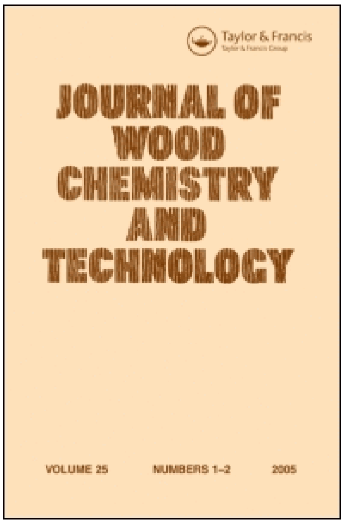

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Structural and Concentration Effects on the Diffuse Reflectance Ftir Spectra of Cellulose, Lignin and Pulp

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STRUCTURAL AND CONCENTRATION EFFECTS ON THE DIFFUSE REFLECTANCE FTIR SPECTRA OF CELLULOSE, LIGNIN AND PULP

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ABSTRACT

Experiments were conducted to determine the effect of sample type and concentration on the diffuse reflectance infrared fourier transform (DRIFT) spectra of unbleached softwood kraft and thermomechanical pulps, microcrystalline cellulose (Avicel) and kraft lignin (Indulin AT). The absorption of characteristic bands, in Kubelka-Munk units, was followed as a function of sample concentration in potassium bromide, and, in the case of the two pulps, was also determined on handsheets. Anomalous dispersion occurred at concentrations of 1% or below. This phenomenon resulted in a decrease of absorption of specific bands with increasing concentration and was particularly significant for kraft pulp, less important for thermomechanical pulp and microcrystalline cellulose, and practically absent in pure kraft lignin. These effects of specular reflectance could not be completely eliminated by diluting the sample in a non-absorbing matrix, as previously claimed, but could only be minimized at low concentrations.

INTRODUCTION

Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy is a very useful and convenient means of obtaining spectra of wood, pulp and paper. Qualitative information on chemical functionalities and quantitative information, based on the linear relationship predicted between response and concentration by the Kubelka-Munk theory, can be retrieved from the spectra. Initially introduced in 1978[1,2], this technique is dedicated to the analysis of solid samples with rough surfaces and can be either performed on neat samples or on samples dispersed in a non-absorbing matrix such as an alkali halide powder. However, the DRIFT spectrum of a neat sample can be very different from that of a dilute dispersion. Phenomena like saturation and anomalous dispersion are involved and can cause distortion of the spectra.

It was recently reported, for example, that spectral distortions in the region of the strongest bands can occur in the DRIFT spectra of pulp handsheets[3], of artificially weathered wood surfaces[4] and of wood surfaces of different roughness produced by sanding the wood with sandpaper of different grit[5]. These authors report distortions in the 1200-950 cm^{-1} region with a great loss of intensity around 1030 cm^{-1}. In addition, a shift to higher wavenumber has been described for the DRIFT spectra of handsheets of increasing grammage [3]. In all cases, the use of neat solid samples seems to be the cause of the distortions and this effect appears to be a function of the grammage of the handsheets[3] or of the roughness of the surface[5].

These anomalies have been attributed to specular reflectance and could result in a reduction or elimination of important bands, which could, in turn, produce misleading information. For example, Fuller[6] has shown that the spectrum obtained by subtracting the spectrum of blank paper from that of ink-coated paper is largely different from the transmission spectrum of the ink. This is due to the fact that the type and extent of spectral distortions are not the same in both samples, and, consequently, the difference spectrum is also highly distorted. A large number of similar examples of distorted spectra can be found in the literature[7-11], although the authors make no reference to this phenomenon.

Several claims have been made that spectral distortions could be reduced or eliminated by recording spectra of fibres[3] or powdered organic materials[12] diluted in a non-absorbing matrix. However, the information available in the literature concerning the effect of dilution of wood and pulp samples in a non-absorbing matrix is contradictory. Whereas Schultz *et al.*[13] stated that spectral quality is improved for wood samples diluted with potassium chloride, Berben *et al.*[14] found no real advantage of diluting pulp samples with potassium bromide. On the other hand, Backa and Brolin[7] showed a slight improvement in the quantitative prediction of the amounts of cellulose, hemicellulose and lignin by partial least squares analysis of the spectra of diluted pulps.

