Determination of pulp characteristics by diffuse reflectance FTIR

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ABSTRACT *We have assessed a method based on diffuse reflectance infrared Fourier transform spectrometry (DRIFT) for the rapid determination of lignin and carbohydrates (arabinose, galactose, glucose, mannose, and xylose) in pulp. The method can also be used to assess process properties such as pulp yield.*

KEYWORDS
Carbohydrates
Chemical analysis
Kraft pulp
Lignin
Wood

Infrared spectroscopy has long contributed to our qualitative understanding of the chemical structure of wood and pulp. Rapid Fourier transform infrared (FTIR) spectrometers, which are able to analyze both liquid and solid samples, became commercially available a decade ago. Since then, interest in quantitative measurements has grown, and several methods for estimating the content of lignin and carbohydrates in wood and pulps have been proposed. To our knowledge, none of these methods have been adopted as a routine industrial method, partly because of poor precision and insufficient information about their limitations.

The need for a quantitative interpretation of spectra requires efficient numerical methods. The partial least squares (PLS) analysis meets these requirements by extracting all relevant spectral data and providing error warnings, which were normally not included in the methods previously used.

Our purpose in this study was to develop a robust, rapid DRIFT method (diffuse reflectance infrared Fourier transform spectrometry) for analyzing pulp characteristics such as lignin content, carbohydrate content, and pulp yield.

Materials and experimental procedures

Pulp samples

Unbleached kraft pulps of Norway spruce (*Picea abies*) and Scots pine (*Pinus silvestris*) prepared in our laboratory were used as calibration and test sets. The pulp was analyzed for monomeric sugar composition (*1*), kappa number (*2*), and total and screened yields. Yield determination was based on the ratios of dry weights of the total pulp and screened fractions after defibration on a water jet defibrator (0.2-MPa water pressure, 2-mm-hole diameter) to the dry weight of wood. In addition, mill kraft pulp samples were obtained from MoDo, Ornskoldsvik, Sweden.

The air-dry pulp samples were milled in a Wiley-mill equipped with a 40-mesh screen. Some samples were further subdivided into finer fractions using sieves with openings of 355, 250, 212, and 160 μm, according to the ASTM E-11 standard.

A laboratory balance equipped with an infrared drying unit (Mettler LP16) was used to dry the samples to constant weight prior to IR analysis. Some of the samples were mixed with potassium bromide (1:16 by weight of sample to KBr) in a glass tube by vigorous shaking.

FTIR measurements

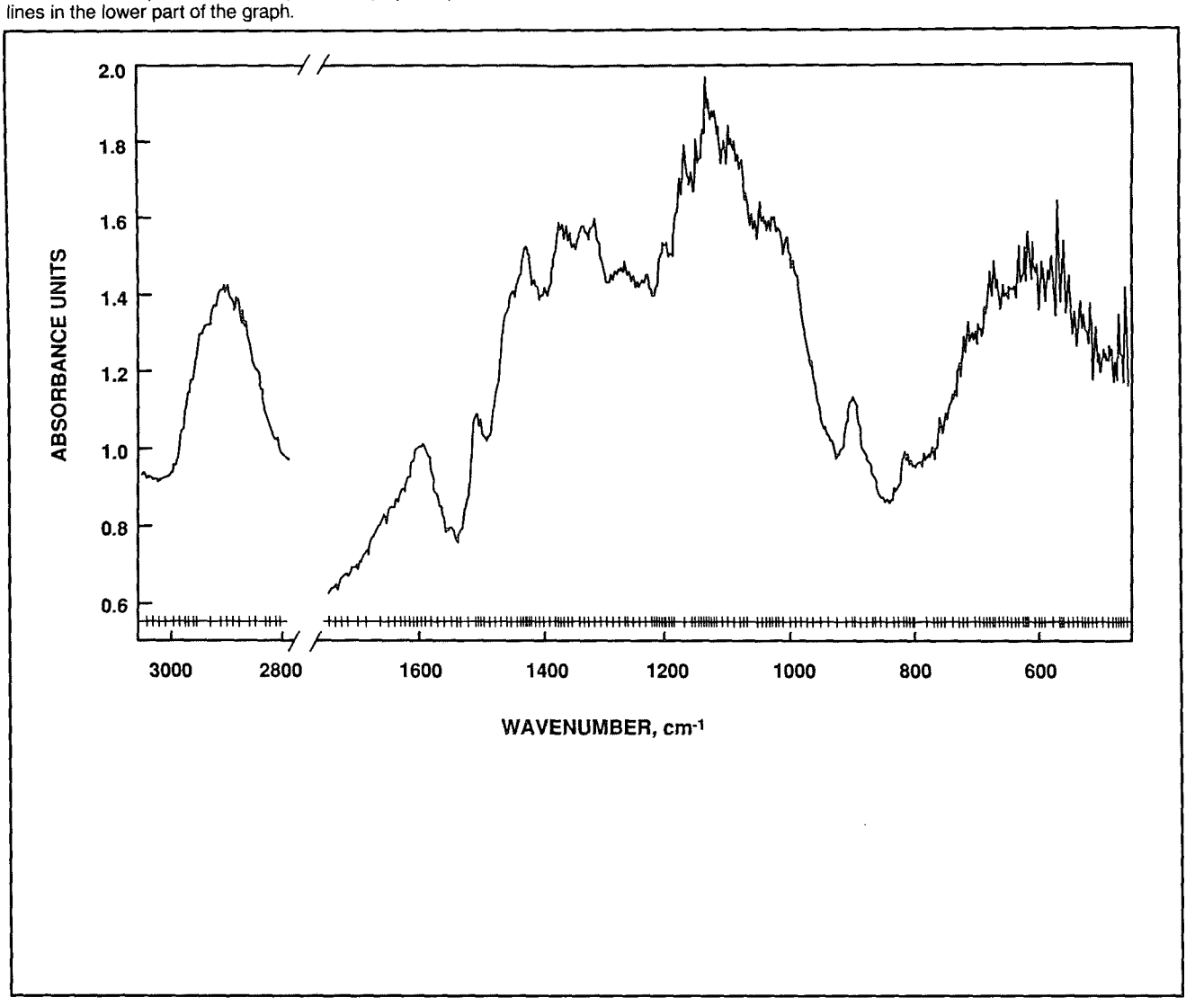
In the case of unmilled samples, the sample cup was half filled with KBr, and a mat of fibers was placed on top. Milled samples, mixed with KBr or neat, were placed in the sample cup and were leveled off gently using a cover glass. The sample cup was placed in a Spectratech DRIFT cell. When used, the blocker device was adjusted to achieve an energy level of 150±10 (arbitrary units) at the detector. The lower working limit of the detector was 100. Without using the blocker device, the energy level was approximately 500.

