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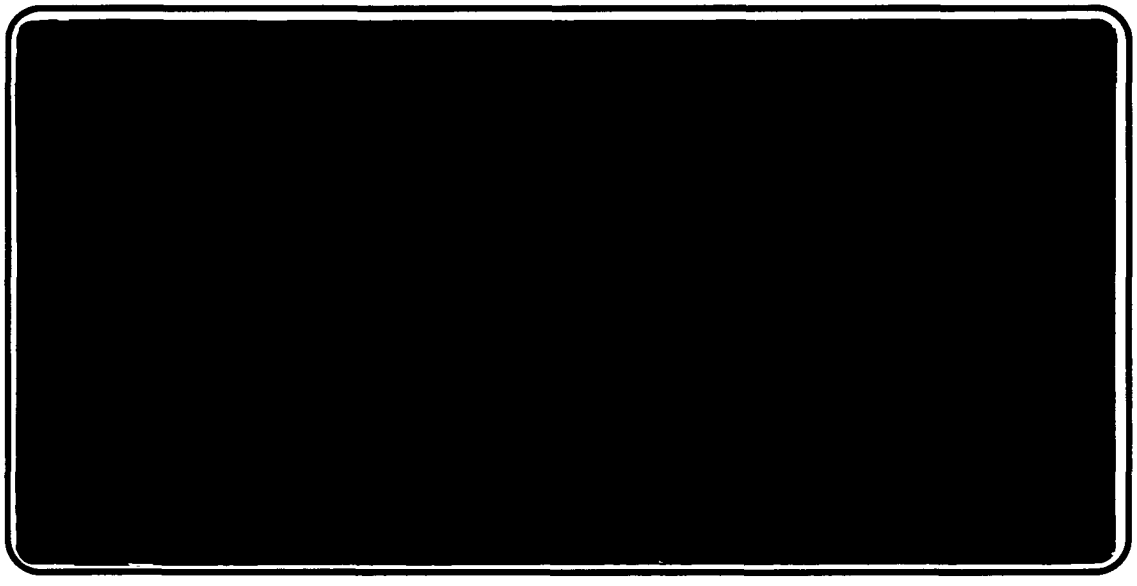

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LIGNIN DETERMINATION BY FT-IR

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Lignin Determination by FT-IR

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Abstract

The lignin content of pulp is determined from its diffuse reflectance infrared spectrum by an algorithm that calculates the degree of overlap between two spectra. The lignin:cellulose fraction correlates with kappa number, a titrimetric measure of lignin. Essentially no sample preparation is required, and the procedure is insensitive to variations in moisture content. The algorithm is able to detect changes induced by exposure of pulp to NO_2.

Diffuse reflectance FT-IR spectroscopy has long been promoted as a rapid means of determining lignin in pulp (1-7). The method is convenient, but suffers in precision vis-a-vis the standard titrimetric procedure (8). Much of the imprecision arises from background variability and from the absence of a signal associated exclusively with lignin. In this paper we develop a new approach to determining kappa number, an indirect measure of lignin content.

Berben et al. (1) used the absorbance of a characteristic lignin band at 1510 cm^{-1} to estimate kappa number. Since cellulose also absorbs in this region, the band intensity was measured after a spectrum of cotton linters (a pure form of cellulose) had been subjectively subtracted out. The residual 1510 cm^{-1} absorption was quite small, and since the subtraction step introduces substantial uncertainty, kappa number could be determined to only within $\pm$10 units (1).

Schultz et al. (2) used five absorption bands ratioed to a

sixth to express lignin content, and a similar multiple band approach was taken by Grandmaison et al. (3). Backa and Brolin (4) used partial least squares analysis with absorptions at 232 discrete wavenumbers. Sample preparation included milling and drying to constant weight. A precision of 2.75% was obtained after removal of outliers.

We have recently described (9) another approach to quantifying constituents in multicomponent spectra based on minimizing the complexity (i.e. the number of lines) of a spectrum. The complexity of a multicomponent spectrum must decrease if a constituent is completely removed from it. One measure of complexity is the integrated area (positive and negative) of the first derivative. Thus, if a fraction of a component spectrum is subtracted stepwise from the target spectrum and a derivative taken at each stage, then the component spectrum will be factored out at the point at which the derivative minimizes.