This lack of consensus led us to investigate the effect of concentration on the DRIFT spectra of various samples. Two softwood pulps, a thermomechanical and an unbleached kraft, as well as pure cellulose (Avicel) and kraft lignin (Indulin) were selected for the study. The absorption of characteristic bands in Kubelka-Munk (K-M) units, was followed as a function of sample concentration in potassium bromide, and, for the two pulp samples, was also determined on handsheets. By treating the data in various ways, we have attempted to gain some insight into these dispersion phenomena and have made recommendations for improving the reliability of the measurements.

DIFFUSE REFLECTANCE THEORY

General

The general theory for diffuse reflectance at scattering layers within powdered samples is similar in form to the Beer-Lambert law and (for an infinitely thick layer) can be expressed by the Kubelka-Munk equation[15] as:

$$f(R_\infty) = (1 - R_\infty)^2/2R_\infty = k/s \tag{1}$$

Where R_∞ is the absolute reflectance of the layer, k is the molar absorption coefficient, and s the scattering coefficient. Typically, a measurement of the absolute reflectance, R_∞, of a sample is avoided by measuring the diffuse reflectance of the sample r_∞ relative to a selected non-absorbing standard. In this case, Equation 1 becomes[16]:

$$f(r_\infty) = (1 - r_\infty)^2/2r_\infty = k/s \tag{2}$$

For an absorber dispersed in a non-absorbing matrix, k is equal to

2.303 ac, and Equation 2 can be rewritten as:

$$f(r_\infty) = \frac{2.303\ ac}{s} \tag{3}$$

where *a* is the molar absorptivity and *c* the concentration. Consequently, a diffuse reflectance spectrum converted to K-M units should therefore appear similar to an absorption spectrum. Thus, the Kubelka-Munk theory predicts a linear relationship between the diffuse reflectance measurement and the concentration of each band, provided that *s* remains constant.

Deviations from the Kubelka-Munk Theory

The primary difficulties associated with diffuse reflectance measurements involve "anomalous dispersion". The nature of anomalous dispersion in optics concerns large or abrupt changes in the absorption index, k, which leads to sharp changes in the index of refraction, n[17]. When a beam of infrared radiation is focused onto the surface of a powdered or matte sample, three different effects can occur which could lead to non-linear Kubelka-Munk plots [6,18]: reduction of the penetration depth, true specular interaction and diffuse specular interaction. As the sample concentration is increased, the effective penetration depth decreases. At high concentrations, the intensity of absorption bands might be expected to deviate negatively from linearity, simply as a result of the reduction in the penetration depth[18].

The **true specular** interaction is a simple reflection from a crystal surface which reflects away at an angle that is equal to the incident angle. This radiation has not been absorbed by the sample and, because it is reflected, the intensity is a function of the refractive index and the absorption index of the sample. For weakly absorbing samples, true specular reflectance depends on some of the properties of the sample and on the optical geometry used for the reflectance measurement[19]. Near the absorption maxima, specular reflectance increases, and shifts to higher wavenumber are observed for the absorption band maxima. $f(R_\infty)$ may even start to decrease with increasing concentration as demonstrated by Brimmer and Griffiths for caffeine[18].

The **diffuse specular reflectance** is caused by radiation which has not been absorbed but has undergone multiple "mirror-like" reflections within the sample. This radiation may emerge at any angle relative to incident radiation and is indistinguishable, optically, from the "true" diffuse reflectance which contains information about the absorptivity of the sample. For high absorbing bands (mainly below 2000 cm^{-1}) the measured diffuse reflectance spectrum is a mixture of the true and the specular components of diffuse reflectance. This mixing is responsible for spectral distortions which can be partially corrected by a mathematical operation known as the Kramers-Kronig transformation[20-22]. In order to eliminate interference from specular reflectance, it was found in one study[23] that the use of polarized incident beam in order to discriminate between specular (true and diffuse) and diffuse reflectance is ineffective for powdered samples. However, Brimmer and Griffiths[12], who make a distinction between true and diffuse specular reflectance, have reported that only true specular reflectance can be eliminated by the use of crossed polarizers.

A device that physically blocks the specular components has been proposed[24] but suffers from high energy loss. Backa and Brolin[7] have observed an increase in the precision of quantitative determination of cellulose, hemicellulose and lignin content of pulps by DRIFTS using a blocker device. However, important distortions remained present in their pulp spectra.

