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INFRARED ANALYSIS FOR PROCESS CONTROL IN THE PULP AND PAPER INDUSTRY

[1]Herbert Furumoto, Uwe Lampe, Hans Meixner, Christoph Roth

Summary

Parameters important for process control in the pulp and paper industry, e.g. strength properties, can only be measured at much expense in the laboratory and are thus not available for immediate control or adjustment. With infrared analysis and modern software for assessment of the spectra, these parameters become available for fast on-line measurement. Almost all chemical and physical information on paper, pulp or the timber are contained in the infrared spectra. It is however not possible to make unambiguous connections between this information and the spectral bands, since these are generally very broad and often overlap. The relations between the chemical composition and the parameters, important for process control, are often insufficiently well known. By the application of an innovative evaluation of the spectra, it can be shown that it is possible to determine the paper and pulp strengths like breaking length, burst strength, CMT (Concora Medium Test) and others, directly from the spectra.

1. Infrared spectroscopy

Infrared spectroscopy is a well established chemical analysis technique. Infrared covers the electromagnetic spectrum between 700 nm and 3 000 µm, corresponding to an energy level of between 1.24 eV and 0.41 meV. The visible light area starts at the shorter wave length and microwaves at the higher wave length. The various spectral infrared ranges and the type of interaction between electromagnetic radiation and the matter is shown in **Figure 1**.

The molecular vibrations, especially the basic fundamental vibrations, remain localized between the individual atoms, and are essentially de-coupled from one another. The most important vibration bandwidths for paper and pulp in the MIR range (Medium Infrared Range) are shown in **Figures 2 and 3**.

The vibration energy depends on the mass of the atoms involved or the atomic groups and the binding energy between the atoms. Qualitatively, the interdependency can be defined as follows:

- as the mass of the atoms increases, then the vibration energy decreases (wave number)
- as the binding energy increases, then the vibration energy also increases (wave number),

e.g. a carbon-double bonding absorbs more energy than a carbon single bonding.

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[1] Dr. Ing. Herbert Furumoto, Schenkstr.146, 91052 Erlangen; Dr. rer. nat. Uwe Lampe, Beim Kloster Dohren 13, 21614 Buxtehude; Prof. Dr. rer. nat. Hans Meixner, Max Planck Str. 5, 85540 Haar; Dr. rer. nat. Christoph Roth, 4-21-5 Denenchofu, Ota-ku, Tokyo 145-0071,

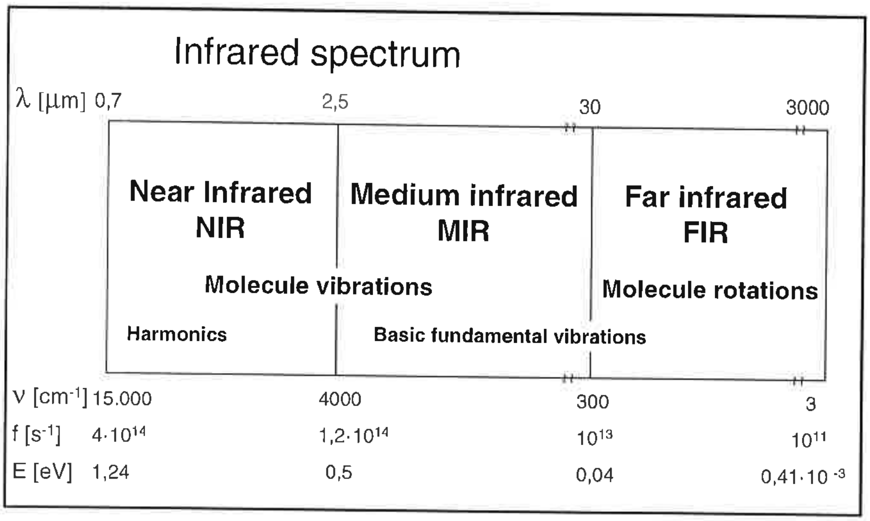
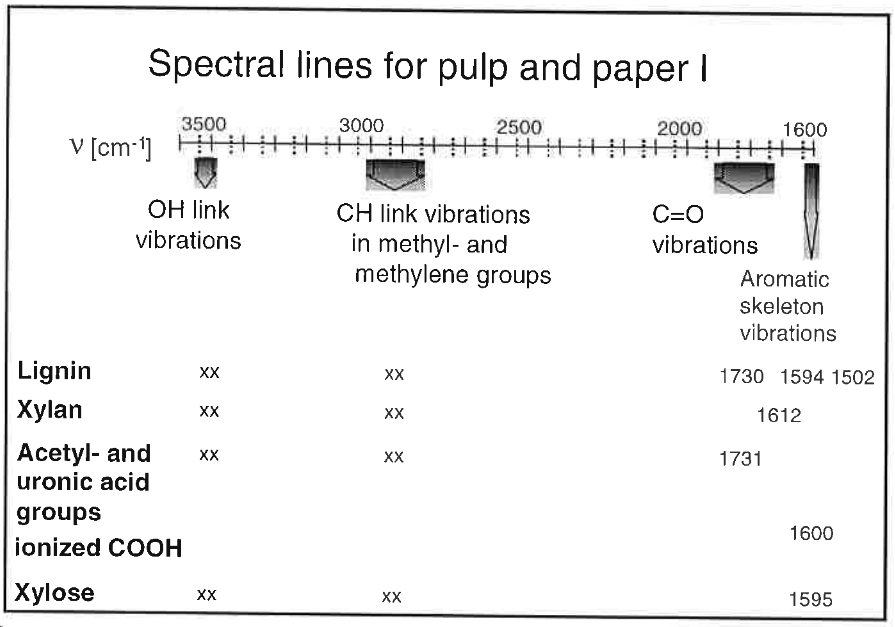