Consider the spectra in Fig. 1. The Fig. 1A spectrum is of an unbleached loblolly pine Kraft pulp. The Fig. 1B trace is a library spectrum of Kraft softwood lignin. Fractions of the Fig. 1B spectrum were incrementally subtracted from Fig. 1A, 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 is illustrated in Fig. 2. The minimum at about 0.18 indicates that 18% of the Fig. 1B spectrum is contained in (or overlaps with) Fig. 1A.

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 since it is the major component of pulp. A derivative minimization as described above was conducted with a spectrum of cotton linters (a pure form of cellulose), and the result is included in Fig. 2. 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} were obtained for the several Kraft pulps and for the one sulfite pulp listed in Table 1. Regression against kappa number led to

$$\text{kappa no.} = -23.5 + 191\ f'_{lig} \quad (n=14;\ r=0.99) \qquad (1)$$

and the relationship is illustrated in Fig. 3. 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.

The f'_{lig} values used in Fig. 3 were averaged from two spectra, and duplicates agreed to within 12%. One of the pulps (VAL 3) was visibly inhomogenous, 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 the NO_2 treated unbleached pulps listed in Table 1 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 underestimate 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.

Fig. 4 illustrates spectra of an unbleached pulp (A), the corresponding NO_2 treated pulp (B), and the corresponding bleached NO_2 treated sample (C). Equation 1 correctly estimates kappa numbers from the Fig. 4A and Fig. 4C spectra but the f_{lig} obtained from Fig. 4B is too low. Fig. 4B contains a shoulder at about 1750 cm^{-1}, but this alone would not cause the deviation, since the location of the minimum in plots of area vs. scaling factor tends to be unaffected by the presence of additional signals. We attribute the low f_{lig} value to the slight flatten-

ing of the envelope in the 1000-1500 cm^{-1} region. The change is subtle, but is evidently sufficient to reduce the overlap between the pulp and lignin spectra.

An important component of our procedure is that it considers all the spectral information rather than discrete preselected bands. It is unnecessary for a signal in the mixture to be associated exclusively with any pure component band. 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 (Fig. 5B and C) of pulps varying only in moisture content. The results are provided in Table 2. Clearly, water does not add significantly to the uncertainty. The "0% moisture" pulp (Fig. 5A) was oven dried at 105°C for 4 hours, 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 2 for the dried pulp is very different from those of the others.

In conclusion, a rapid algorithm has been developed for determining kappa number in pulp. No sample preparation other than air-drying is necessary and data handling is completely objective and automated. Precision depends upon sample homogeneity.

Materials and Methods

Spectra were collected (500 scans/spectrum) in duplicate in the DRIFT mode at 4 cm^{-1} resolution on a Nicolet 7199 FTIR spec-

trometer equipped with a liquid nitrogen cooled MCT detector and a Harrick Praying Mantis diffuse reflectance cell. Disks were cut from air-dried pulps and pressed flat with a Noble and Wood sheet press at 200 psi for 5 minutes. In some cases multiple disks were stacked in the sample cup to position the sample in the focal point of the diffuse reflectance cell.

For the experiments in Table 2, a regular air-dried pulp was moisturized by exposure to steam for 1 minute. Moisture content was determined gravimetrically after oven drying at 105°C for 4 hours, and the oven-dried material was used for the "0% moisture" entry in Table 2.

Spectra were referenced to KBr, converted to an ASCII file through the LabCalc (Galactic Industries) package and trimmed to 440 data points in the 400-4000 cm^{-1} region. Kappa numbers were measured by the TAPPI standard method (8).

Acknowledgment

We thank Kyle Reed for providing us with several pulps along with their associated kappa numbers.

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Captions to Figures

Fig. 1 Spectra of softwood Kraft pulp (A) and softwood lignin (B).

Fig. 2 Dependence of area of the derivative on scaling factor.

Fig. 3 Relationship between f'_{lig} and kappa number.

Fig. 4 Spectra of softwood pulp exposed to (A) 0%, (B) 8% NO_2 and (C) 8% NO_2 followed by oxygen bleaching.

Fig. 5 Spectra of softwood pulp containing (A) 0%, (B) 4.2% and (C) 33.9% moisture.

