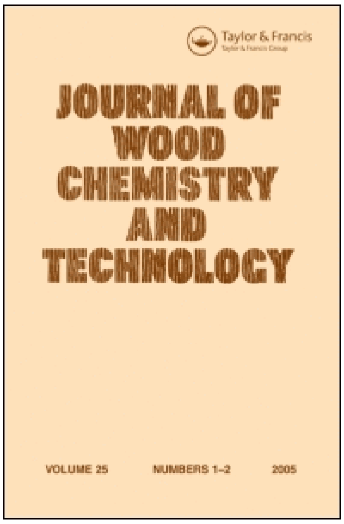

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PHOTOACOUSTIC FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY OF MECHANICAL PULP BRIGHTENING

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To D.A.I. Goring, with every good wish for a satisfying and productive "retirement".

ABSTRACT

The technique of photoacoustic Fourier transform infrared spectroscopy (FTIR-PAS) was applied to the study of mechanical pulp brightening with hydrogen peroxide. Intensities relative to three internal standard peaks (3400, 1510 and 1056 cm^{-1}) were used since the absolute photoacoustic signal intensities were not reproducible. The internal standard method yielded a reproducibility of better than 5% and made it possible to observe significant changes in the 1750-1600 cm^{-1} region upon brightening with peroxide. The peak intensities were found to decrease due to alkaline deacetylation (1740 cm^{-1}), and to the net removal of conjugated carbonyl structures (1650 cm^{-1}).

INTRODUCTION

Studies in the area of wood chemistry are always made complicated by the insolubility of the material. In the case of lignin, this difficulty can be circumvented by the use of model compounds or lignin preparations, and by solid-state characterization methods. In the case of mechanical pulp brightening, several studies using lignin model compounds[1-4] and on milled wood lignin or other preparations[2,5-7] have been reported. Studies involving the characterization of the lignin in the wood itself have been fairly rare[8-11]. In these studies ultraviolet, visible and infrared spectroscopic methods were used. Infrared spectroscopy in particular seems very appropriate to the study of mechanical pulp brightening since it can generate a great deal of structural information about solid materials. The main disadvantage of the technique lies in the need for sample preparation, either as a thin sheet or as a potassium bromide pellet. However, recently, the techniques of diffuse reflectance[12] and photoacoustic detection[13,14], which require no sample preparation, have been introduced to the field of Fourier transform infrared (FTIR) spectroscopy.

Photoacoustic spectroscopy is a method in which the sample is irradiated in a closed cell with intensity-modulated light. The absorption of radiation causes the sample temperature to increase. Heat is transferred from the sample surface to a coupling gas present in the cell, causing the pressure to rise in the cell. Since the incident light is modulated, so is the pressure variation which can be monitored by means of a sensitive microphone. The theoretical aspects of photoacoustic spectroscopy (PAS) are described by Rosencwaig[15-16] and recent applications of PAS in conjunction with FTIR are described in a few reviews[13,14,17].

The photoacoustic technique has recently been employed in the study of lignocellulosics. Gould studied the ultraviolet and visible photoacoustic spectra of lignin[18], while Harbour et al. used the technique in the UV, visible, near- and mid-infrared regions, for cellulose, paper and wood samples[19]. Photoacoustic FTIR measurements on bleached kraft paper have been reported, with particular emphasis on the effect of surface area on signal intensity[20].

The main drawback of the photoacoustic technique is that the absolute peak intensities are not readily quantified. However, the technique has been used successfully for the quantitative analysis of a mixture of isotopically different potassium nitrate samples, using peak ratios instead of absolute peak intensities[21]. The aim of the present paper is to show that the method of peak ratios in FTIR-PAS can be used to detect the chemical changes that occur during mechanical pulp brightening.

EXPERIMENTAL

Pulp Preparation

Chips of black spruce wood (picea mariana) were refined in a Bauer 187 atmospheric discharge double disk (60 cm diameter) refiner at the Abitibi-Price Research Centre in Mississauga, Ontario. The pulp was Soxhlet-extracted with acetone (24 hours), dried, chelated (2% consistency, 0.5% EDTA on pulp), and Soxhlet-extracted with water (14 hours).