A Bruker IFS 66 FTIR spectrometer with a DTGS detector was used for collecting the interferograms. For each sample, 100 scans were collected and averaged in the wave number range of 3300–450 cm^{-1} with a resolution of 2 cm^{-1}. The interferograms were apodized by use of the Happ-Genzel function and were subsequently Fourier transformed. The reflectance spectra were expressed as ratios to a background of KBr and were processed to absorbance spectra in absorbance or Kubelka-Munk (K-M) units.

Data processing

The intensities at wave numbers 10

1. Absorbance spectra of a neat pine kraft pulp sample recorded with the use of blocker. Selected spectral data points are shown as vertical lines in the lower part of the graph.



cm^{-1} apart throughout the spectral range (except the range of 2800–1750 cm^{-1}) were chosen to represent the spectrum. In addition, a few wave numbers were chosen according to pertaining literature (*3*, *4*) to make a total of 232 wave numbers (**Fig. 1**).

The data interpretation was carried out by partial least squares analysis using the SIMCA package from SEPANOVA AB, Enskede, Sweden (*5*).

The method

Method development

To be rapid and not overly laborious, methods used in industrial analysis must permit an assessment of the uncertainty of the measurement. Moreover, factors affecting the precision and applicability of the method must be known. The simplification of methods to meet the need for rapid analysis generally conflicts with the need for precision and accuracy. One of the factors often neglected in this respect is sample preparation, which is important in DRIFT (*6*, *7*).

The FTIR analysis encompasses a number of operations, some of which are known to improve the quality of the spectra. These operations, however, are sequentially dependent on each other and are therefore difficult to evaluate. Hence, we employed a factorial design (**Table I**) using a subset of 16 pine kraft pulp samples to study the quantitative features of the operations. The evaluation was based on the standard error of prediction (SEP) as defined by Geladi *et al.* (*19*):

$$SEP = \sum_{i=1}^{I_{pred}} (c_i - \hat{c}_i)^2 / I_{pred} \qquad (1)$$

where

I_{pred} = total number of samples predicted

c_i = "true" value of the analyte concentration in Sample i

$\hat{c}_i$ = predicted value of the analyte concentration in Sample i.

(Here, the "analyte" is the chemical species or structure being analyzed.)

Partial least squares analysis (*5*, *8*) was used as the calibration method. The accuracy of the method (in terms of the standard error of prediction) can often be increased by adding extra PLS dimensions to the model. This practice, however, increases the complexity of the prediction model, with increasing sensitivity to errors in the data set. The optimum number of PLS-dimensions can be selected by the use of crossvalidation (*4*) as has

I. Plan of factor analysis

Variable				Partial least squares dimension									
A	B	C	D	1	2	3	4	5	6	7	8	9	10
+	+	+	+	95.0	89.6	29.9	17.1	9.2	7.0	4.3	2.7	1.4	0.8
+	+	+	-	65.1	49.1	31.0	21.3	12.8	9.1	6.8	4.9	3.2	1.6
+	+	-	+	96.1	88.6	28.8	16.0	9.0	5.8	3.6	1.6	0.9	0.3
+	-	+	+	81.1	75.8	31.0	18.1	10.7	7.0	4.5	2.9	1.4	0.6
-	+	+	+	98.2	72.6	28.8	18.1	12.8	7.3	4.2	1.9	0.7	0.3
-	-	+	+	89.6	68.3	32.0	20.3	13.8	9.9	6.3	3.8	2.2	1.2
-	+	-	+	78.7	72.8	27.3	16.0	10.4	6.8	3.5	1.5	0.6	0.3
-	+	+	-	47.0	32.0	23.5	17.1	10.7	7.5	4.1	2.2	1.2	0.5
+	-	+	-	81.1	34.2	30.9	25.6	13.9	8.9	7.4	6.0	4.3	2.8
+	-	-	+	74.7	68.3	28.8	13.9	8.1	5.3	3.1	1.8	0.7	0.4
+	+	-	-	65.1	49.1	29.9	19.2	12.8	8.5	6.5	4.7	3.4	1.4
+	-	-	-	77.9	35.2	30.9	24.5	12.8	8.3	7.0	5.5	4.2	2.5
-	+	-	-	48.0	32.0	28.8	22.4	14.9	8.3	5.2	3.1	1.9	1.0
-	-	+	-	71.5	49.1	33.1	23.5	18.1	11.7	9.0	6.4	5.2	2.8
-	-	-	+	95.0	60.8	27.7	16.0	10.7	6.4	4.6	2.6	1.2	0.6
-	-	-	-	68.3	50.2	29.9	19.2	13.9	11.7	8.9	6.4	4.4	2.9
Factor response													
A				4.98	6.52	1.26	0.38	-2.00	-1.22	-0.32	0.28	0.26	0.10
B				-5.76	5.48	-2.04	-1.74	-1.18	-1.12	-1.58	-1.60	-1.28	-0.96
C				3.10	1.72	1.02	1.74	1.18	0.92	0.52	0.46	0.28	0.16
D				23.06	33.24	-0.46	-4.66	-3.16	-2.32	-2.60	-2.56	-2.34	1.38
Factor interactions													
AB				7.38	10.24	1.54	-0.38	0.76	1.34	1.38	1.02	0.86	0.40
AC				-0.98	0.16	0.08	0.38	-0.20	0.12	0.18	0.28	-0.02	0.16
AD				-8.62	5.44	-0.58	-1.72	-0.68	-0.12	-0.46	-0.48	-0.34	-0.18
BC				1.26	-1.52	-1.42	-1.74	-1.58	-0.54	-0.38	-0.26	-0.36	-0.10
BD				12.66	7.12	0.86	1.46	0.70	0.68	0.86	0.76	0.82	0.68
CD				1.76	2.24	1.26	1.18	0.90	0.82	0.60	0.50	0.28	0.16
Estimation of the standard deviation is based on three and four factor interactions.													
s				3.33	3.22	0.95	2.30	1.08	0.44	0.27	0.20	0.18	0.10