Table 1. Characteristics of pulps used[1]

		kappa no.
LP103B	Unbleached Kraft	39.5
LP136A	Oxygen Bleached Kraft	34.0
LP136B	Oxygen Bleached Kraft	29.2
LP136C	Oxygen Bleached Kraft	19.5
LP130C	Oxygen Bleached Kraft	17.6
SULF117	Unbleached Sulfite Pulp[2]	122
LP103C	Unbleached Kraft, 2% NO_2 treated[3]	39.0
LP103D	Unbleached Kraft, 4% NO_2 treated[3]	38.4
LP103E	Unbleached Kraft, 6% NO_2 treated[3]	37.2
LP103F	Unbleached Kraft, 8% NO_2 treated[3]	39.0
LP103G	Unbleached Kraft, 10% NO_2 treated[3]	36.8
LP130E	Oxygen Bleached Kraft, 2% NO_2 treated	21.2
LP130I	Oxygen Bleached Kraft, 4% NO_2 treated	16.5
LP130K	Oxygen Bleached Kraft, 8% NO_2 treated	21.2
VAL2	Unbleached Kraft Linerboard	70.2
VAL3	Unbleached Kraft Linerboard	73.5
DC2926	Bleached Larch Kraft	24.4
DK2926	Bleached Larch Kraft	18.5
EA2926	Bleached Larch Kraft	11.1

[1]loblolly pine, unless otherwise indicated
[2]hardwood mix
[3]not used in the eq. 1 regression

Table 2. Variation of kappa number with moisture content

Percent moisture	f_{lig}	$f_{linters}$	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

