Interpreting multicomponent infrared spectra

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ABSTRACT *The complexity of a multicomponent spectrum decreases as constituents are removed from it. This decrease is reflected by a reduction in intensity of the first derivative. If the spectrum of a candidate constituent is subtracted stepwise from a multicomponent spectrum and a derivative is taken at each stage, then the candidate constituent will be identified in the mixture if the derivative minimizes. An application of this procedure to the determination of lignin in pulp is presented.*

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Testing

Infrared spectroscopy has long been used in the paper industry for qualitative identification of spots, stickies, and the like. The technique works well if the component can be easily recognized from the overall spectrum of the sample, but this is frequently not the case. If a sample contains multiple components with overlapping spectra, visual identification of any one component can be uncertain.

The problem is essentially one of pattern recognition. Traditionally, one overlays the absorption spectrum of a candidate component with that of the sample and attempts to find at least a partial match, either visually or through regression analysis. We have devised an alternative approach (*1*, *2*) based on the fact that if a constituent is exactly removed from a multicomponent spectrum, the number of bands remaining in the difference spectrum must decline. In other words, the overall complexity (i.e., the detail, the smoothness, or the number of lines in a spectrum) will decrease if the spectrum of a component is exactly removed from it.

An operational measure of complexity is the area (positive and negative) of the first derivative of the spectrum. Thus, if a candidate spectrum is progressively subtracted from the target and a derivative is taken at each stage, then the candidate component will be positively identified if the derivative minimizes.

Results and discussion

Consider the spectrum in **Fig. 1**. Figure 1A consists of the spectrum composed of two signals (left) and the spectrum's derivative (right). As one of the signals is progressively removed, the absolute value of the overall intensity (positive and negative) of the first derivative decreases until the signal is exactly stripped out in Fig. 1B. Further stripping of the signal increases the intensity of the derivative (Fig. 1C). Thus, the derivative, which relates to spectral complexity, minimizes when a component is exactly removed. Hence, in principle, the intensity of the derivative can be used as a tool for identifying component spectra.

Consider now the spectrum in **Fig. 2**. Figure 2A contains components from Figs. 2B and 2C. A computer program was written to subtract various fractions n of the Fig. 2B spectrum from Fig. 2A and to take a derivative after each stage. A plot of the absolute intensity (integrating both positive and negative intensities) of the derivative is plotted against n in **Fig. 3**. The minimum occurs at $n = 0.85$, indicating that 85% of the Fig. 2B spectrum is contained in the Fig. 2A spectrum. A similar analysis shows that 24% of the Fig. 2C spectrum is contained in Fig. 2A.

The technique has been used to determine kappa number from the infrared spectrum of pulp. Several attempts to do so have been reported (*3–8*). Berben *et al.* used the absorbance of a characteristic lignin band at 1510 cm^{-1} to estimate kappa number (*3*). Since cellulose also absorbs in this region, the band intensity was measured after a spectrum of cotton linters had been subjectively subtracted. The residual 1510-cm^{-1} absorption was quite small, and since the subtraction step introduces substantial uncertainty, the kappa number could be determined to only within ±10 units (*3*).

Schultz *et al.* (*4*) used five absorption bands ratioed to a sixth to express lignin content, and a similar multiple band approach was taken by Grandmaison *et al.* (*5*). Backa and Brolin

used partial least squares analysis with absorptions at 232 discrete wavenumbers (*6*). Sample preparation included milling and drying to constant weight. A precision of 2.75% was obtained after the removal of outliers.

Consider the spectra in **Fig. 4**. The Fig. 4A spectrum is that of an unbleached loblolly pine kraft pulp. The Fig. 4B trace is a library spectrum of kraft softwood lignin. Fractions of the 4B spectrum were incrementally subtracted from the Fig. 4A spectrum, and a derivative was taken after each step. A plot of the integrated area (positive and negative) of the derivative vs. the scaling factor applied to the lignin spectrum showed a minimum at 0.18, indicating that 18% of the Fig. 4B spectrum is contained in (or overlaps with) the Fig. 4A spectrum.