Factor A denotes the mixing of potassium bromide (+) or neat samples (-).
Factor B denotes the use of blocker (+) or not (-).
Factor C denotes the use of K-M transformation (+) or absorbance (-) spectra.
Factor D denotes the use of multiple scattering coefficient (+) or internal standard (-) for normalization of spectra.

been done in this work.

Thus, we have aimed at an SEP as low as possible at a minimum number of PLS dimensions. Throughout the development of the method, the PLS modeling was consecutively based on 3/4 of the data, leaving 1/4 for predictions, until all samples were predicted.

Calibration techniques

The relevant literature on quantitative IR analysis reports the use of different calibration techniques. These techniques range from fairly simple correlations of a single intensity to multivariate methods such as PLS analysis.

In the use of linear regression of single absorption bands to analyte concentration, it is presupposed that the bands are assigned to the analyte and that the matrix does not contribute to the variance in absorption intensity. Many of the descriptors used in industry, such as "kappa number" and "yield," do not have a unique chemical definition. For example, the contributions to the kappa number from different lignin structures (different absorption bands) vary with the raw material, the degree of delignification, and the delignification process. This suggests that the use of linear regression of single absorption bands should be restricted to a limited experimental domain. As an example of quantifications in DRIFT analysis based on linear regression, Berben *et al.* (*9*) related the intensity of the 1510-cm^{-1} band to the lignin content of pulp.

To extend the range over which the predictions may be made or to assess composite analytes, two or more absorption bands are used, representing more than one chemical structure in the analyte. A method commonly used in these cases is stepwise regression analysis. This method suffers from the same limitation, that spectral bands should not overlap but must be linearly dependent on the analyte concentration. Some further constraints are that the spectral bands used must be orthogonal and that the number of calibration samples must exceed the number of spectral bands used. Grandmaison *et al.* (*10*) and Pakdel *et al.* (*11*) utilized a nonlinear least squares multiple regression analysis to determine partially converted lignocellulosics and wood, respectively. Schultz *et al.* (*4, 12, 13*) used MINITAB stepwise regression analysis in estimating lignin and

monose sugar composition in pulp.

IR spectra of wood pulp are at least partly composed of overlapping spectral bands. These bands may be resolved by the use of multivariate techniques, such as principal component regression analysis and partial least squares regression analysis (*5, 8*). By using these techniques, all inherent information in the spectra may be used for quantification. A further advantage is that the number of samples may be less than the number of spectral bands. Wallbacks *et al.* (*14*) determined the Klason lignin, glucose, xylose, and galactose content of birch kraft pulp using the PLS calibration technique.

Many FTIR instruments utilize principal component regression analysis for quantifications (as for example in Bruker's QFAKTOR software). This type of analysis differs from PLS analysis in that it separates the spectral data into principal components, using these as orthogonal factors in a stepwise regression. On the other hand, PLS calculates the principal components of the analyte matrix and of the spectral data matrix, then it allows tilting of the resultant principal components (of analyte and spectral data) relative to each other to obtain an optimal calibration. PLS is thus more effective than principal component regression analysis.

Since the purpose of our work includes the prediction of complex descriptors, our choice of calibration methods was PLS.

Sample preparation

The particle size generally plays an important role in light scattering. Fuller and Griffiths studied azobenzene and reported considerable changes in bandwidths and relative intensities with particle size, with the bandwidths decreasing with reduction in particle size (*15*). Childers and Palmer, working with brominated polystyrene beads, found that the spectral peaks were resolved only for particles with diameters less than 100 μm (*7*). Berben *et al.*, however, found no appreciable difference in the quality of IR spectra between milled and unmilled pulp samples (*9*).

To assess the importance of particle size, we compared 11 unmilled pulp samples to their milled (<40 mesh) counterparts with respect to the pooled SEP. Based on absorbance spectra normalized by an internal standard, the milled samples had significantly lower SEP than the unmilled samples (at 95% confidence). Furthermore, three milled pine kraft pulp samples (**Table II**) were divided into different size fractions by means of a standard sieve. The mean of the predicted assays did not substantially differ between the fractions. However, the precision of the predictions was superior for the fines fraction (<160 μm) than for the fractions for larger particles. It is therefore advisable to mill the sample to small particle sizes.

II. The influence of particle size on the prediction error of a determinant vector consisting of kappa number, xylose content, and total yield. The calculations are based on 4 PLS dimensions from internal standard normalized K—M spectra.

Fraction, μm	*Fraction distribution, %*	*Pooled SEP, %*
Combined sample	100.0	0.30
$250 < x < 355$	5.0	1.22
$212 < x < 250$	6.6	1.21
$160 < x < 212$	13.2	1.09
$x < 160$	74.9	0.30

Samples for DRIFT analysis are usually diluted by potassium bromide to improve the spectral quality (in a visual sense). Fuller and Griffiths (*15*) showed that for the analysis of azobenzene, a nonlinear relation between concentration and absorbance (given in Kubelka-Munk units) occurs when the sample-to-diluent ratio exceeds 0.3. This finding was supported in an analysis of carbazole (*6*). Childers and Palmer (*7*) stated that nonlinearities occur at a sample-to-diluent ratio >0.2 in the analysis of Prussian blue powder. They interpreted these nonlinearities as saturation effects that occur when the depth of penetration of the incident light becomes independent of absorptivity. This situation is normally encountered in strongly absorbing samples. Specular reflectance has also been suggested as a reason for nonlinear behavior (*6, 10, 16*). Schultz *et al.* (*4*) stated that spectral quality is improved for wood samples diluted with KCl.