Pulp Brightening

Brightening was carried out at 12% consistency with a 2.5% charge of hydrogen peroxide, 5% 41° Bé sodium silicate, 2% sodium hydroxide and 0.05% magnesium sulphate. The pulp was mixed with the bleaching solution and placed in a water bath at 50°C for 3 hours. The pulp was then taken out and the consistency was lowered to 0.6%. The pH of the resulting slurry was adjusted to 5.5 by addition of 10% sodium bisulphite solution. The pulp was then filtered, washed, and dried in a vacuum oven at 45°C. In all cases a blank experiment was run under the same conditions using pulp and a liquor identical to the brightening one except for the absence of peroxide.

Sodium Hydroxide Pretreatment

Some of the pulp was treated with a basic solution prior to brightening. The pretreatment liquor was identical to that used for the brightening except that no hydrogen peroxide was present. The pretreatment was carried out for 6 hours under the same conditions of temperature and consistency as the brightening process.

Sample Preparation

Although good quality spectra were readily obtained on pulp sheets, it was found that grinding the pulp in a Wiley mill (60-mesh screen) had a beneficial effect on the signal-to-noise ratio of the resulting FTIR-PAS spectra. After grinding, the samples were dried a second time in a vacuum oven at 45°C.

Spectroscopic Measurements

A Mattson Cygnus 25 FTIR spectrometer with an EG&G Princeton Applied Research Model 6003 photoacoustic cell was employed. The sample holder had a 5 mm diameter and was 1 mm deep. The output from the cell was fed to an EG&G Princeton Applied Research Model 6005 preamplifier and thence to the detector input of the spectrometer.

Photoacoustic FTIR spectra were obtained by averaging 100 scans at a resolution of 8 cm^{-1} (measurement time of 4 minutes). The interferometer mirror velocity was 0.084 cm/sec. A double-sided interferogram and a triangular apodization function were used to generate the spectra. The latter were ratioed to a background spectrum of carbon black (Fisher Norit A) obtained at the same instrumental settings. Baseline correction was carried out with the routine provided in the instrument software. To obtain more reproducible results the baseline correction program was applied twice to each spectrum. For each sample, spectra of ten different aliquots were recorded and then baseline corrected so that the data could be averaged and the amount of scatter could be estimated.

RESULTS AND DISCUSSION

Photoacoustic FTIR spectra of the untreated pulp are shown in Figures 1 (original spectrum) and 2 (baseline corrected). For comparison, a conventional transmission spectrum is shown in Figure 3. The same peaks appear in both the photoacoustic and

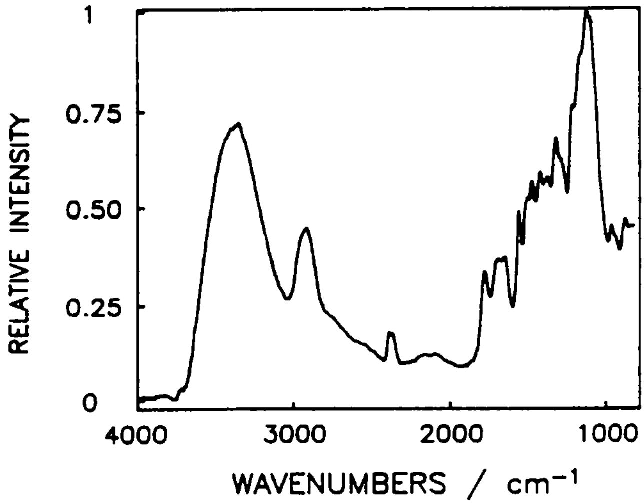

Figure 1. FTIR photoacoustic spectrum of refiner mechanical pulp (normalized to the highest peak.)

transmission spectra, although their relative intensities do differ. This is not unexpected since, unlike the transmission intensity, the photoacoustic signal intensity depends on the modulation frequency of the infrared radiation, according to the Rosencwaig-Gersho theory[22] and, in FTIR, each wavelength is modulated at a different frequency[14].