Figure 1. Spectral ranges of infrared light.
(λ wavelength, ν wave number, f frequency, E energy)



	OH link vibrations	CH link vibrations in methyl- and methylene groups	C=O vibrations / Aromatic skeleton vibrations
Lignin	xx	xx	1730 1594 1502
Xylan	xx	xx	1612
Acetyl- and uronic acid groups	xx	xx	1731
ionized COOH			1600
Xylose	xx	xx	1595

Figure 2. Important spectral lines for pulp and paper in the medium infrared range.

Thus, if the absorption shifts, it can be assumed that the binding strength changes, e. g. hydrogen bridge linkages always weaken of the actual hydrogen bonding. Its absorption is therefore shifted to lower energy levels. From the theory, we know that the bonding between paper fibers and the bonding within the fibers is essentially due to hydrogen bridge linkages between the cellulose molecules. Thus, the number and the strength of these hydrogen bridge linkages can be immediately determined, also in the infrared spectrum, from the shift and extent of the OH peak. This results in a correlation between the strength of the paper or pulp which depends on the number and strength of the hydrogen bridge linkages, and the IR spectra of the paper or pulp. This correlation forms the physical basis for modeling the strength from the IR spectrum.

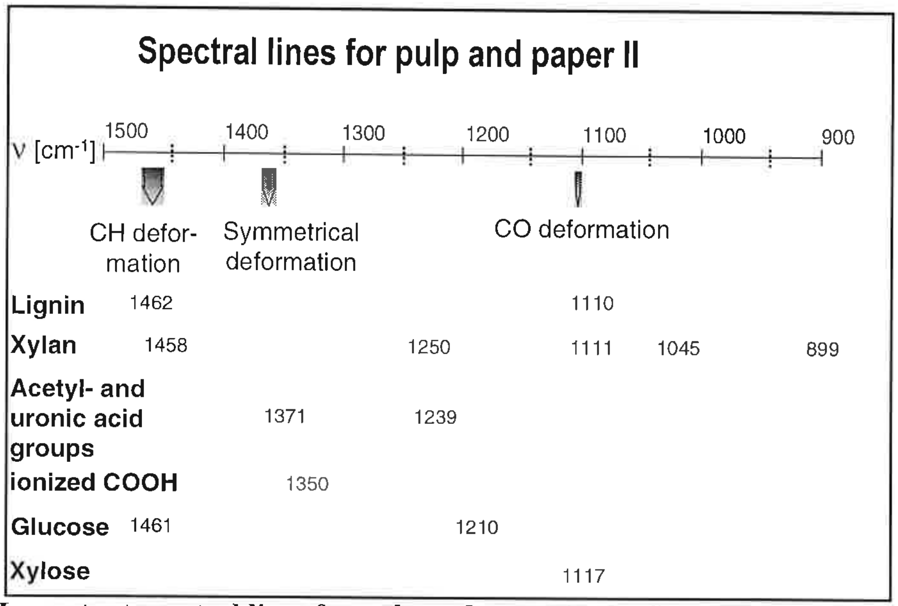


Figure 3. Important spectral lines for pulp and paper in the fingerprint range of MIR.

