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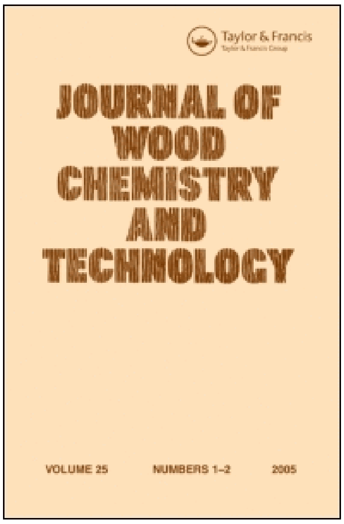

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# An Anomalous Effect in the Drift Spectra of Woods and Papers

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# AN ANOMALOUS EFFECT IN THE DRIFT SPECTRA OF WOODS AND PAPERS

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## ABSTRACT

Diffuse Reflectance Fourier Transform Infrared (DRIFT) Spectroscopy is a very useful and convenient means of obtaining the infrared spectra of woods and papers. However, distortions can occur in the intensities of bands in the region 950-1200 cm$^{-1}$ when the spectra are obtained by reflection directly from wood and paper surfaces due to interference from specularly reflected radiation. Such distortions are reduced in spectra obtained from very thin sheets of paper or from fibres diluted in potassium bromide.

## INTRODUCTION

Infrared spectroscopy is a very useful technique for obtaining information about woods and papers [1,2] and about chemical changes taking place in them resulting from various treatments or exposure in service. Its usefulness has been greatly enhanced by the increase in sensitivity resulting from the combination of Fourier Transform and computer techniques [3].

Scattering at fibre/air interfaces causes problems in the transmission spectra of even thin wood and paper samples. This difficulty has been overcome by dispersing the finely ground material or thin wood section [4,5] or thin paper [6] in alkali halide disks. Well behaved spectra are obtained with the intensities of the bands in the spectra of woods and papers being able to be related to the intensities of bands in the spectra of the components [5]. These techniques have some disadvantages. Thin sectioning requires special equipment and skills and fine grinding exposes the material to local heat. Obtaining the FTIR spectrum by direct measurement of the radiation reflected off the surface of wood or paper would seem to overcome these difficulties. Two techniques which have been used are multiple internal reflectance [2,7,8] (MIR) and diffuse reflectance [9-14] (DRIFT). Infrared spectra obtained by different techniques should be characteristic of the chemical structure of the sample, independent of the geometry of the experiment and able to be compared directly. Some differences are inevitable because of the different physics involved in the transmission, MIR and DRIFT sampling methods [15,16]. For example, the effective thickness of the absorbing layer, and therefore the amount of radiation absorbed, varies with frequency in MIR experiments. However, much larger differences can occur in DRIFT spectra of woods and paper. It is important to be able to distinguish those which arise from different physics from those which arise from optical distortion.

## RESULTS AND DISCUSSION

The effects of sampling technique on the FTIR spectrum of *Eucalyptus regnans* cold soda pulp are shown in Figure 1. In the transmission spectrum (Fig. 1A) the most intense absorptions occur between 1030 and 1060 cm $^{-1}$. A DRIFT spectrum of the surface of a paper sheet made from the same fibres is shown in Figure 1B. This spectrum clearly differs from the transmission spectrum in the region 950-1200 cm$^{-1}$. Overall the bands are less intense relative to the other bands in the spectrum and the strongest band occurs at 1133 cm$^{-1}$ instead of 1056 cm$^{-1}$. Moreover, there has been a very large reduction in intensity in the region 1030 and 1056 cm$^{-1}$. Figure 1C shows the DRIFT spectrum of the same fibres dispersed in finely ground potassium bromide. The intensities in the 950-1200 cm$^{-1}$ region of this spectrum are now much more like those of the transmission spectrum in Figure 1A but differ in having the peak at 1112 cm$^{-1}$ slightly more intense than the peak at 1056 cm$^{-1}$.