It was found that the absolute peak intensities of photoacoustic spectra were not very reproducible for spectra of different aliquots of the same material. The main reason for this lies in the difficulty in packing the cell reproducibly, since the signal is sensitive to the surface area[20], and a densely packed sample gives a lower signal than a loosely packed one. To circumvent this problem three internal standard peaks were used to

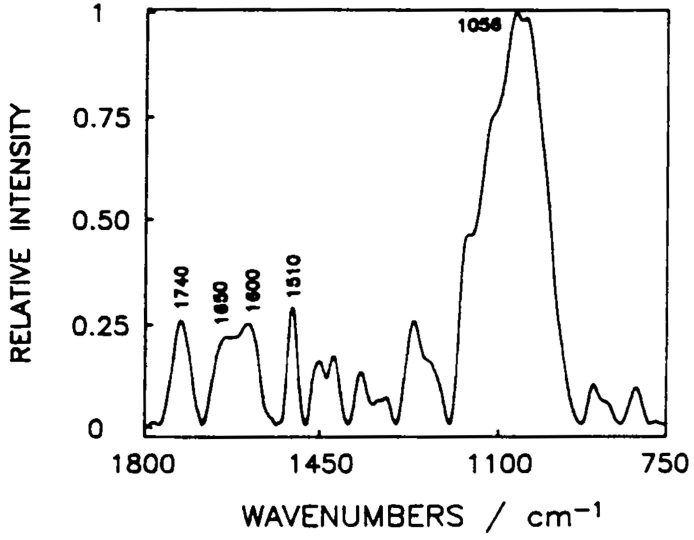

Figure 2. Baseline corrected FTIR photoacoustic spectrum of the refiner mechanical pulp in the region from 1800 to 750 cm^{-1} (normalized to the highest peak).

obtain relative intensities: the peak at 1056 cm^{-1} assigned to C-O stretching vibrations[23], the broad peak centered around 3400 cm^{-1} corresponding to O-H stretching[24], and the peak at 1510 cm^{-1} ascribed to an aromatic skeletal vibration[24]. The first two peaks were chosen because they are strong and represent groups that are common in both the lignin and the carbohydrates. Since these groups are plentiful it seemed unlikely that they would be subject to drastic depletion upon brightening. The peak at 1510 cm^{-1} was chosen because it is a pure lignin vibration and is well-defined in the spectra. The precision of the method was estimated by repeating measurements on ten different aliquots of each sample

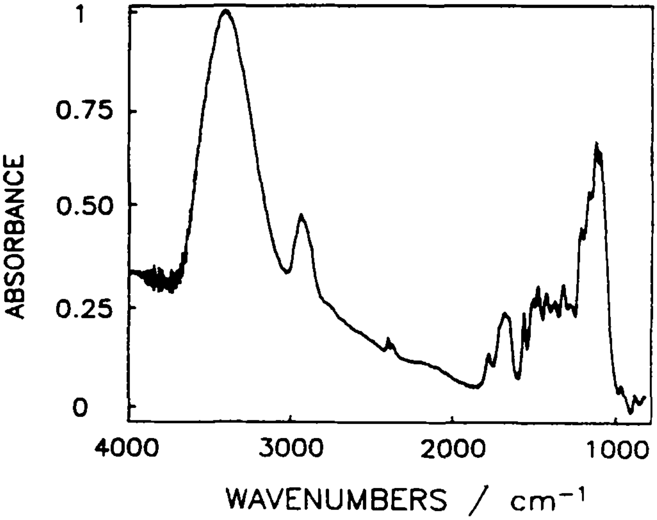

Figure 3. FTIR transmission spectrum of refiner mechanical pulp in a potassium bromide pellet (normalized to the highest peak).

and the use of t-test statistics[25]. If no baseline correction was used, the reproducibility of the relative intensities was found to be around 10%, while if the spectra were baseline corrected as shown in Figure 2, it was better than 5%. The baseline correction method made it possible to remove the effect of coherent background noise in the cell. It is very difficult to know exactly where the baseline actually is, but the fact that all the spectra were similar in shape, and were corrected in the same manner may explain the better reproducibility obtained upon baseline correction.

Unextracted pulp was used in the first set of experiments but the dissolution of extractives in the brightening liquor led to changes in the infrared spectra that were difficult to interpret in terms of the brightening action alone. Even pulp that had been both acetone- and water- extracted showed significant changes throughout the spectra on treatment with alkali. For this reason it was important to have good blank samples obtained under identical conditions without the addition of brightening agent. As will be seen below, the alkali in the peroxide bleaching liquor

TABLE 1

Brightness Values of the Pulp Samples

Sample	Brightness Elrepho, %
Untreated pulp	58
Blank[(a)]	56
Peroxide brightened	70
Pretreated pulp[(b)]	55
Pretreated blank[(c)]	53
Pretreated peroxide brightened	68

(a) Blank refers to pulp treated with liquor containing no peroxide, under bleaching conditions (3 hours).