Figure 1

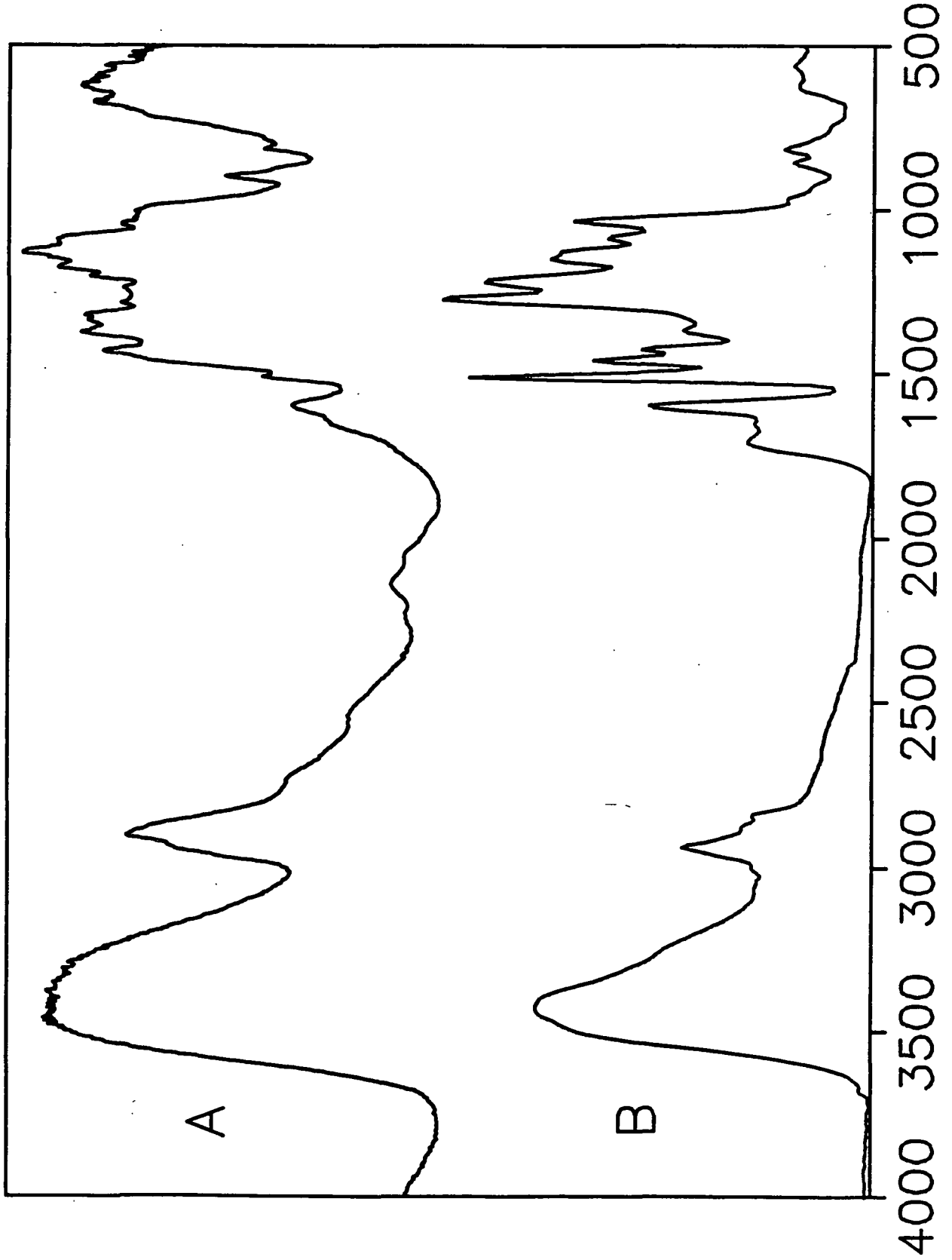

Figure 2

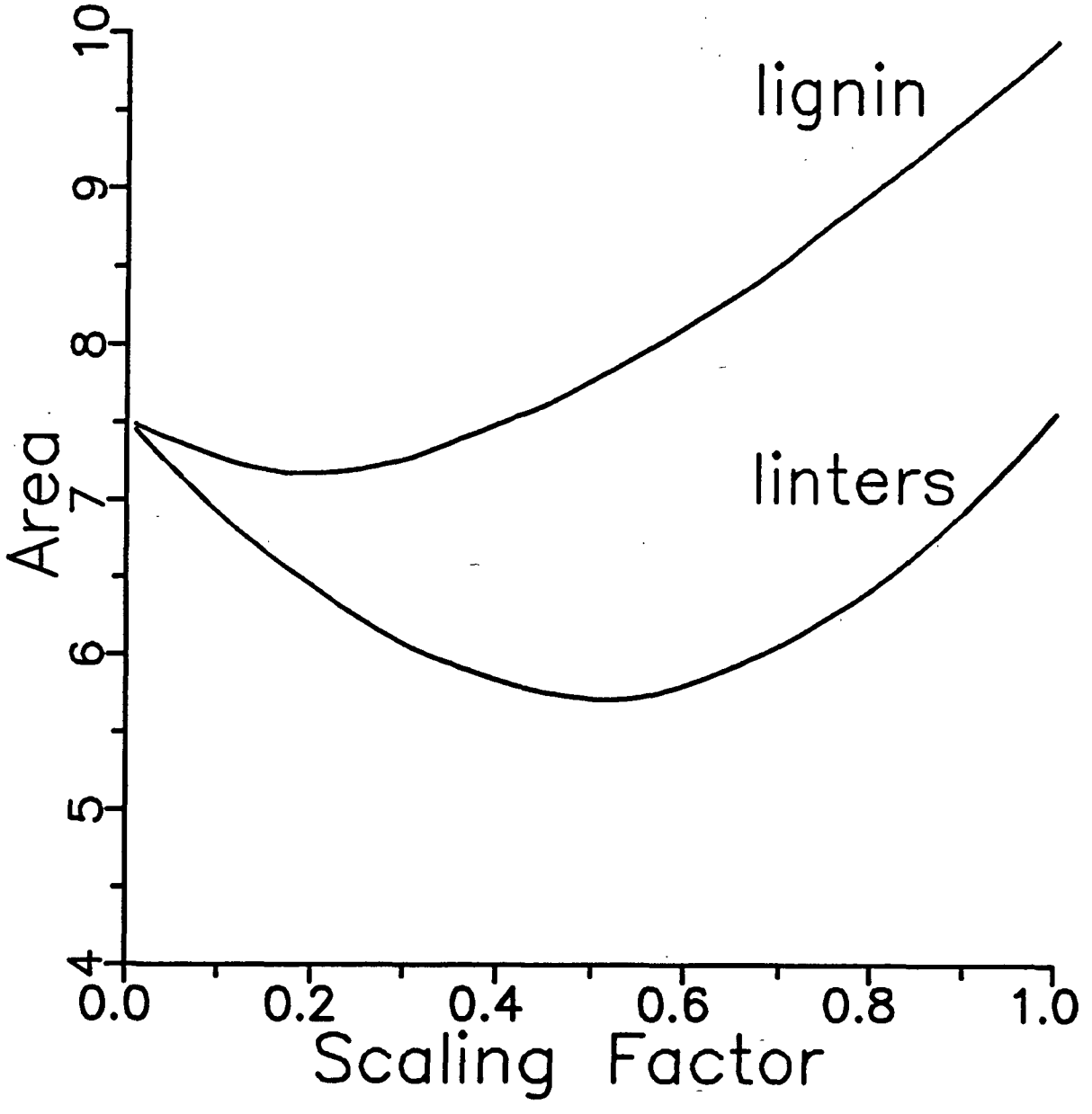
lignin
linters
Area
10
9
8
7
6
5
4
0.0
0.2
0.4
0.6
0.8
1.0
Scaling Factor