The lignin scaling factor needs to be normalized in order to compensate for interferences and for spectral variability. The obvious choice for a reference is cellulose because it is the major component of pulp. A derivative minimization as described was conducted with a spectrum of cotton linters. The ratio of the lignin:linters minima is designated as f'_{lig} and is expected to be a measure of the lignin content relative to the cellulose (cotton linters) content. Values of f'_{lig} for several kraft pulps and one sulfite pulp were regressed against kappa number, which led to Eq. 1:

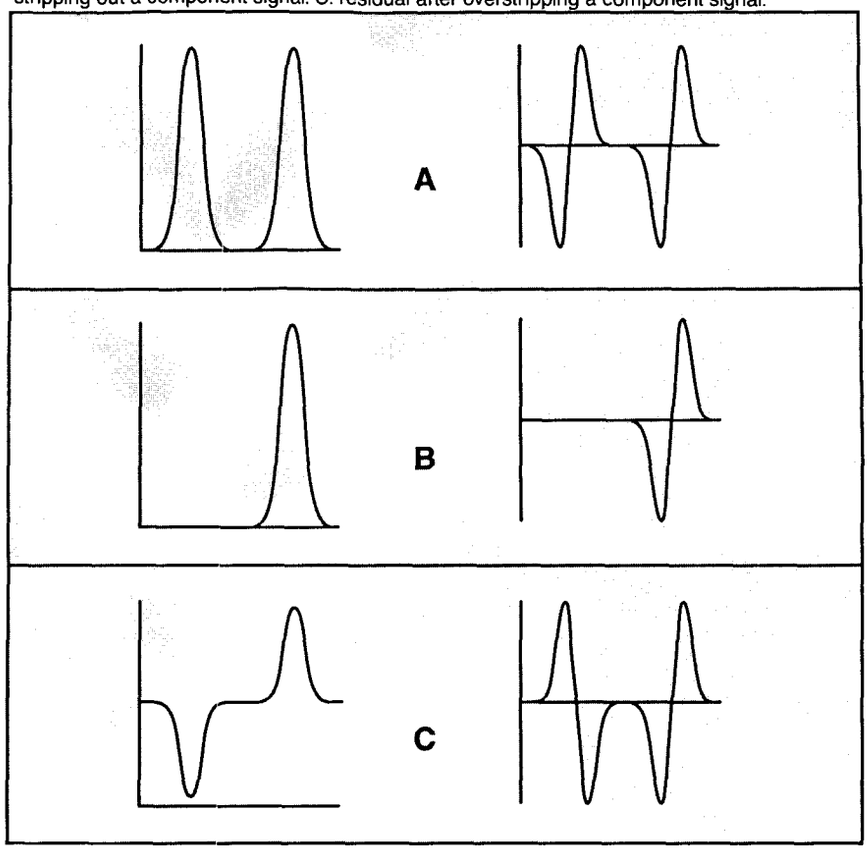
$$\text{kappa no.} = -23.5 + 191\, f'_{lig} \qquad (1)$$

for which the number of values, n = 14 and the correlation coefficient r = 0.99.

The relationship is illustrated in **Fig. 5**. The quality of the fit is unchanged if a spectrum of hardwood lignin is used to determine f'_{lig}. This is consistent with the general spectral similarity between hardwood and softwood lignin. Consequently, it appears that a single equation may apply to softwoods, hardwoods, and to mixtures thereof.

The magnitude of the intercept may initially appear to be too large, since lignin-free material has a kappa number of zero. However, the spectra of lignin and cotton linters are not orthogonal. We found (through derivative minimization) that 11.2% of the lignin spectrum was contained in a spectrum of cotton linters—i.e., f'_{lig} for cotton linters was 0.112. This leads to a value of about 2 for the kappa number of cotton linters, which is of the order of the uncertainty of the estimation.