(b) Pretreated refers to pulp that was treated for 6 hours with liquor containing no peroxide, under bleaching conditions.

(c) Pretreated blank refers to pulp treated as in (b) then treated as in (a).

caused substantial changes in the IR spectra, independent of the peroxide. For this reason, a sample of the extracted pulp was pretreated for six hours with alkali under bleaching conditions with no peroxide present to try and isolate the changes due to alkali from those due to the brightening process.

The effects of the treatments on pulp brightness are shown in Table 1. The blank treated with bleaching liquor but no peroxide showed a 2-point drop in brightness; a moderate gain in brightness was observed with peroxide. Even after a 6-hour pretreatment with base, which darkened the pulp substantially, a further 2-point drop in brightness was observed when a blank bleaching treatment was performed. The brightness gain on peroxide-bleaching this pretreated pulp was the same as for the untreated pulp, but the final brightness was, of course, much lower.

Table 2 shows the percent change in the relative intensities of the IR bands between the peroxide treated sample and the corresponding blank. The intensity changes are shown relative to the three peaks used as internal standards. The scatter in values within each row indicates the precision of the measurements. Interpretation of the changes in intensities is not straightforward and the following interpretation of the chemical changes in the fibre is tentative. The largest change was found at 1650 cm^{-1} which corresponds to the C=O stretch of various conjugated carbonyl groups such as α-carbonyls, α,β-unsaturated aldehydes, and various quinones[6]. This decrease was in line with the results of

TABLE 2

Percent Change in Relative Intensities Between Peroxide Brightened Pulp and Blank.

Peak position ν (cm^{-1})	Percentage change in relative intensities		
	A_ν/A_{1056}	A_ν/A_{1510}	A_ν/A_{3300}
1740	+ 1	- 1	+ 1
1650	- 8	-10	- 8
1600	- 5	- 6	- 4
1510	+ 1	---	+ 2

studies on groundwood[10], thermomechanical pulp[11], and on milled wood and enzymatically isolated lignins[6,7].

A significant decrease was also seen in the 1600 cm^{-1} peak which corresponds to an aromatic skeletal vibration, but not in the 1510 cm^{-1} peak which is also due to an aromatic vibration. However, the peak at 1600 cm^{-1} is known to be intensified by the presence of α-carbonyl groups[26] and, in addition, carboxylate groups are known to absorb in this region. Polčin and Rapson[10] and Bezúch et al.[11] found slight increases in this peak for TMP brightening. However, in the present study, if the spectrum of the brightened pulp was compared to that of the original pulp instead of to that of the blank sample, an increase in the 1600 cm^{-1} peak was found. In this case, though, a large decrease was also observed in the 1740 cm^{-1} peak, which could be assigned to deacetylation of hemicellulose[10] due to the alkalinity of the medium and not to the oxidative properties of the peroxide. Deacetylation or hydrolysis would also lead to the formation of carboxylate groups in the strongly alkaline medium, thus causing an increase in the 1600 cm^{-1} band. Comparing the brightened sample with the blank, no significant change was found in the 1740 cm^{-1} band (because deacetylation occurred in both cases) and the 1600 cm^{-1} peak also showed no increase. In fact, the 1600 cm^{-1} peak showed a decrease that is probably due to a decrease in α-carbonyl content.

Previous work on lignin model compounds and milled wood lignin has shown that aromatic rings are attacked by peroxide, leading to the formation of quinone groups[3,5]. Quinone formation should lead to a decrease in the peak at 1510 cm^{-1}, corresponding to the aromatic skeletal C=C vibration. However, in the present study, the peak at 1510 cm^{-1} was found to be invariant, within experimental error. This was also reported in work by Polčin and Rapson[10] who presented additional ultraviolet-visible data showing no significant decrease in the aromaticity of the pulp.

Quinone formation should have other effects. The peak at 1650 cm^{-1}, should increase due to the quinone C=O stretching vibration, contrary to the observed behaviour. For the peak at 1600 cm^{-1}, the situation is more complicated: a decrease in aromaticity should lower its intensity, while the formation of quinone C=C bonds should have the opposite effect. Since no decrease was observed for the 1510 cm^{-1} peak, it is most likely that changes in the 1600 cm^{-1} absorption are not due to changes in aromaticity.