Off-axis geometry of optics has been found somewhat effective for reducing the specular reflection in the case of calcium carbonate and caffeine[25] but ineffective in the case of Ottawa sand[23]. Brimmer and Griffiths[12] have shown that diffuse specular reflectance of organic materials is unaffected by optical geometry and can only be eliminated by dilution of the neat sample in a non-absorbing matrix. In the present report no distinction is made between true and diffuse specular reflectance.

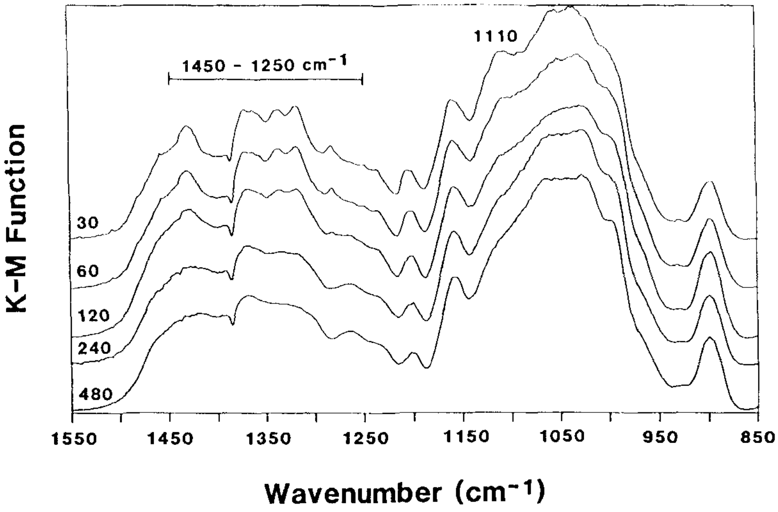

FIGURE 1: DRIFT spectra of Whatman filter paper (2% in KBr) at various grinding times (indicated in seconds at the extreme left of each spectrum).

RESULTS AND DISCUSSION

Effect of Grinding Time and Particle Size

Sample grinding in a vibratory mill exposes the material to local heat which could result in its degradation. In order to assess the effect of grinding on the DRIFT spectra of pulp fibres, spectra (1550-850 cm^{-1}) of Whatman filter paper at 2% concentration in KBr were recorded at various grinding times. As indicated in Figure 1, flattening of bands in the 1450-1250 cm^{-1} area (1430,1336,1317 and 1282 cm^{-1}) and at 1110 cm^{-1} occurred when the grinding time exceeded 60 seconds. Grinding times above 60 seconds should therefore be avoided because they induce spreading of specific bands and cause loss of resolution. A total grinding time of 60 seconds (sample alone and sample in KBr) was adopted for all the samples in this work.

It is well known that particle size is a key parameter in DRIFT spectroscopy. Faix and Böttcher[26] have recently shown that spectroscopic data of wood (transmission and diffuse reflection) are influenced by the particle size of the milled wood. However, in the case of pulp, the pulping processes insure an almost complete defibration of the fibres and the particle size in a pulp sample is therefore the dimension of the fibres themselves. The diameter of fibres is in the 10-50μm range which is the recommended particle size for DRIFT spectroscopy. Scientific evidence to the effect that particle size is not a factor can be found in a previous study done by Michell[3] where DRIFT spectra of cold soda pulp handsheets indicate that diffuse specular reflectance is only a function of the concentration of fibres (grammage of the handsheet).

Effect of Sample Type and Concentration

Figure 2 shows some spectra of the cellulose (AVI), UNBK, TMP and kraft lignin (IND) series. For the Avicel, UNBK and TMP series, the spectra were normalized to 1 K-M unit at the maximum of the 1423-1431 cm^{-1} band, whereas spectra from the IND series were normalized to 1 K-M unit at the 1515 cm^{-1} band. For the Avicel, UNBK and TMP pulp series, the effects of increasing concentration can be described in a similar manner. In the 1800-1200 cm^{-1} region, there were no detectable effects and all normalized spectra were almost identical. However the spectra differed greatly in the 1200-800 cm^{-1} region. The principal effect was a general reduction of absorption with increasing concentration. Furthermore, these effects begin at concentrations as low as 1% and possibly lower. In the case of handsheets, the 1030 cm^{-1} band was almost completely eliminated and there was appearance of several new bands. Specular reflectance is reported to be particularly significant in the area of highest absorption, yet the weakly absorbing 898 cm^{-1} band was also strongly affected and its intensity was relatively reduced as the sample concentration was increased. It was also apparent that the AVI and TMP series were less affected by specular reflectance than the UNBK series.