1. Gaussian signals and their derivatives. A: two equivalent Gaussians. B: residual after stripping out a component signal. C: residual after overstripping a component signal.

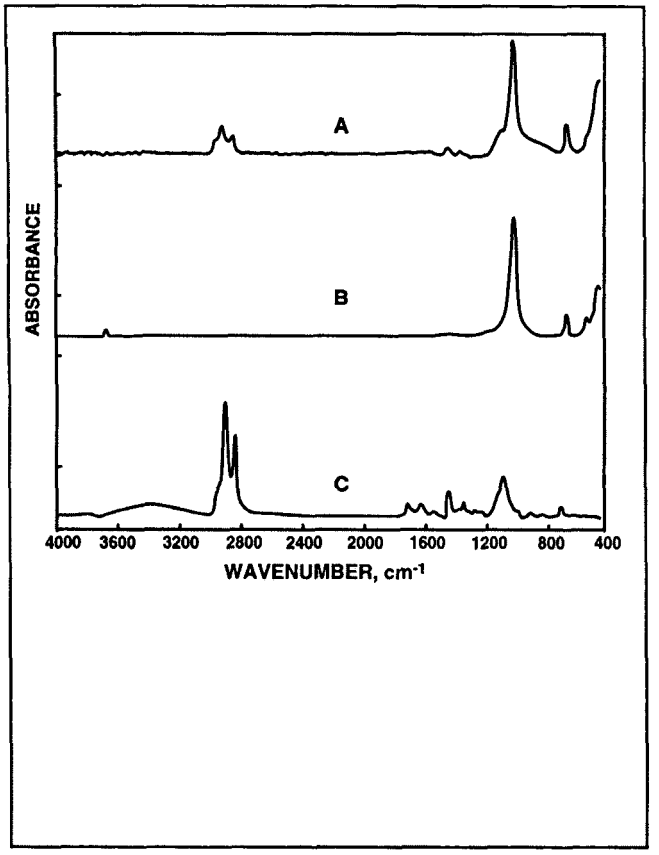


The f'_{lig} values used in Fig. 5 were averaged from two spectra, and duplicates agreed to within 12%. One of the pulps was visibly inhomogeneous, and the duplicates differed by 22%. It would seem that the approximately 6-mm^2 area of the pulp sample exposed to the beam does not fully represent the pulp, and it is likely that greater replication will improve accuracy.

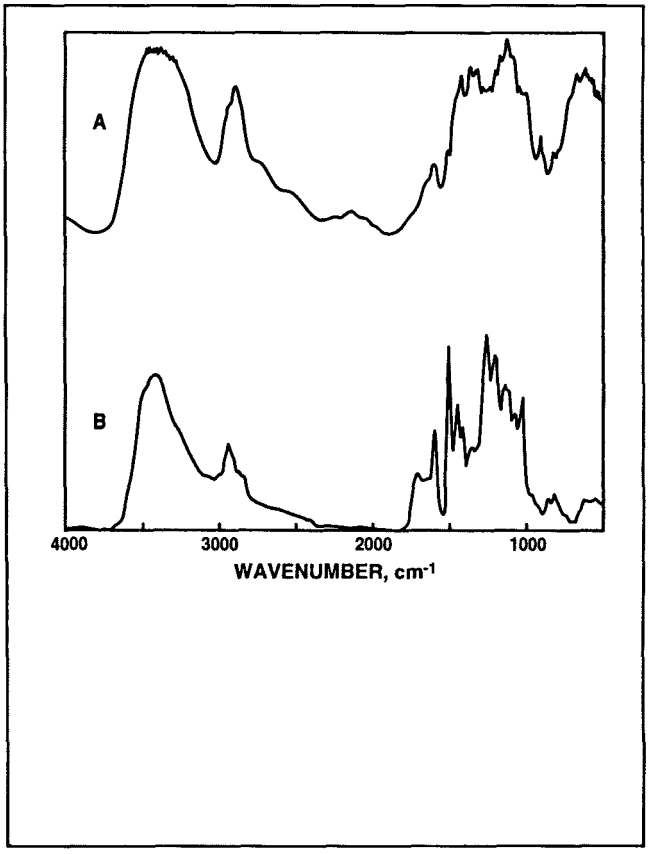
Equation 1 consistently underestimates kappa numbers of NO_2-treated unbleached pulps by an average of 23 units. Exposure to NO_2 probably alters the infrared spectrum of the lignin; certainly, the electronic spectrum is altered, as indicated by a yellowing of the exposed pulps. A change in lignin structure would reduce the overlap between the lignin and pulp spectra and lead to an underestimation of lignin content as observed. However, once the NO_2 treated pulps are bleached, they are accommodated by Eq. 1. This indicates that the altered lignin is largely removed during bleaching; the residual native lignin is then again recognized by our algorithm.