Figure 3

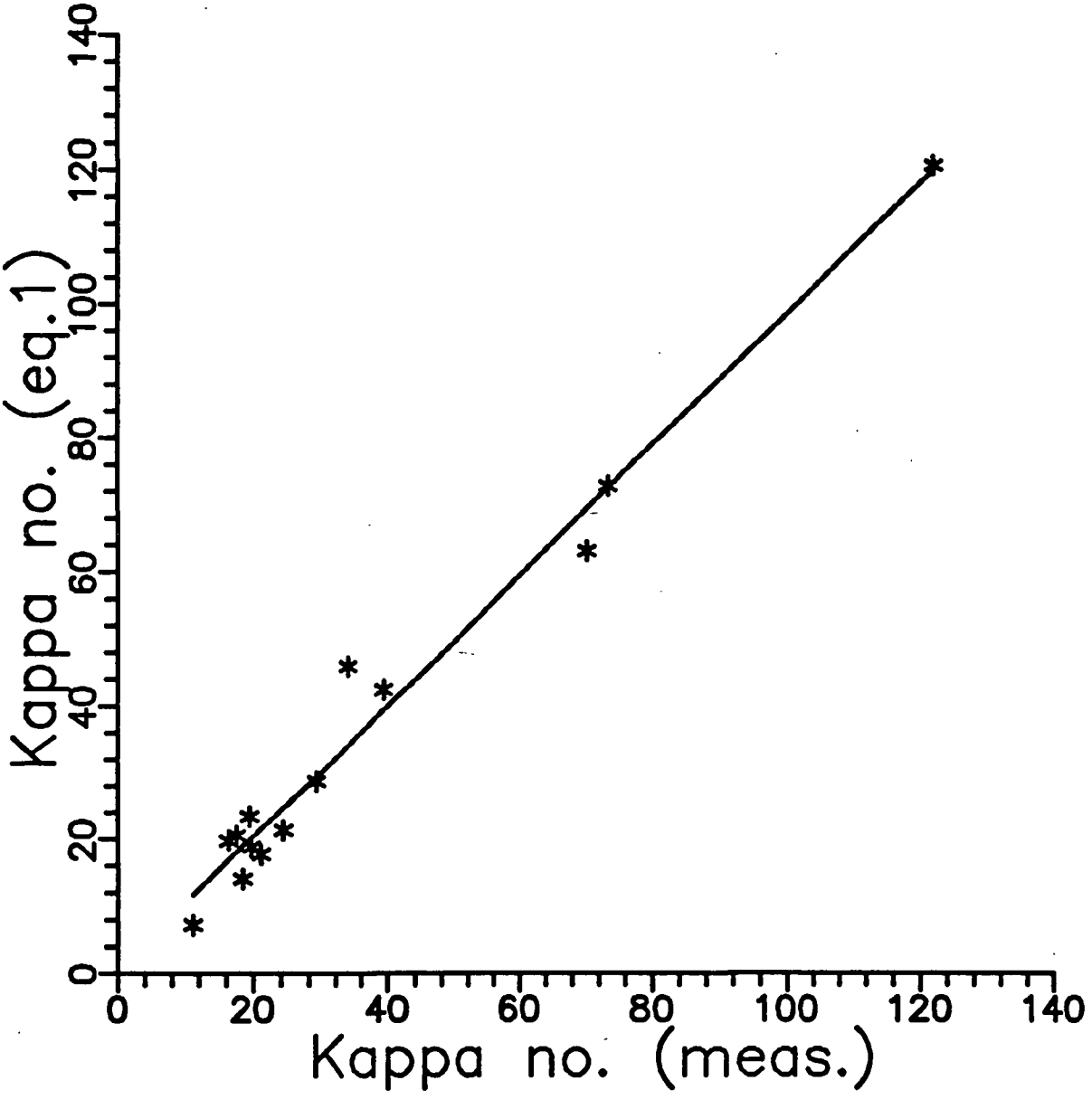

Figure 4

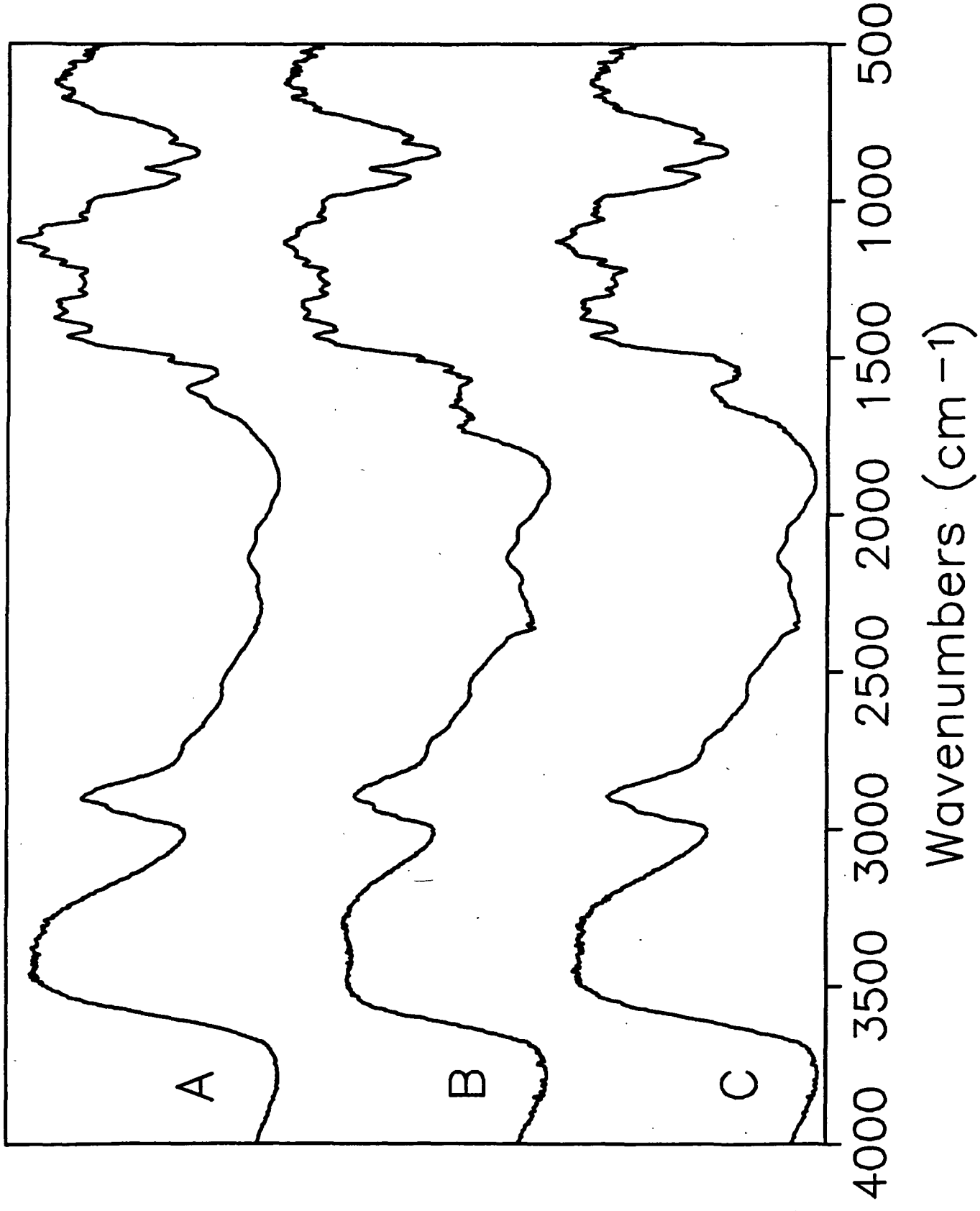

Figure 5