In analyses of coals with low mineral content (*6*), of aspirin (*7*), and of pulp samples (*9*), no improvement or only a slight improvement in the spectral quality was found on dilution with KBr or KCl.

In our work, the subset of pine kraft pulp samples was analyzed both neat and diluted with potassium bromide. We concluded from factor analysis (Table I) that dilution with KBr has a negative effect on the modeling of differences in baseline level and slope (*8*), which is reflected in the first two PLS dimensions. This effect can be due to sample inhomogeneity. However, the dilution causes a slight improvement in precision in the prediction of the analytes. This effect may be due to a diminished risk of saturation effects.

The sample cell

In practical DRIFT applications, the radiation reflected from the samples is due to both diffuse reflectance and specular reflectance. Specular reflectance is defined as IR radiation reflected from the sample surface without penetration. Specular reflectance may therefore distort the quantitative analysis. To reduce the influence of specular reflectance, the sample is diluted in a low absorbing matrix (KCl or KBr). The use of polarizers has been proposed as well (*17*). Different optical geometries of the DRIFT accessories may also influence the amount of the specular component (*18*). The physical rejection of specular reflectance with a "blocker device" has also been proposed and recommended for quantitative purposes (*16*).

To evaluate the influence of the blocker device, we analyzed the subset of pine kraft pulp samples with the blocker active. The factor analysis showed that the use of blocker strongly improves the prediction power. The use of blocker led to a less variable baseline level, which positively affects the PLS modeling. In the prediction of carbohydrates, a positive effect is

noticed, which may be explained by a decrease in the influence of specular reflectance (*16*).

Signal transformation

The reflectance signal impinging on the detector undergoes a transformation to yield a linear relationship to the quantitative properties sought. There are two main transformations, the absorbance and the Kubelka-Munk (K-M) transformations.

Lambert-Beer's law relates the absorbance to the concentration of the analyte, with the absorption of radiation at a specific wave number being linearly proportional to the concentration. For ideal diffuse reflectance of an infinitely thick layer of dilute samples in low absorbing matrices, the K-M theory relates the sample absorption coefficient of radiation to the reflected energy and thereby to the analyte concentration, separating the effect of scattering from the true effect of absorption.

In quantitative DRIFT analysis of pulp or wood samples, intensities have been given in absorbance as well as in K-M units. Schultz *et al.* related absorption signals to analyte concentration for samples diluted with potassium chloride (*4*). Grandmaison *et al.* used intensities in K-M units for diluted samples and in absorbance units for neat samples, but they used only the Kubelka-Munk technique for quantification because of spectral quality considerations (*10*). Berben *et al.* used spectra in K-M units as well as in absorption units for neat samples (*9*). They found that the detector signal given in absorbance units correlates to the lignin content of the pulp, whereas that given in K-M units does not. Pakdel *et al.* used K-M transformed spectra for the analysis of dilute samples (*11*).

As the factor analysis of data (Table I) shows, the absorbance signal, independent of the other factors, is better suited for PLS analysis given in absorbance units than in K-M units. This difference might be due to the nonlinear behavior of the K-M transformation, possibly as a result of variations in the scattering coefficient. Spectra recorded in absorbance instead of K-M units give a better modeling in the second and sixth PLS dimensions. In the second dimension, the slopes and intercepts of the random baselines are modeled (*8*).

Normalization of spectra

The IR spectra obtained are seldom directly comparable since baseline levels differ between samples. To make it possible to compare spectra quantitatively, the spectra are normalized. Our approaches to normalize spectra in this work involve the total energy norm, an internal standard peak in the spectrum, and the multiple scattering correction.

First, the total energy norm is defined by the integral of absorbed energy in the spectrum. After normalization, the data matrix has the form

$$[X] / \Sigma \text{ absorbed energy}$$

where $[X]$ denotes the spectrum absorbance matrix. Second, the internal standard norm is based on an internal standard peak in the spectrum. The data matrix has the form

$$[X] / x_{istd}$$

where x_{istd} denotes the signal (absorbance or K-M) at the internal standard wave number. Finally, the multiple scattering coefficient is derived by linearizing the spectra used for multivariate analysis. Here, the individual spectra are represented as linear functions of a mean spectrum using linear regression analysis, according to Eq. 2:

$$X = a / \bar{X} + b + \epsilon \qquad (2)$$

where

- X = individual spectrum matrix
- $\bar{X}$ = mean of individual spectrum matrices
- a, b = constants
- ϵ = deviation from the linear model.

This equation allows a separation of light scattering and absorbance (*19*).

Schultz *et al.* (*4*) used separate internal standards for different pulp components. They used the 1048 cm^{-1} peak as the internal standard for lignin, the peak at 1461 cm^{-1} for glucose, and the peak at 1117 cm^{-1} for xylose. Schultz and Glasser employed one of the bands at 1600, 1513, or 1425 cm^{-1} as internal standards in analyzing lignin (*12*). Grandmaison *et al.* took the peak at 1505 cm^{-1} as the internal standard peak for lignin and the peak at 1595 cm^{-1} for glucose and xylose (*10*). Faix *et al.* (*20*) and Niemz *et al.* (*21*) made use of a peak at 897 cm^{-1}, but this absorption band is prone to increase as a result of treatment that leads to decreasing cellulose crystallinity (*22*). Pakdel *et al.* used bands of 1100 cm^{-1} to analyze Klason lignin, 1210 cm^{-1} to analyze glucose, and 1595 cm^{-1} to analyze xylose (*11*).

