 64 scans. Background spectra were obtained with the FMIR unit in the spectrophotometer without having a sample against the crystal.

The difference spectra in Figs. 1C and 2C were obtained by using the computer to adjust the pairs of spectra in Figs. 1A and 1B and 2A and 2B, respectively, so that the integrated absorptions in the region 3,050–2,750 cm<sup>-1</sup> (C–H stretching region) were equal and then performing the subtraction on each pair.

#### RESULTS AND DISCUSSION

Commercial multiple internal reflection crystals are available offering up to 25 internal reflections. These reflections take place over an area of 50 × 20 mm. To obtain suitable samples ca. 1.5 mm in thickness, O'Brien and Hartman (1969) used a cutting and glueing technique. Veneers might also be used. However, samples prepared by these means are rather stiff and unconformable. The present technique involves joining microtomed sections together against a backing of double-sided adhesive tape. The compressibility of the tape assists in overcoming variability arising from uneven sectioning and other causes of surface roughness.

Some differences are to be expected between the absorption and FMIR spectra of wood. First, one arises from the bulk, while the other arises from the surface of the sample. Second, there is a dependence of the intensities of the bands in the FMIR spectra on frequency arising from variation in the depth of penetration with frequency. Harrick (1967) showed that the depth of penetration (d) of the wave into the medium is given by

$$d = \lambda/2\pi[\sin^2\theta - (n_2/n_1)^2]^{1/2} \quad (1)$$

where  $\lambda$  = wavelength,  $\theta$  = angle of incidence (45°),  $n_1$  = refractive index of KRS-5 prism ( $\sim 2.38$ ),  $n_2$  = refractive index of wood ( $\sim 1.55$ ).

For the range 2,000–600 cm<sup>-1</sup> (5.0–16.7  $\mu$ m) studied here, the depth of penetration will vary from 2.8 to 9.4  $\mu$ m.

Difference spectroscopy is a very useful technique for showing changes in samples and is now achieved simply with Fourier Transform Infrared Spectrophotometers.

Figure 1 shows the FMIR infrared spectra of a tangential surface of *Pinus radiata* wood, a similar surface after oxidation with hydrogen peroxide and the difference spectrum.

For comparison, Fig. 2 shows the corresponding infrared absorption spectra obtained by using the sandwich technique with two 15- $\mu$ m tangential sections of the same wood (Harrington et al. 1964). Overall, the peaks in the absorption spectra are better defined than those in the FMIR spectra. The frequencies of the peaks in the corresponding spectra in the two groups are the same. The most