2. Quantitative evaluation of spectra: Chemometrics

Infrared analysis reaches its limits, if the spectra become too complex, i. e. if the spectral bands are too wide and many of the bands overlap. Pulp and paper spectra belong to this particular class, as they contain several different organic components, and further, macro molecules having a different size. A clear assignment is only possible for just a few molecule groups. Comprehensive laboratory investigations have been carried-out, especially regarding to pulp and wood, using infrared spectroscopy. In the pulp area, the main focus was on chemical analysis, for example, the measurement of the lignin content[1,2,3], the fine structure and the properties of the cellulose[4] and in the wood area, in the classification[5] and the quality with regard to pulp production[6].

The developments made in various chemometric techniques represented a significant step forward when it came to the quantitative analysis of spectra Special mention should be given here to two techniques - the Principle Components Analysis (PCA) and the Partial Least Square (PLS) in latent variables. For PCA, the measured wavelengths of the spectra (original variables) are modeled using linear combinations, which are independent of one another. These contain, as main components, the factors of the linear combinations, the so-called scores. The largest possible part of the variation of the spectrum is explained with the 1st main component pc_1. The second main component pc_2 explains the largest proportion of the remainder; the third, fourth etc. appropriately follow. Generally, this technique can be defined as follows:

$$\text{Spectrum}^{n}\,(\text{wave number}) = \Sigma_{j=1\rightarrow n}\, pc^{n}_{j} * \text{score}_{j}(\text{wave number})$$

Spectrum ^{n}(wave number) -	n plotted spectra,
pc^{n}_{j} -	main components,
score_{j}(wave number) -	spectral dependency, independent of the individual spectrum

The PLS technique is principally the same, however the breakdown is already made, taking into account the target quantity to be calculated, e. g. a strength. This means, that the algorithm becomes significantly more complex.

The two techniques have the following advantages:

- complete spectral ranges are used for evaluation, and not individual values from the spectra
- non-systematic disturbances, such as noise etc., are not included in the evaluation
- the data quantities are significantly reduced, and
- the spectral ranges, with the highest information contents for the required target quantity, are automatically identified.

The chemometrics technique requires training sets with a known composition and known properties. In addition to the chemical composition of the samples, this technique can be used to directly calculate physical properties[7]. Chemometric techniques can themselves learn the correlation between the spectra and the target quantities using the training sets, without any additional analytical knowhow. Good results are obtained, for example, with reference to wood classification, i. e. by measuring the infrared spectrum of the wood followed by a chemometric evaluation, the wood type and even the area from where the wood came can be determined[5,6]. This article will now show how chemometrics can be used to determine the mechanical properties of pulp and paper.

3. Carrying-out the measurements

An FTIR spectrometer was used for the measurements, which covers the medium- and near infrared ranges. The spectra themselves were recorded in the near infrared range from 1 – 2.5 µm and in the medium infrared range from 2.5 - 25 µm with a resolution of 2 cm^{-1}. For pulp and paper, with a basic weight of less than 100 g/cm^2, the measurements were made by transmitting infrared light through the paper, and for thicker papers, the diffuse reflection technique was used. In both cases, a high reproducibility of the spectra was seen. 100 spectra were recorded and averaged for each sample. The NIR spectrum of pulp is shown as an example in **Figure 4**.

A training set of laboratory sheets with known mechanical properties was available for the two experiment programs for paper and pulp. Models were generated to calculate the mechanical properties from the infrared spectra. They consist of pre-processing the spectra and chemometric methods, whereby the PLS technique was proven to be especially successful. The models were optimized using the training set, whereby a "cross-validation" was made, i. e. always one data set (properties and spectra) was removed from the training set, the model trained with the remaining data and the mechanical properties of this sample calculated. This procedure was applied to all of the data sets, i. e. a dedicated model was generated for each spectrum, which only differed slightly from all of the other models. In order to investigate how the model behaved with new unknown spectra, a test set (minimum 25% of the data) was used, which was only used to calculate the mechanical properties. In this case, it involved samples, which to some extent, deviate significantly from the training set samples. The result of the test set was extremely important when evaluating the various models. It was shown, that there are many models, which provide excellent results for the training set, but on the other hand, provide poor results for the test set. These models are generally characterized by a high PLS rating or many input variables.