Wallbacks *et al.* used the multiple scattering correction (*14*).

We have found that normalization of the data generally improves the quantitative information contained from the IR analysis. The difference between normalized (Internal Standard 897 cm^{-1}) and nonnormalized data is significant at the 95% confidence level, based on a four-dimensional PLS model determining kappa number, pulp yield, and monose sugar composition. However, no difference between the internal standard method (897 cm^{-1}) or the total energy norm has been found at the same confidence level.

According to the factor analysis of Table I, the multiple scattering correction is superior to the internal standard normalization with regard to prediction power. The number of PLS dimensions used to achieve a certain standard error of prediction increases compared to the internal standard technique when the multiple scattering correction is used. This difference arises because the first two PLS dimensions in the internal standard case do not contain information about the chemical composition of the samples. Moreover, the better baseline correction obtained by internal standard normalization emphasizes this effect.

Further improvement may be possible by an initial normalization by internal standard to compensate for differences in baselines and by subsequent normalization using the multiple scattering correction to reduce variations in the light scattering.

Some of the factors studied in our work are partly, in a complex manner, affecting the same physical phenomena. As an example, the specular reflectance can be affected in different stages of the analysis: in sample preparation by dilution with KBr, in the instrumental analysis by using the blocker device, and in the data manipulation by using the multiple scattering correction. These interactions suggest that an intricate cooperative effect could be discerned, which is demonstrated by the following inter-

pretation of two-factor interactions extracted from the factor analysis in Table I.

The two-factor interaction between the dilution with KBr and the use of blocker has a negative influence on the prediction model. The more likely interpretation is, however, that by using neither KBr nor blocker, the scattering is uncontrolled. Both of these factors obstruct a smooth linear modeling. By using either of the two interacting factors, the model will improve, since the scattering and specular reflectance are diminished. Also, the power to predict the analyte concentration improves, since the noise from noninformative (specular) reflection is reduced.

No significant effects have been encountered by the use of either KBr and K-M simultaneously or KBr and absorbance simultaneousyly, which is contrary to most results reported in the literature.

The simultaneous use of an internal standard and neat samples simplifies the modeling of differences in baselines (PLS, first and second dimensions). The prediction ability is, however, superior when multiple scattering correction and KBr are used simultaneously, presumably as a result of better modeling of scatter differences and perhaps because of a lack of linearity between the internal standard chosen and some of the spectral bands used for predicting the concentrations of the analytes.

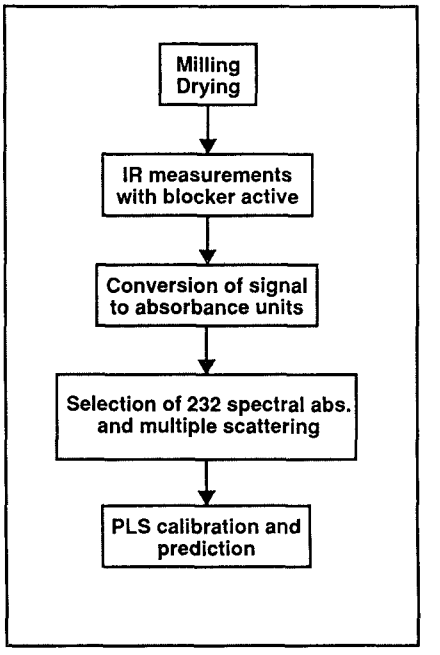
The use of a blocker reduces the relative level of scattering so that the K-M transformation can be used. The simultaneous use of blocker and K-M thus readily facilitates the modeling of the baseline of the sample by diminishing the differences in baseline intercepts. The simultaneous use of blocker and internal standard also permits a good modeling of differences in baselines. The use of internal standard without using blocker at the same time impairs the method's ability to predict the analyte concentrations.

As the result of the method development, a scheme of analysis was adopted as diagrammed in **Fig. 2.**

In this work, the only sample treatments recommended are milling of the sample to pass a 40-mesh screen and drying to constant weight prior to the IR measurement. The dilution by KBr recommended by many others can be omitted to simplify the sample treatment. Apart from saving time and achieving better homogeneity, the advantages of avoiding KBr addition are that the sample is less sensitive to hygroscopic conditions during preparation and storage and that the calibration samples can be reused. The IR measurements should be made using blocker. Correction of selected spectral absorbances by multiple scattering correction is recommended before PLS calibration and prediction.

The method is sensitive to samples ratioed to different backgrounds. Consequently, all samples in the calibration and test set should be related to the same KBr background. Automation of the last steps of the analysis will result in a method that is easy to use, even for unskilled personnel.

2. General scheme of analysis



Applications of the method

Determination of pulp yield

The pulp yield is not easily monitored, especially in continuous processes. The importance of determining yield increases with increasing raw material costs and the desire to extend the delignification during pulping. Much effort has been devoted therefore to developing methods for determining pulp yield. The weighing of raw material and pulp produced has been recommended but is impracticable (*23*). The preferred method is the utilization of baskets with a defined amount of raw material immersed in the digester. These methods, however, are restricted to discontinuous processes.

In practice, the yield is normally estimated from a kappa number-yield relationship established by laboratory cooking. Janson and Teder (*24*) further developed the yield determination based on kappa number determinations by taking into consideration the carbohydrate degradation that occurs in less selective delignification processes.