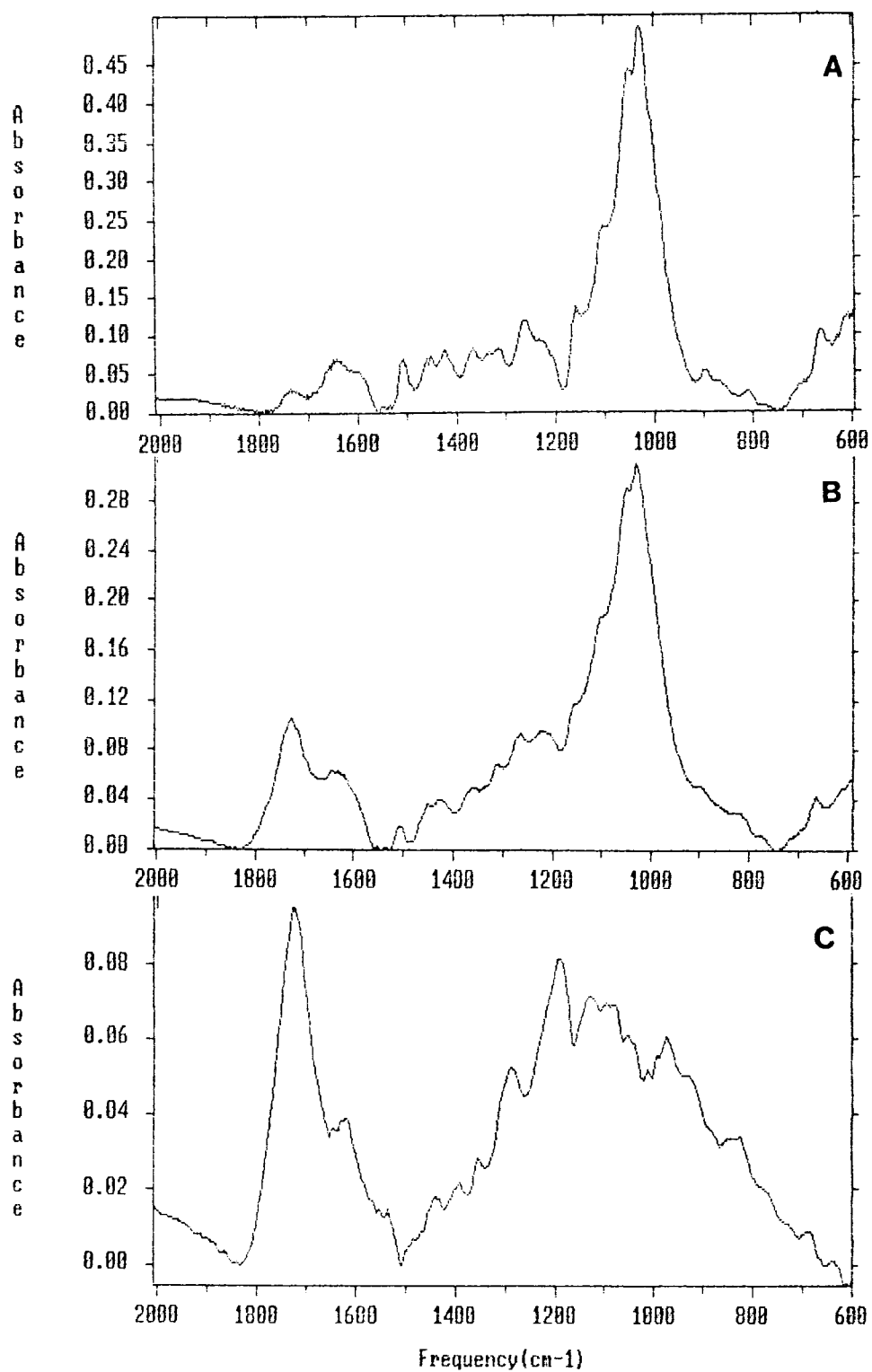


FIG. 1. FMIR infrared spectra of A. Tangential surface of *Pinus radiata* wood. B. Same surface treated with Fe<sup>++</sup> and 30% (aq) H<sub>2</sub>O<sub>2</sub>. C. Difference spectrum (B-A).