Another effect which has been attributed to specular reflectance by other authors is a shift of specific bands to higher wavenumbers

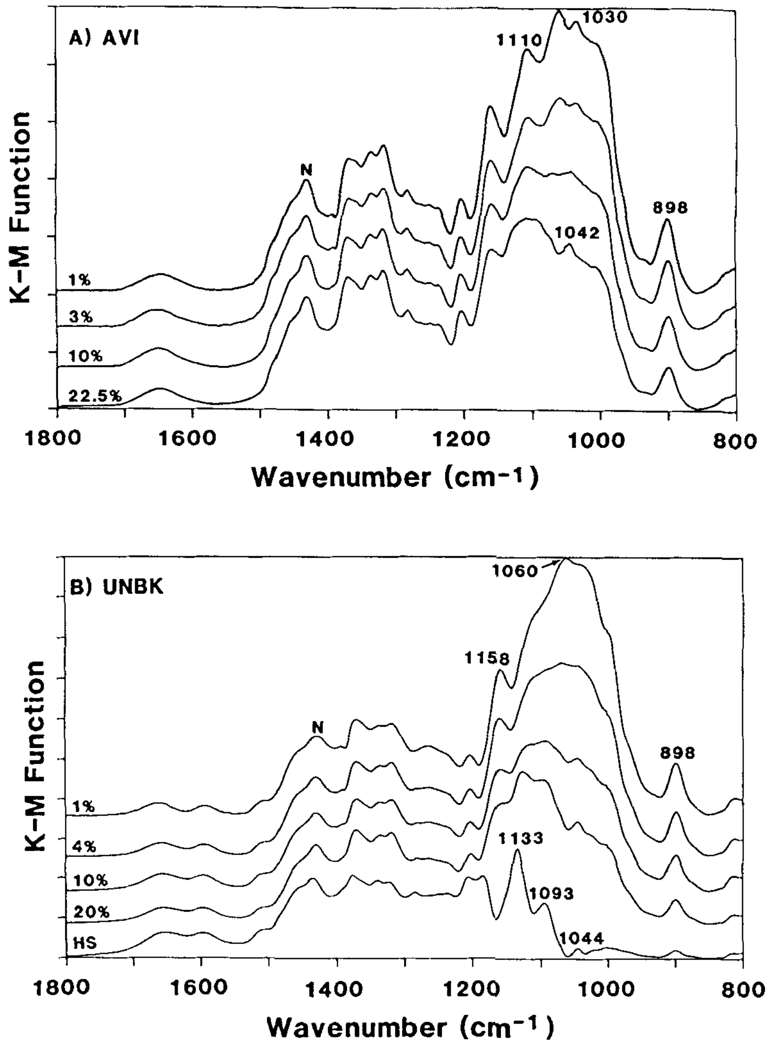

FIGURE 2: DRIFT spectra at different concentrations of samples in KBr (indicated in percent at the extreme left of each spectrum, the symbol HS denotes handsheets) A: microcrystalline cellulose (AVI), B: unbleached kraft pulp (UNBK), C: thermomechanical pulp (TMP) and D: kraft lignin (IND). The letter N in each figure indicates the peak at which the spectra were normalized to 1 K-M unit.