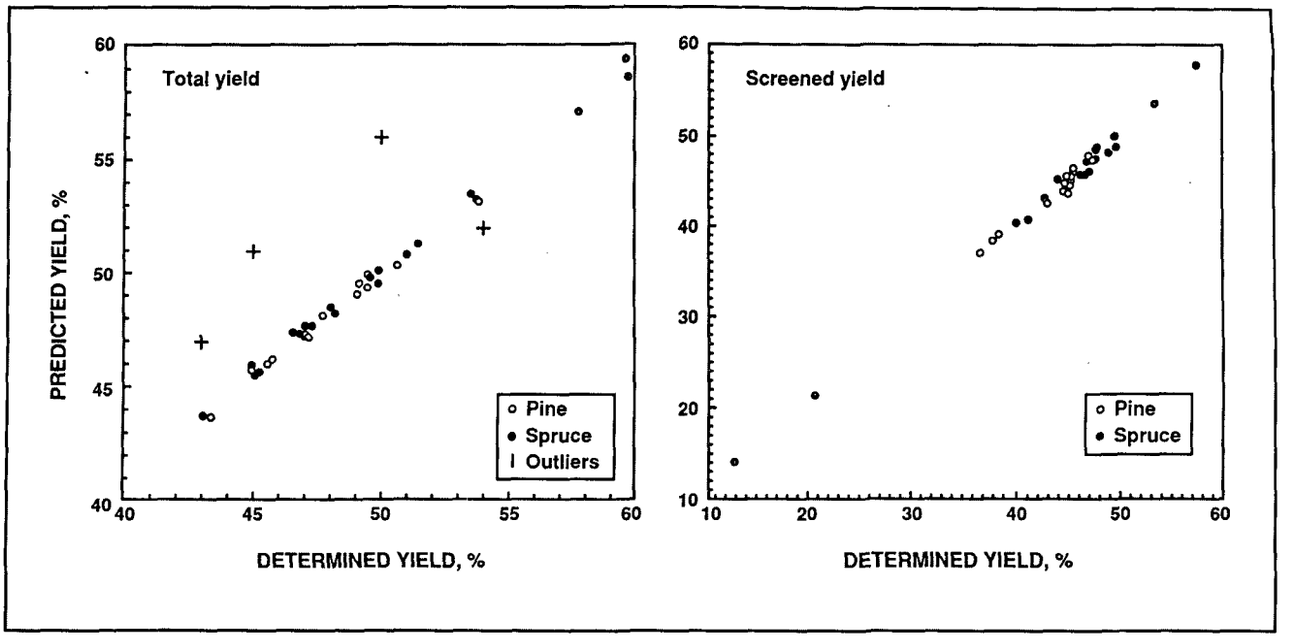
Chemical changes in the pulp during the course of delignification lead to changes in the IR spectrum and make possible a calibration of pulp yield. Softwood kraft pulps over a wide range of total and screened yields have been prepared in the laboratory. The raw material was selected to cover and even exceed the outermost limits with regard to chip dimensions and knots content encountered in a mill. Both plots in **Fig. 3** are based on the same data set, consecutively using 33 samples as the calibration set and leaving 2 samples for prediction until the analytes of all 35 samples have been predicted.

A relationship between kappa number and yield was established using linear regression analysis. The yield was also determined by the method of Janson and Teder (*25*). The results are presented in **Fig. 4.**

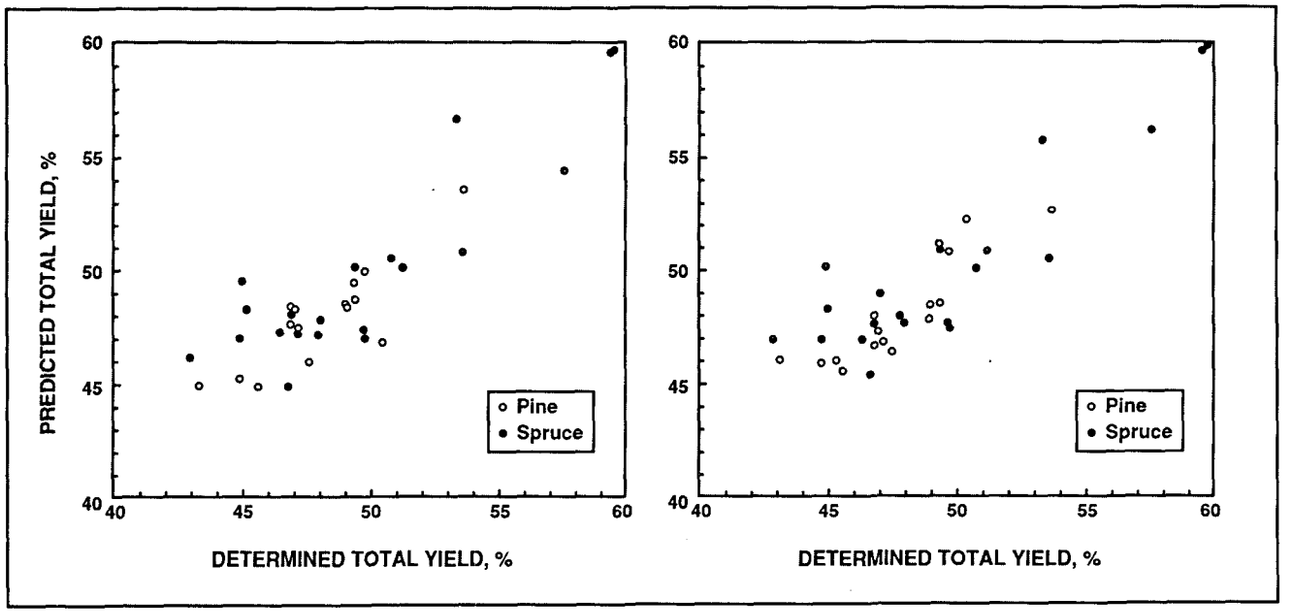
As Figs. 3 and 4 show, the precision of the IR method is superior to that of the other methods. The lack of precision in the kappa number-yield relationship is caused by strong variations in chip quality. This relationship therefore has a limited range of validity. The method of Janson and Teder (*24*) has a larger validity range because it compensates for carbohydrate losses, but it is apparently sensitive to variations in chip quality. In our use of the Janson and Teder method, the calculation constants used (*25*) may not fully apply to our set of pulps and may contribute to an inferior precision than obtained under normal mill conditions.