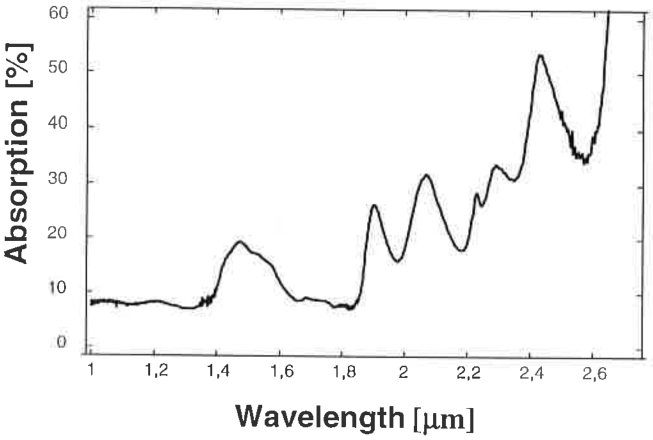


Figure 4. NIR spectrum of bleached hardwood kraft.

4. Results and discussion

4.1 Waste paper

The goal of the first experimental program was to measure the quality of waste paper using infrared spectroscopy. The quality, which is defined by various strength properties, was to be directly calculated from the infrared spectrum. This mean that an evaluation algorithm was to be developed, which can calculate all of the mechanical properties, listed below, from the measured infrared spectrum.

The experimental program consisted of sheets, which were produced from three different waste paper grades: Waste paper collected from stores, from domestic households, and carton. The pulp grades were either used individually or ground and unground in defined mixtures. The spectra for this experimental program were plotted in the medium (MIR) and near infrared (NIR) ranges. The results shown here, are based on the MIR measurements; the measuring accuracy is only slightly decreased, if the NIR spectra are also used. A model was generated and optimized for each of the mechanical properties CMT (Concora Medium Test), SCT (Short Span Compression Test), RCT (Ring Crush Test), breaking length, burst strength and tensile strength. All of the strength values can be measured with a similar accuracy using the IR analysis. As an example, the measurement of the CMT value is shown in **Figure 5**. The result of the infrared analysis in comparison to the value, which was measured in a paper laboratory, is provided for every sheet. The IR analysis data was recovered from the cross-validation of the training sets. It indicated good correspondence between the two measurements. The essential trend of the CMT values was also reflected in the IR analysis - there were only statistical deviations. The measurement error was 7.5 N and the correlation coefficient 0.89.

The reasons for the measuring error of the IR analysis are as follows:

- Inhomogeneous sheet structure, as the infrared analysis only involves a low paper surface area (the radiation diameter is only a few mm), significant measuring signal variations were obtained. Five IR measurements were averaged in order to reduce this variance.
- As the sheet weight of 120 g was not always able to be precisely set, all of the laboratory values were normalized to the basic weight. The basic weight measurement error is also included and the inaccuracy of the normalization equation, which was empirically determined.
- Measuring error in the reference measurement: The measuring error of the infrared analysis cannot be less than the measuring error of the reference measurement made in the laboratory.

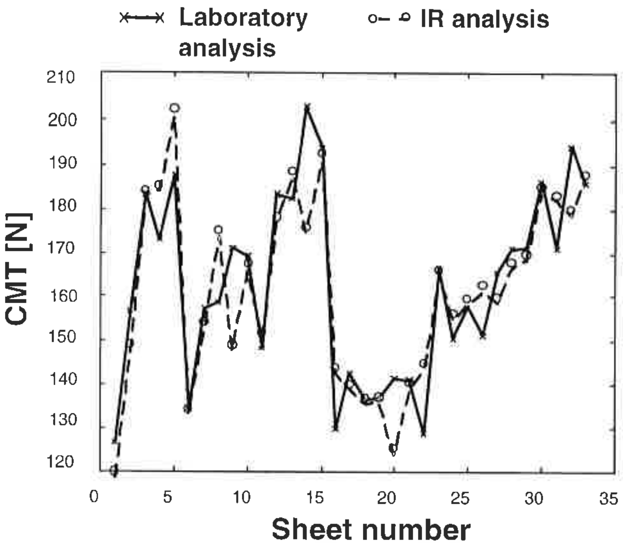


Figure 5. Comparison between the measured values from the IR analysis and the laboratory measurements.
(cross-validation in the training set)

The model was initially optimized for the CMT value, and then without essential modifications, also used for the other mechanical quantities. This is why the measuring errors for these quantities are somewhat higher; however, they lie in the same range as for the CMT measurement. All of the values are listed in **Table 1**.