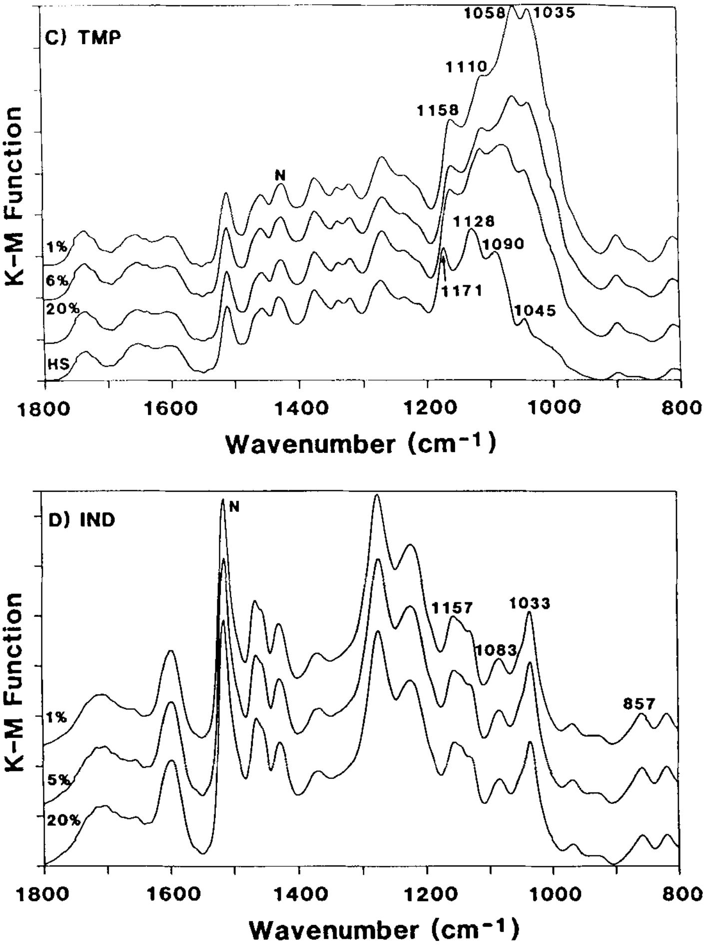

FIGURE 2. Continued

with increasing concentration[3,17]. Similar apparent shifts of absorption maxima can also be observed in Figure 2 (B and C) when comparing the 1% sample with the handsheet. For the TMP sample (Fig. 2(C)), these apparent shifts are: from 1158 cm^{-1} to 1171 cm^{-1}; from 1110 cm^{-1} to 1128 cm^{-1}; from 1058 cm^{-1} to 1090 cm^{-1} and from 1035 cm^{-1} to 1045 cm^{-1}. Surprisingly, no frequency shift was observed for the 898 cm^{-1} band.

In contrast, the DRIFT spectra of kraft lignin (Fig. 2(D)) were remarkably similar, regardless of concentration. It appears, therefore, that there is no specular reflectance component in the DRIFT spectra of lignin even at a concentration of 20% in KBr. If this is true, we conclude that the specular component present in a pulp sample at concentrations as low as 1% or lower is caused by structural features of the cellulosic fibres.

In order to make a more detailed analysis of the anomalous dispersion effect in DRIFT as a function of concentration, three specific frequencies were selected: the 898 cm^{-1} band (857 cm^{-1} for Indulin), an affected low absorption band; the 1030 cm^{-1} band, an affected high absorption band; and the 1430 cm^{-1} band which seems to be unaffected by anomalous dispersion.

Figure 3 shows the absorption intensities (in K-M units) for the 1430, 1030 and 898 cm^{-1} bands of the different samples as a function of concentration and for handsheets in the case of the UNBK and TMP pulps. For all three frequencies, the Indulin exhibited a linear relationship from 0-10% concentration and deviated negatively at higher concentration due to saturation effects resulting from a reduction in penetration depth. As discussed previously, anomalous dispersion is not an important part of the Indulin spectrum, even at a concentration of 20%. For the 1430 cm^{-1} band (Figure 3A), Avicel showed an almost linear relationship over the entire range of concentration, whereas the TMP and UNBK pulps deviated slightly from linearity at concentrations beyond 8 and 4% respectively. This deviation was somewhat more important for UNBK than TMP.

For the 1030 cm^{-1} and 898 cm^{-1} bands (Figure 3 B and C), strong deviations from linearity were observed for Avicel, TMP and UNBK. These deviations begun at concentrations below 3% and increased with increasing concentration. For the handsheet samples, the absorption decreased drastically and approached zero in the case of UNBK at 1030 cm^{-1}. This means that the absorption of UNBK has been almost completely eliminated by anomalous dispersion in the area of maximum absorption (1060-1030 cm^{-1}) and that this process begins at a very low concentration of fibres in a non-absorbing matrix. Another