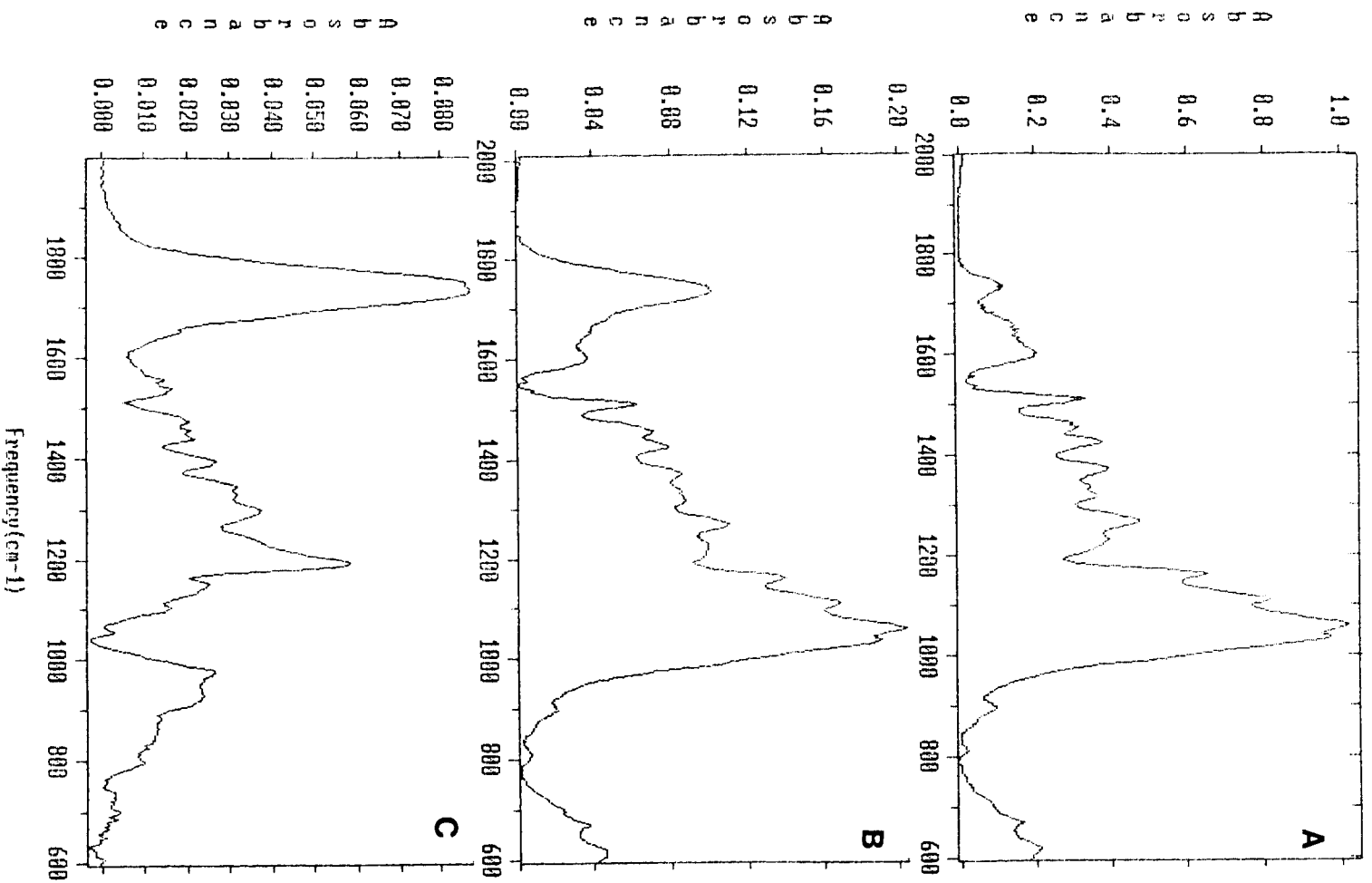


Fig. 2. Infrared absorption spectra of A. Sandwiche of tangential sections of *Pinus radiata* wood. B. Same sections treated with Fe³⁺ and 30% (aq) H₂O₂. C. Difference spectrum (B-A).

marked variations are to be found in the region  $1,150\text{--}1,000\text{ cm}^{-1}$  of the difference spectra, but this is not surprising as it is a region of intense absorption in the parent spectra and therefore very sensitive in the difference spectra to any mismatching in the subtraction procedure.

The strongest peaks in the FMIR difference spectrum (Fig. 1C) are found near  $1,730$ ,  $1,620$ ,  $1,290$ ,  $1,190$ ,  $1,130$  and  $974\text{ cm}^{-1}$ . In the absorption difference spectrum (Fig. 2C), the major peaks are near  $1,735$ ,  $1,390$ ,  $1,290$ ,  $1,190$  and  $978\text{ cm}^{-1}$ . The expected effect of the treatment with hydrogen peroxide is oxidation. The  $1,730\text{ cm}^{-1}$  band in the reflectance spectrum of similarly treated cellulose was assigned to a C=O stretching vibration of carboxyl groups (Jenkin 1976). Other vibrations of carboxyl groups give rise to a peak near  $1,400\text{ cm}^{-1}$ , a doublet between  $1,300$  and  $1,200\text{ cm}^{-1}$  and a peak between  $980$  and  $930\text{ cm}^{-1}$  (Flett 1951; Freeman 1952).

#### CONCLUSION

The simple technique described above enables the FMIR infrared spectra of wood surfaces to be obtained with a quality nearly equal to that of the infrared absorption spectra from wood sections and sufficiently good to give useful information concerning chemical changes when the surfaces are treated with reagents such as hydrogen peroxide. Moreover, the specimens are much more robust than in the case of thin wood sections used for absorption spectra. Studies of the changes in the chemistry of wood surfaces treated with a wider range of reagents will be reported shortly.

#### ACKNOWLEDGMENTS

The author thanks Messrs. Y. Ilic, J. P. Yuritta, and J. Ward for their skilled cutting of sections.

#### REFERENCES

- FLETT, M. STC. 1951. The characteristic infrared frequencies of the carboxylic acid group. *J. Chem. Soc.*:962-967.
- FREEMAN, N. K. 1952. Infrared spectra of branched long-chain fatty acids. *J. Am. Chem. Soc.* 74: 2523-2528.
- HARRICK, N. J. 1967. Internal reflection spectroscopy. P. 30. John Wiley and Sons, New York, London, Sydney.
- HARRINGTON, K. J., H. G. HIGGINS, AND A. J. MICHELL. 1964. Infrared spectra of *Eucalyptus regnans* F. Muell and *Pinus radiata* D. Don. *Holzforschung* 18:108-113.
- HON, D. N.-S., AND S.-T. CHANG. 1984. Surface degradation of wood by ultraviolet light. *J. Polym. Sci.: Polym. Chem.* 22:2227-2241.
- HSE, C.-Y., AND B. S. BRYANT. 1966. The infrared analysis of thin wood sections by attenuated total reflectance. *J. Jap. Wood Res. Soc.* 12(4):187-191.
- JENKIN, D. J. 1976. Infrared spectroscopy of chemically oxidized wood. *J. Appl. Polym. Sci: Appl. Polym. Symp.* 28:1309-1320.
- MARCHESSAULT, R. H. 1962. Application of infrared spectroscopy to cellulose and wood polysaccharides. *Pure Appl. Chem.* 5:107-129.
- O'BRIEN, R. N., AND K. HARTMAN. 1969. Infrared spectra of wood surfaces by attenuated total reflectance spectroscopy. *Pulp Paper Mag. Can.* 70:T122-T124.
- TSCHAMLER, H., K. KRATZL, R. LEUTNER, A. STEINNGER, AND J. KISSER. 1953. The infrared spectra of microscopic wood sections and of some model substances. *Mikroskopie* 8:238-246.
- ZAVARIN, E. 1984. Activation of wood surface and nonconventional bonding. Pages 349-400 in R. Rowell, ed. *The chemistry of solid wood. Advances in Chemistry Series No. 207* ACS, Washington DC.