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		Measuring error	Measuring range
Freeness	SR	4.2	35 - 73
Breaking length	km	0.3	3.4 – 6.3
Tensile strength	N	34	515 - 834
Burst strength	kPa	20	205 - 389
CMT	N	7.5	126 - 202
RCT	kN/m	0.06	1.0 – 1.5
SCT	kN/m	0.14	2.1 – 3.3

— N

Table 1. Measuring error and measuring range for the strength properties of waste paper.

Laboratory sheets were produced from comparable fibers and combined to form a test set, to investigate how the model responded to unknown spectra, i. e. none of the spectra were plotted in the training set. However, as waste paper is not a homogeneous material with constant composition materials and quality, the subsequently produced sheets of the test sets differ, regarding their composition, to the sheets of the training set. The CMT values calculated from the IR measurements of the test sheets are compared to the measurements made in the paper laboratory in **Figure 6**. The good result obtained from generalizing the model for unknown spectra proves the reliability of the system.

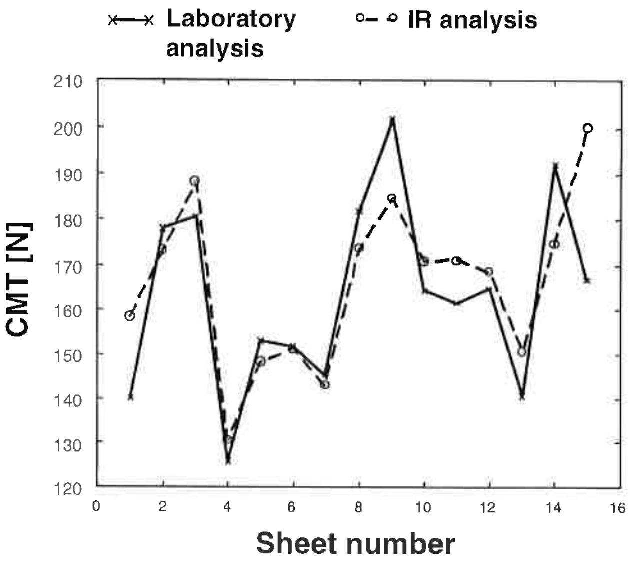

Figure 6. Comparison of the measured values of the IR analysis to the reference measurements (test set).

4.2 Pulp

A second experimental program was involved with measuring the mechanical properties of pure pulp. In this case, the measurements were made in the NIR, by transmitting the infrared light through the pulp. The experimental program comprised approx. 100 sheets of bleached softwood kraft and bleached hardwood kraft and CTMP pulp. All of the pulps had different degrees of freeness. As the mechanical properties are very dependent on the pulp type, in this case, a two-stage model was used, which first classifies the pulp. From the spectrum, the sheet was then assigned one of the three pulp classes. This classification worked error-free, as the differences were clearly visible in the spectrum. The total model structure with the classifier and the three individual pulp models is shown in **Figure 7**. After the classification, the selected pulp model calculates the pulp strength. The difference between bleached hardwood kraft and bleached softwood kraft has often been investigated, especially by carrying-out measurements on the wood[5, 6]. It is interesting to note, that these differences are also clearly visible for the pulp.

The measurement of the breaking length is shown as example in **Figure 8**; the results of the IR analysis in comparison to the laboratory measurement are shown. Additional strength parameters are measured using the IR analysis, whereby the freeness, the burst strength and the E-module can be measured with a similar relative accuracy.

The measuring errors of the strength properties are listed in **Table 2**, which comprise the errors of the IR analysis and the reference measurements. A comparison with the results from the waste paper measurements in Table 1 indicates that the errors have the same order of magnitude.