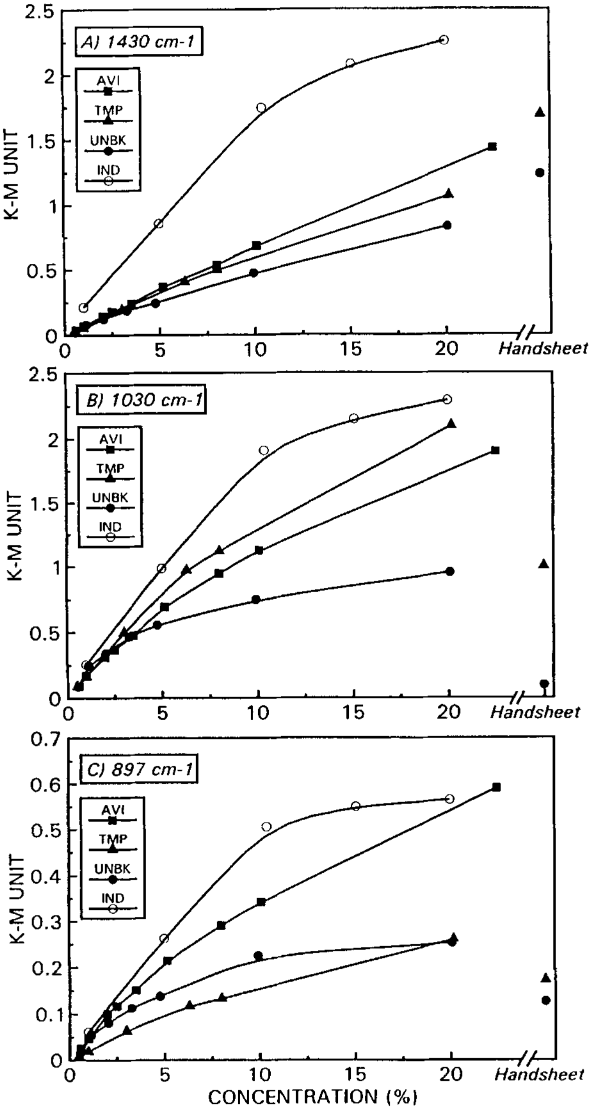

FIGURE 3: Absorption intensities (in K-M unit) of the AVI, UNBK, TMP and IND series as a function of concentration at A) 1430 cm^{-1}, B) 1030 cm^{-1} and C) 897 cm^{-1}. Data points identified by HS are for the neat handsheets and cannot be related to a specific concentration.

observation from Figure 3 was that the extent of anomalous dispersion is different for each type of sample. In decreasing order of importance, the effect of anomalous dispersion is: UNBK > TMP ≈ Avicel while Indulin is almost unaffected.

These results can be rationalized on the basis of structural differences and orientation effects in the various samples examined[27]. McKenzie and Koenig have also shown that orientation is a significant factor in the DRIFT spectrum of E-glass fibres[28]. The overall orientation of cellulose microfibrils is greater for a pulp fibre than it is for microcrystalline cellulose such as Avicel, which has been acid hydrolysed and has an average particle size of 50 μm before milling and probably a shorter effective length of orientation. Orientation is probably non-existent in purified lignin and consequently little or no distortion was detected. This could also explain why a high lignin TMP pulp is less affected by anomalous dispersion than a low lignin kraft pulp. The concentration of ordered cellulose microfibrils is lower in TMP, and so the extent of anomalous dispersion is also lower compared to UNBK at the same concentration in Kbr. However, morphological and structural differences between pulps can also be responsible for the different behaviour of the pulps.

As far as the shift to higher wavenumbers reported previously [3,18] is concerned, it is difficult to explain that increasing the sample concentration could cause a shift in the vibrational frequency of a specific chemical bond. We propose instead that the broad band in the region of 1200-900 cm^{-1} in the spectrum of a pulp at low concentration is the result of the overlapping of a number of different bands. The decrease in absorptivity of stronger bands due to specular reflectance, may give rise to the appearance of new weaker bands. This is particularly evident for the handsheet spectra (Fig.2 (B and C)).

To verify this assumption, we have plotted in Figure 4 the second derivative of the UNBK spectra in the 1225-875 cm^{-1} area. In a second derivative spectrum, the features of the original spectrum are enhanced, and negative peaks correspond to the peaks and