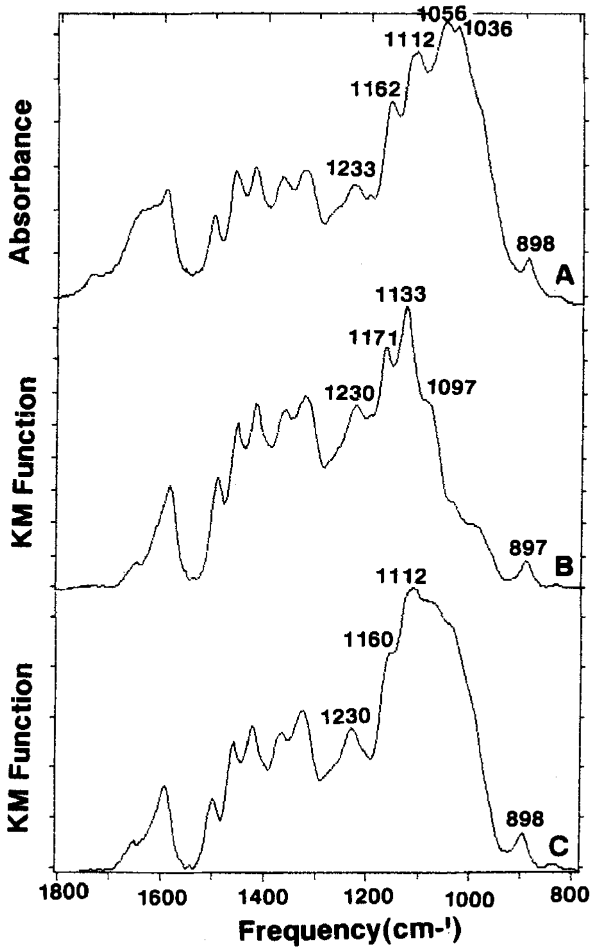

FIGURE 1. FTIR spectra of eucalypt cold soda pulp fibres. A. Transmission spectrum of fibres in fused potassium bromide. B. DRIFT spectrum of paper sheet (60 g/m$^2$) composed of the fibres. C. DRIFT spectrum of the fibres diluted with potassium bromide.

In Figure 2 are shown the DRIFT spectra of handsheets of varying grammage (60-7.5 $g/m^2$) of a similar pulp. Bands in the spectra show a progressive change with changing grammage with the most intense band shifting in frequency from 1133 $cm^{-1}$ to 1110 $cm^{-1}$ with concomitant shifts in other bands in this region. There also seems to be a reduction in a broad absorption which appears to underly the region 1400-950 $cm^{-1}$. The DRIFT spectrum of the lowest grammage (7.5 $g/m^2$) sheet in Figure 2 is quite similar to that of Figure 1C in which the fibres have been diluted with potassium bromide. These spectra may approximate that of the true DRIFT spectrum of the fibres which differs from the transmission spectrum in Figure 1A because of the different physics whereas differences in the other spectra in Figure 2 and the spectrum in Figure 1B result from optical distortion.

Since observing the distorted spectra I have noticed a number of similar examples in the literature. In a paper [9] on the DRIFT spectra of hardwoods and softwoods the spectrum of balsawood would appear to be normal but the spectrum of redwood shows distortion in the region 950-1200 $cm^{-1}$. The DRIFT spectra of Douglas fir and of quaking aspen show similar attenuation of band intensities in the region 950-1200 $cm^{-1}$ [10]. The DRIFT spectra of Southern pine in a paper [11] on the spectroscopic analysis of wood treated with chromated copper arsenate and of Southern yellow pine in a paper [12] on the effect of sulfur dioxide on wood surfaces also show the attenuation of bands in this region. Examples are also available of the same effect in the DRIFT spectra of papers. DRIFT spectra of drafting paper and duplicating paper [13] show an even greater loss of intensity around 1050 $cm^{-1}$. Similarly the DRIFT spectrum of a paper sheet made from unbleached pulp of Kappa Number 30 is strongly attenuated in the same frequency range [14].