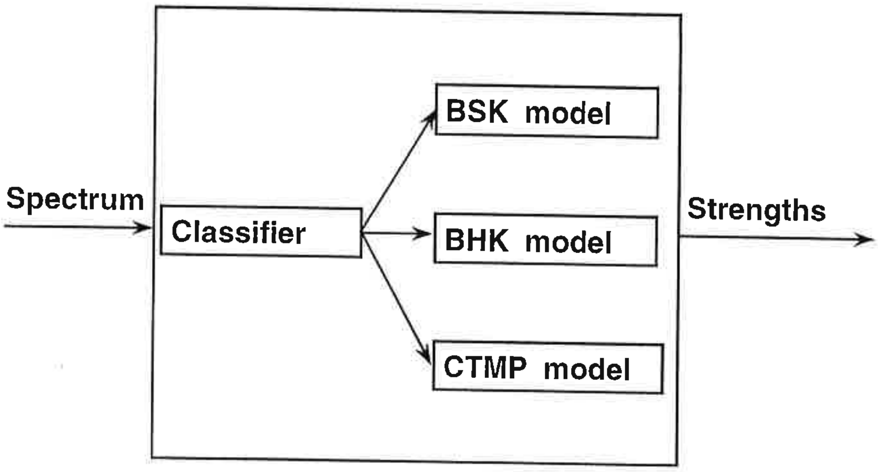

Figure 7. Model structure for calculating the strength of pulp types.
(BSK = Bleached Softwood Kraft,
BHK = Bleached Hardwood Kraft)

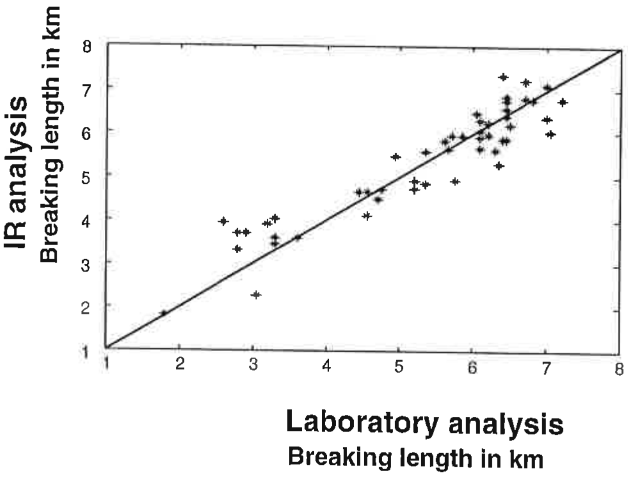

Figure 8. Comparison between the measured values of the IR analysis with the laboratory measurements for the breaking length of pulp.

		Measuring error	Measuring range
Freeness	SR	4.9	12-53
Breaking length	km	0.5	1.8 – 7.3
Burst strength	kPa	34	90 - 420
E module	N/mm^2	331	1150 - 5150

Table 2. Measuring errors and measuring range for the strength properties of pulp.

5. Glance into the future

It was able to be demonstrated that it is possible to define the mechanical properties of pulp and paper using infrared. Strengths and freeness can be measured using innovative spectra evaluation, based on chemometric techniques. A training set, tailored to the measuring problem, allows the numerical algorithms to "learn" the interrelationships between the spectra and the mechanical properties. This know-how can then be used to evaluate unknown test sheets, in order to calculate their strength.

Training sets, tailored to the special application, allow, in a small input range, low measuring errors to be achieved. Often, the product spectrum for a particular application is low, i. e. the paper grades to be measured do not significantly differ. By optimizing the evaluation software in this input area, would permit a significant improvement in the measuring error. If products, which differ significantly, are to be measured, a classifier, as described above for measurements made on pulp, could result in a higher measuring accuracy.

The systems presented here could be used in the process- and quality control. For process control, the mechanical paper properties of a continuous paper web can be measured online, e.g. using a measuring frame across to the paper web (cross profile). It would then be possible to control the stock preparation and paper machine using the paper quality values.

The second application involves the quality monitoring. In this case, a single infrared spectrometer can replace many different test units, as the strength parameters can be calculated from the infrared spectrum. It is not necessary to keep the paper or pulp in a climatized environment, which means that measurements can be made faster. Generally, it is not necessary to prepare special samples.

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