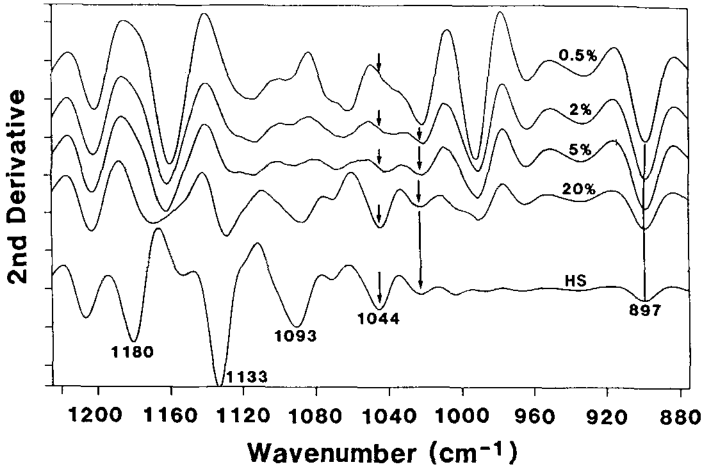

FIGURE 4: Second derivative DRIFT spectra of unbleached kraft pulp (UNBK) at different concentrations (indicated in percent at the extreme right) in KBr and of the handsheet sample (HS). The arrows represent the position of the peaks gradually disappearing (at ~1020 cm^{-1}) and of those emerging (at ~1044 cm^{-1}) with increasing pulp concentration.

shoulders present in the original absorption spectrum. It is evident from Figure 4 that the 898 cm^{-1} band and the 990 cm^{-1} shoulder, which both appear as negative peaks in the second derivative spectra, disappear almost completely as the concentration is increased, but without any shift in frequency. Others peaks (1158,1116,1060 and 1020 cm^{-1}) gradually disappear and new ones (1180,1133,1093 and 1044 cm^{-1}) emerge.

Thus, the elimination of the strong cellulose absorption from the handsheet spectrum has allowed lignin and hemicellulose bands to emerge. It is also significant to note that at intermediate pulp concentration (e.g. 5 or 20%), both sets of peaks (those disappearing and those emerging) can be seen in the spectrum as indicated by the arrows in Figure 4. This is evidence that no frequency shift has occurred.

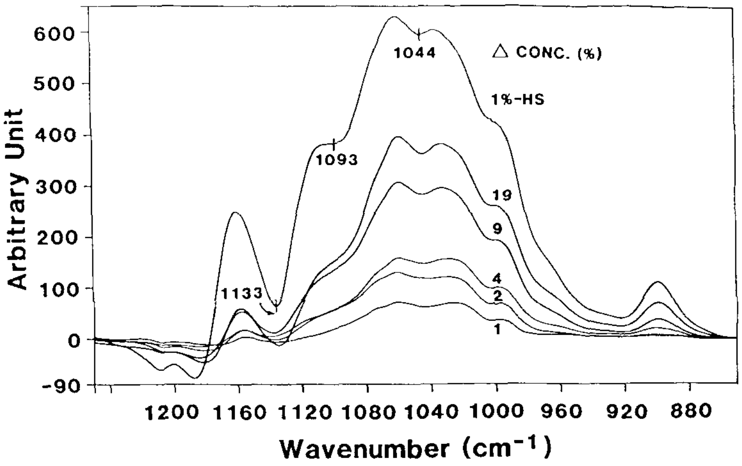

FIGURE 5: Difference DRIFT spectra produced by subtracting normalized spectra of UNBK at different concentrations from the 1% normalized spectrum. Concentration differences are indicated on each spectrum.

Assuming that the specular reflectance is specific to cellulose in wood, pulp or paper, the information which is lost when increasing the concentration of fibres in a non-absorbing diluent should have the characteristics of the pure cellulose absorption spectrum. This is illustrated in Figure 5 which shows a series of difference spectra for the UNBK samples. Normalized spectra of different concentrations have been subtracted from the 1% concentration normalized spectrum. Difference spectra are identified by this concentration difference. The [1%-HS] spectrum is the difference spectrum obtained by subtracting the normalized handsheet spectrum from the 1% concentration spectrum. These difference spectra are very similar to the pure absorption spectrum of cellulose (Fig.2 (A)) and indicate that information has been lost from both high and low absorption bands. The most striking feature of these spectra, however, is that all the valleys corresponds to the maxima of the bands present in the handsheet spectrum (Figure 2(B and C)). These maxima were also those assigned to lignin bands

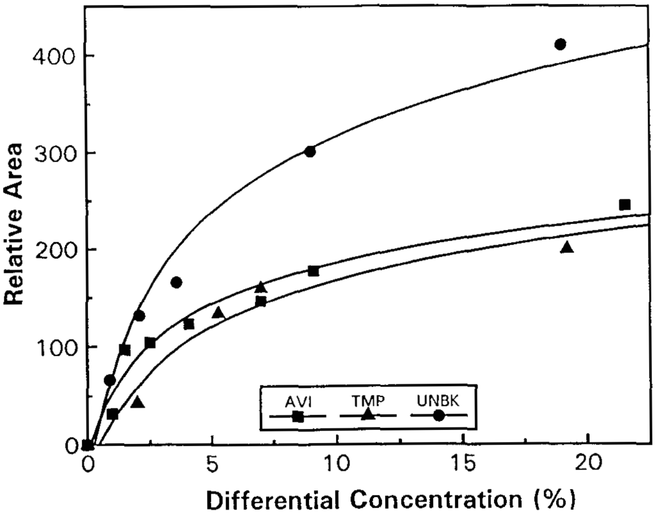

FIGURE 6: Area under the difference spectrum of UNBK, TMP and AVI in KBr as a function of concentration difference.