In general, the major cause of distortion in diffuse reflectance spectra is specular reflection [17] and this has its greatest effect in the vicinity of the strongest bands in the spectrum as is shown in Figures 1 and 2. The results show that distortion can be reduced by either dilution of the fibrous sample with potassium bromide or by using a much thinner sample. Optical distortion is important because it can eliminate the strongest bands in the spectrum of a paper [13], it can complicate comparisons between the spectra of woods where the level of distortion varies between samples depending on surface texture [9] and it

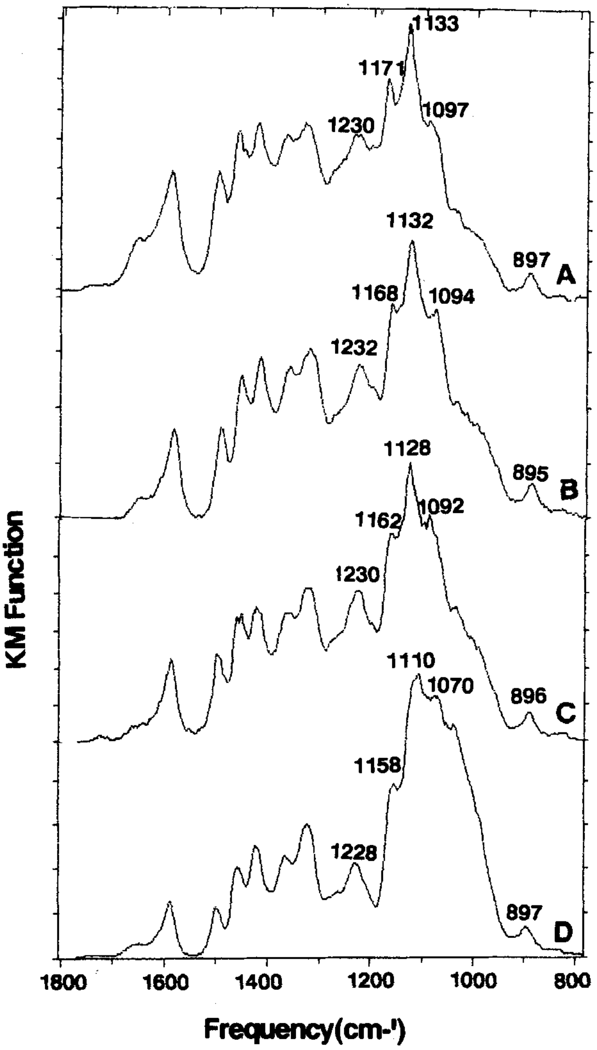

FIGURE 2. DRIFT spectra of handsheets of eucalypt cold soda pulp fibres. A. 60 g/m$^2$. B. 30 g/m$^2$. C. 15 g/m$^2$. D. 7.5 g/m$^2$.

can affect the linear relationship predicted between response and concentration by Kubelka-Munk theory. If such distortions are not avoided misleading conclusions may be drawn from the spectra.

## EXPERIMENTAL

The preparation of the eucalypt cold soda pulp has been described [18].

The spectra were obtained by using a Mattson Alpha Centauri Fourier Transform Infrared Spectrophotometer equipped with a water cooled source, a computer controlled iris and a DTGS detector. The spectra were obtained at a resolution of 4 $cm^{-1}$ and are averages of 128 scans except for the transmission spectra which are averages of 64 scans. The methods used for sampling the DRIFT [3] and transmission spectra [5] have been described. The instrumental software was used to convert the measured reflectances to values of the Kubelka-Munk function $F(R_\infty)$ where

$$F(R_\infty) = K/S = (1-R_\infty)^2/2R_\infty$$

R is the diffuse reflectance of the sample, K is the absorption coefficient and S is the scattering coefficient.

## CONCLUSIONS

Measurement of DRIFT spectra of woods and papers by reflection directly from the material's surface is a very convenient way of obtaining the spectrum of the material without the risk of artefacts being introduced in preparation. However, spectral distortion may occur in the region of the strongest bands of spectra obtained in this way. Spectra need to be obtained in ways which avoid this distortion otherwise misleading conclusions may be drawn.

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