An important component of our procedure is that all the spectral information is considered rather than discrete preselected bands. It is unnecessary for a signal in the mixture to be associated exclusively with any one component. Perhaps the most useful feature of our technique is its relative insensitivity to interferences in comparison to absorbance-based techniques. A common variable in pulp is the moisture factor, and in order to determine the effect of water on kappa number, we collected spectra of pulps varying only in moisture content. The results are provided in **Table I**; clearly, water does not add significantly to the uncertainty. The "0% moisture" pulp was oven dried at 105°C for 4 h, a process that removes volatiles and causes structural changes in the pulp. Our technique picks up the change, and the f'_{lig} value in Table I for the dried pulp is very different from those of the others.□

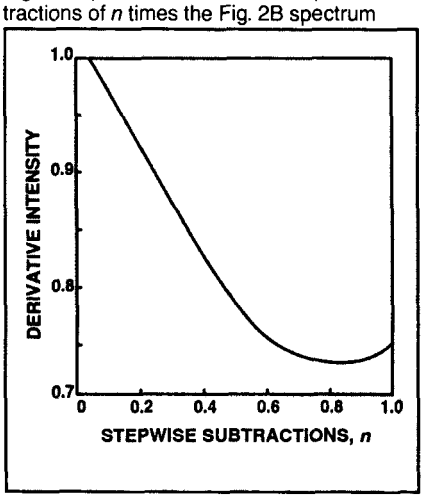
2. Spectrum of a Mixture A including components from B and C



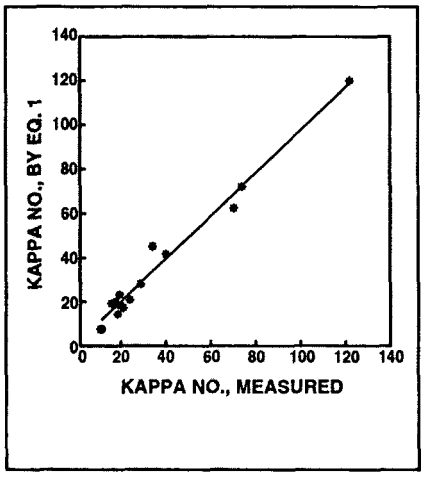
4. Spectra of softwood kraft pulp (A) and softwood lignin (B)



3. Absolute intensities of derivatives of the Fig. 2A spectrum taken after stepwise subtractions of *n* times the Fig. 2B spectrum



5. Dependence of the area of the derivative on the scaling factor



1. Variation of kappa number with moisture content

Moisture, %	F_{fig}	$F_{linters}$	f'_{lig}	*Kappa no.*
0	0.054	0.314	0.16	...
4.2	0.108	0.520	0.21	16.6
33.9	0.099	0.493	0.20	14.7

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