in Figure 4 (HS). This further confirms that such bands are in fact present in all the pulps spectra, but, except for the handsheet sample, are largely masked by the cellulose absorption.

The total area under the difference spectra can be related to the total amount of information on absorptivity which is lost when increasing the concentration of the sample in DRIFT. Figure 6 shows the increase of total area of the difference spectra from 1190 to 850 cm^{-1} as a function of the concentration difference, for the unbleached kraft pulp (UNBK), thermomechanical pulp (TMP) and the microcrystalline cellulose (AVI). The order of importance of anomalous dispersion which was established previously from Figure 3 (UNBK > TMP ≈ AVI) is confirmed in Figure 6. The loss of information is about twice as important for kraft pulp as for thermomechanical pulp. Furthermore, variations in anomalous dispersion are relatively more important at concentrations below 5%. Consequently, specular reflectance effects cannot be completely eliminated by diluting the sample in a non-absorbing matrix, as claimed by other authors, but can only be minimized at low concentrations.

CONCLUSIONS

- Specular reflectance causes anomalous dispersion in the spectra of cellulose, pulp and paper even when these are diluted to low concentrations in a non-absorbing matrix.
- Anomalous dispersion results in a decrease of absorption with increasing concentration in the 1200-800 cm^{-1} region for both high and low absorptivity bands.
- This effect appears to be dependent on the type and structural features of the sample. It is particularly significant for kraft pulp, less important for thermomechanical pulp and microcrystalline cellulose, and practically absent in pure kraft lignin.
- The shift in frequency of DRIFT bands with increasing sample concentration, reported by other authors, is in fact caused by the progressive disappearance of specific cellulose bands in a more complex spectrum and by the emergence of bands characteristic of the lignin and hemicelluloses.
- To improve the reliability of DRIFT measurements on wood, pulp or paper, samples must be diluted to 5% or below and the concentration must be kept rigorously constant from sample to sample. In addition, comparison between different types of pulps at the same concentration should take into account the fact that dispersion phenomena may vary with sample type.

EXPERIMENTAL

Sample Preparation

The samples examined were a microcrystalline cellulose (Avicel, FMC Corp.), an unbleached softwood kraft pulp (UNBK), a softwood thermomechanical pulp (TMP), and kraft lignin (Indulin AT, Westvaco Co.). The klason lignin content of UNBK and TMP were 4.5% and 28.2%, respectively. Air-dried samples were milled in a steel ball vibratory mill (Wig-L-Bug, Crescent Co.) for 30 seconds in order to remove fibre bundles. Each sample was diluted to the desired concentration with potassium bromide (FTIR grade, Aldrich Chem.) and milled again for 30 seconds in the same apparatus. Each milled sample was transferred to the diffuse reflectance sample cup and levelled off gently using a blade. In the case of handsheets (HS) each sample was placed on top of a KBr layer in the sample cup. DRIFT spectra were recorded at sample concentrations ranging from 0.5 to 24% in KBr. In the case of UNBK and TMP, spectra of handsheets at 60 g/m^2 were also recorded.

FTIR Measurements

DRIFT spectra were obtained with a 1725 Perkin Elmer FTIR spectrophotometer equipped with a DTGS detector and a diffuse reflectance accessory with an on-axis geometry and an angle of incidence of 38°. For each sample, 400 scans were collected and averaged at a resolution of 4 cm^{-1}. In all cases, the Happ-Genzl apodization function was used. Spectra were expressed as ratios to a background of KBr and converted to values of the Kubelka-Munk function which represents the k/s ratio and gives an absorbance-like spectrum. Baselines were corrected, in the 1870-800 cm^{-1} region, for the ramping effect of diffuse reflectance. When applying the subtraction procedure, the spectra at different concentrations were normalized according to the intensity of the 1430 cm^{-1} band.

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