Although we have no evidence for quinone formation, it cannot be excluded. Infrared spectroscopy of pulp is not specific enough for quinones; the associated vibrations appear together with other bands (e.g. other conjugated carbonyls at 1650 cm^{-1}, and aromatic double bonds at 1600 cm^{-1}). Also relevant is the observation by Spittler and Dence[5] that the small amount of lignin that is solubilized during the bleaching process is extensively oxidized, but the insoluble fraction shows no significant decrease in aromaticity.

Table 3 shows the percent change of the relative intensities of the IR peaks with respect to the pretreated pulp. Data are presented for the peroxide brightened pretreated pulp, and also pretreated pulp treated under the same conditions as the brightened one but without the addition of peroxide (pretreated blank). The largest change was a decrease in the 1740 cm^{-1} peak due to deacetylation. The peroxide-treated sample showed a somewhat greater change in this region, perhaps due to the greater alkalinity afforded by the presence of the perhydroxyl anion. A noticeable decrease in the aromatic peak at 1510 cm^{-1} was found, indicating that a small quantity of lignin was dissolved in both processes. The amount was very similar in both cases. This

TABLE 3

Percent Change in Relative Intensities for Pretreated Blank and Pretreated Peroxide Brightened Pulp with Respect to the Original Pretreated Pulp.

Peak position	Percentage change in relative intensities					
	Blank[(a)]			Peroxide[(b)]		
$\nu(cm^{-1})$	$\frac{A_\nu}{A_{1056}}$	$\frac{A_\nu}{A_{1510}}$	$\frac{A_\nu}{A_{3300}}$	$\frac{A_\nu}{A_{1056}}$	$\frac{A_\nu}{A_{1510}}$	$\frac{A_\nu}{A_{3300}}$
1740	- 42	- 35	- 42	- 51	- 43	- 47
1650	+ 2	+ 9	+ 2	- 9	0	- 5
1600	- 7	0	- 7	- 4	+ 4	0
1510	- 7	--	- 7	- 9	--	- 5

(a) Difference between pretreated blank and pretreated pulp.

(b) Difference between pretreated peroxide brightened pulp and pretreated pulp.

change made the intensity data relative to the 1510 cm^{-1} intensity invalid. This is a good illustration of the need to use more than one internal standard peak. The peak at 1650 cm^{-1} showed a decrease upon peroxide brightening, corresponding to the removal of conjugated carbonyl chromophores, and a very slight increase upon treatment with the blank liquor.

Table 4 shows the percent change of the relative intensities of the bands between the pretreated brightened pulp and the pre-

TABLE 4

Percent Change in Relative Intensities between Pretreated Peroxide Brightened Pulp and Pretreated Blank.

Peak position ν (cm^{-1})	Percent change in relative intensities A_ν/A_{1056}	A_ν/A_{1510}	A_ν/A_{3300}
1742	-10	- 8	- 6
1650	-11	- 9	- 7
1600	+ 3	+ 4	+ 6
1510	- 2	---	+ 2

treated blank. In this case no significant change was found in the aromatic peak at 1510 cm^{-1}, since lignin was dissolved to the same extent in both the brightening and blank liquors. The change in the band at 1650 cm^{-1} due to conjugated carbonyls was found to be very similar to the one shown in Table 2 for the pulp that had not been pretreated. This correlates well with the similar brightness increase values obtained for the two sets of pulp. The acetyl and ester band at 1740 cm^{-1} showed a significant decrease for the pretreated peroxide brightened pulp with respect to the corresponding blank. This, together with the fact that the aromatic (and carboxylate) peak at 1600 cm^{-1}showed a slight increase in intensity, indicated that the expected decrease due to the removal of α-carbonyl groups was masked by the formation of carboxylate groups from deacetylation.

CONCLUSION

The technique of FTIR-PAS was shown to be useful in the study of mechanical pulp brightening. With baseline correction and the use of three different internal standard peaks (3400, 1510 and 1056 cm^{-1}), a reproducibility of better than 5% was achieved. The main changes observed in the spectra upon brightening were found in the carbonyl region. A net decrease in conjugated carbonyl groups was found in all cases. The main advantage of the technique is that it does not require any sample preparation.

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