In the IR method presented, the selection of spectral data points for the PLS analysis accounts for most of the chemical changes relevant to determining the yield. According to Fig. 3,

3. Prediction of total and screened yields for 35 unknown samples from a model based on 7 PLS dimensions. The model data set contains 33 pine and spruce kraft pulp samples.



4. Prediction of total yield from a kappa number-yield relationship (left) and according to Janson and Teder (*24*) (right)



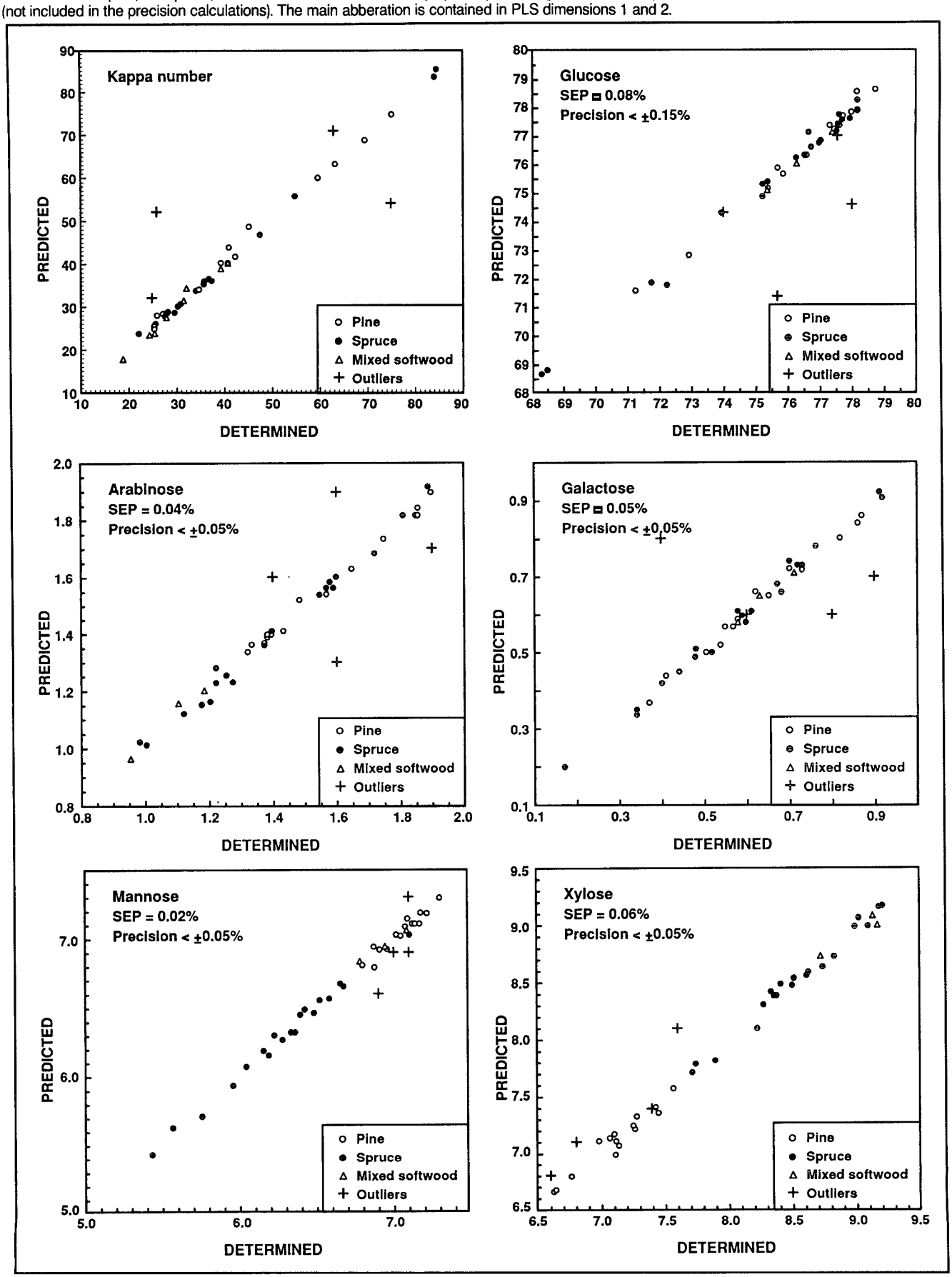
the SEP is 0.46% and 1.18% for total and screened yields, respectively. If we remove 9 samples with abnormally high reject content (>5% on o.d. wood), the SEP improves to 0.02% using a 7-dimensional PLS model.

PLS calibration has the advantage of automatically allowing the detection of samples not coherent with the calibration set (detection of out-lying data ponts), providing a means of controlling the model validity (*5*).

On the basis of this data set of 35 samples, the standard deviation for a total yield at 47% is 0.46%. This value can probably be regarded as an upper limit of uncertainty, since the chip dimension in technical processes is normally less variable than reflected in this model. IR prediction of three samples of softwood kraft pulp from a continuous Kamyr digester revealed a total yield of 45.0% at kappa no. 30.4, which is in close agreement with laboratory kraft cooking of pine wood from the same geographical region (44.6±0.5% at kappa no. 35) (*26*).

The precision of the gravimetric determination of pulp yield in the laboratory has been reported to be ±0.2% based on five replicate samples (*23*). Since the yield determination of the calibration set in this work is based on the dry weight of the total pulp produced, rather than on wet weight corrected for moisture con-

5. Prediction of kappa number, glucose, arabinose, galactose, mannose, and xylose from a model based on 7 PLS dimensions. The total data set contains 15 pine, 20 spruce, and 2-7 mixed softwood kraft pulp samples. + signs denote samples not concurrent with the calibration set (not included in the precision calculations). The main abberation is contained in PLS dimensions 1 and 2.



tent, the accuracy of the calibration data and thus of the predicted data is very high. The only uncertainty remaining is lack of homogeneity in the moisture content of the chips.

Determination of kappa number

A variety of wood species and pulping processes have been examined by IR spectrometry with regard to kappa number. Berben *et al.* (*9*) reached a precision in kappa number determination of duplicate samples of ±10 units at the 95% confidence level. The same researchers estimated their results to be comparable to those of Marton and Sparks (*27*). One reason for this wide variation is the use of calibration sets containing different wood species that have undergone delignification by different delignifying agents (kraft and sulfite cooking), indicating that different types of residual lignin structures give rise to the kappa number. The PLS analysis enables detection of samples dissimilar to the calibration set. In an attempt to predict the kappa number for a birch kraft pulp sample by the softwood calibration model used in this work, we discovered that the sample resided outside the calibration domain.

In our study, the SEP for kappa number determination is 2.75% for the 35 samples mentioned and 7 additional industrial samples of mixed softwood. This precision is concurrent with recommendations on reported accuracy in the SCAN standard for wet chemical determination of kappa number (*2*).

Determination of carbohydrates

A rapid method for determining the carbohydrate composition in pulp is highly desired, especially since such a method would enable selectivity in extended delignification processes to be monitored. Schultz *et al.* (*4, 13*) determined cellulose and hemicelluloses as well as glucose and xylose content in pulp. Wallbacks *et al.* (*14*) determined galactose, glucose, and xylose in pulp. The results of these studies suggest that the prediction error is considerable. Glucose and xylose contents were also determined with varying success in wood samples subjected to heat treatment (*10, 11*).

As shown in **Fig. 5**, all five major monose sugars in pulp can be determined readily by the use of FTIR. These results show that the precision of the FTIR method exceeds that of the classical wet chemical determination (*1*).

Generally, spectroscopic methods are very precise. The accuracy of the FTIR calibration methods is governed by systematic errors (uncertainty) in the reference method used, but the precision of the reference method does not necessarily limit the precision of the calibration method, provided a large enough calibration set is used.

Conclusions

A rapid method based on diffuse reflectance infrared spectrometry has been developed for determining chemical constituents of pulp and pulp yield. The use of blocker to minimize direct reflectance from the sample surface and the use of a mathematical separation (the multiple scattering correction) of the informative and noninformative components of the reflected energy improve the quantification.

This work also shows that homogenization of the sample plays an important role in increasing the precision, and that a thorough modeling of the background is crucial to successful predictions. The method is very precise, and it provides a means of detecting its limitations. The total analysis time necessary is 10–15 min/sample, excluding sample preparation.

The proposed method has been used to assess the pulp yield, a factor that is often impossible to monitor with sufficient precision. The use of FTIR combined with efficient computer-assisted quantification software may thereby open new fields within this industry, both in sophisticated process control and in research.□

Literature cited

1. Theander, O. and Westerlund, E. A., J. Agric. Food Chem. 34(2): 330(1986).
2. Standard method for determination of kappa number, Scandinavian SCAN C1:77.
3. Faix, O. and Beinhoff, O., J. Wood Chem. Techn. 8(4): 505(1988).
4. Schultz, T. P., Tempelton, M. C., and McGinnis, G. D., Anal. Chem. 57(14): 2867(1985).
5. Wold, S., Albano, C., Dunn III, W. J., Edlund, U., *et al.*, Chemometrics, mathematics and statistics in chemistry (B. R. Kowalski, Ed.), D. Reidel Publishing Co., Dordrecht, Holland, 1984.
6. Brimmer, P. J. and Griffiths, P. R., Anal. Chem. 58(11): 2179(1986).
7. Childers, J. W. and Palmer, R. A., Am. Laboratory (3): 22(1986).
8. Haaland, D. M. and Thomas, E. V., Anal. Chem. 60(11): 1193(1988) (Part I and II).
9. Berben, S. A., Rademacher, J. P., Sell, L. O., and Easty, D. B., Tappi 70(11): 129(1987).
10. Grandmaison, J. L., Thibault, J., and Kaliaguine, S., Anal. Chem. 59(17): 2153(1987).
11. Pakdel, H., Grandmaison, J. L., and Roy, C., Can. J. Chem. 67(2): 310(1989).
12. Schultz, T. P. and Glasser, W. G., Holzforschung 40(Suppl.): 37(1986).
13. Schultz, T. P. and Burns, D. A., Tappi 73(5): 209(1990).
14. Wallbacks, L., Edlund, U., and Norden, B., manuscript submitted to Tappi.
15. Fuller, M. P. and Griffiths, P. R., Anal. Chem. 50(13): 1906(1978).
16. Messerschmidt, R. G., Applied Spectroscopy 39(4): 737(1985).
17. Yang, P. W., Mantsch, H. H., and Baudais, F., Applied Spectroscopy 40(7): 974(1986).
18. Hembree, D. M. and Smyrl, H. R., Applied Spectroscopy 43(2): 267(1989).
19. Geladi, P., MacDougall, D., and Martens, H., Applied Spectroscopy 39(3): 491(1985).
20. Faix, O., Patt, R., and Beinhoff, O., Papier 41(12): 657(1987).
21. Niemz, P., Weinhaus, O., Schaarschmidt, K., and Ramin, R., Holzforsch. Holzverwert. 41(2): 22(1989).
22. Michell, A. J., Watson, A. J., and Higgins, H. G., Tappi 48(9): 520(1965).
23. Keays, J. L., Hatton, J. V., and Cortez, R. R., Tappi 52(5): 904(1969).
24. Janson, J. and Teder, A., Nordic Pulp and Paper Res. J. 1(1): 43(1986).
25. Janson, J., Faserforschung u. Textiltechn. 25(9): 375(1974).
26. SPCI-meddelande nr 29 (with addendum) (in Swedish), available from SPCI, Villagatan 1, Stockholm, Sweden, 1977.
27. Marton, J. and Sparks, H. E., Tappi 50(7): 363(1967).

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