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Transform Infrared Spectrometry

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Estimation of lignin in wood pulp by diffuse reflectance Fourier transform infrared spectrometry.

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ABSTRACT

A method for estimating lignin in unbleached pulps using diffuse reflectance Fourier transform infrared spectrometry has been developed. The procedure is based on linear relationships which were found to exist between the area of the 1510 cm^{-1} infrared band, measured on diffuse reflectance difference spectra, and kappa number and Klason lignin. These relationships, which serve as calibration lines for lignin estimation, have been found to apply to a range of hardwood and softwood pulps from high-yield and conventional kraft processes (1-20% lignin, 10-120 kappa) and from the alkaline sulfite anthraquinone process. An unknown sample's 1510 cm^{-1} band area is referred to the calibration line to estimate its lignin content. This method is nondestructive, requires no sample preparation other than drying, employs no calculations, and may be used on samples as small as 0.5 mg.

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Introduction

Methods most often used for quantitative determination of lignin in wood and pulp are time consuming wet chemical procedures. The Klason lignin determination (1) requires about three days. This time may be reduced somewhat by using a small-scale variation of the method (2). Kappa number measurements (3) require about 20 minutes, provided the required reagents have previously been prepared. The relationship of kappa number to Klason lignin varies somewhat with wood species and pulping process (4,5).

Infrared (IR) spectrometry has been employed for the study of lignin in wood and pulp for over 20 years (6-10). Chlorine dioxide modifications of lignin were revealed by varying amounts of reacted and unreacted materials in the sample and reference beams of a dispersive IR spectrometer to achieve equal absorption at 2900 cm^{-1} (8). Differential IR spectra of lignin were obtained with a KBr pellet containing wood meal or pulp in the sample beam and holocellulose in the reference beam. A characteristic of these differential spectra was the extreme care necessary to prepare matched pellets and to balance the energy levels of the sample and reference beams. In many cases the spectra suffered from poor resolution associated with low energy levels characteristic of dispersive IR spectrometers. Using the differential method, about 10% lignin was the lower limit for pulp samples which would permit the recording of spectra (7). A more sensitive, simple, and rapid method for determining lignin via IR has long been sought.

Determination of lignin with a dispersive IR spectrometer was significantly improved by use of the multiple internal reflection (MIR) technique (11). Pulps were made into handsheets and clamped in contact with the MIR prism in the IR

spectrometer. The transmittance difference between the 1510 cm^{-1} lignin peak and the 1310 cm^{-1} carbohydrate peak was found to correlate with lignin content and kappa number. This correlation was increased when the 1310 cm^{-1} peak was set at 45 ± 0.5% T by adjustment of the clamping pressure. Lignin contents as low as 2% were determinable by this method.

The potential of infrared to study wood and pulp components was further enhanced by the advent of Fourier transform infrared spectrometry (FTIR). Increased sensitivity and signal-averaging ability of FTIR instruments permit generation of useful spectra from the surface of ground or powdered samples by diffuse reflectance (12). This technique has recently been used by Schultz _et al._ to characterize hardwood chips which had been pretreated by a rapid steam hydrolysis (RASH) process (13). The pretreated samples were air dried, ground in a specified ratio with KCl, and their diffuse reflectance FTIR spectra were obtained. Manipulation of the absorbances of 18 peaks with a microcomputer yielded predicted lignin, glucose, and xylose contents which correlated with the measured amounts of these components in the samples.

Exploratory work was initiated in this laboratory several years ago to examine the possibility of determining lignin in unbleached pulps by diffuse reflectance FTIR. It was hypothesized that if the diffuse reflectance spectrum of an unbleached pulp is obtained and a carbohydrate spectrum is subtracted from it, a lignin spectrum should result. The intensity of the lignin spectrum should be proportional to the lignin content of the pulp. Such spectra would provide the basis for a method of lignin determination which is rapid and requires minimal sample preparation. The method would be validated by correlation with Klason lignin and/or kappa number.

Initial unpublished results revealed a linear relationship between IR absorbance at 1500-1510 cm^{-1} and kappa numbers of pulps from one wood cooked to varying degrees. Efforts were then directed at learning whether the correlation between IR absorbance and lignin content varies with wood species and pulping processes. This investigation has documented the validity of the FTIR lignin method and has demonstrated its ease, simplicity, nondestructive nature, and utility with small samples.

Results and discussion

Diffuse reflectance difference spectra

An unbleached pulp and a cotton linters cellulose reference material were ground to pass a 40-mesh screen, and each was mixed 1 part to 19 parts of KCl. Diffuse reflectance spectra were recorded, and difference spectra (pulp minus linters) were plotted as Kubelka-Munk (K-M) units (12) and as absorbance. In addition, diffuse reflectance difference spectra were obtained with samples neither ground nor mixed with KCl; it is likely that these measurements included radiation from specular as well as diffuse reflectance.

All of the spectra exhibited sharp and well defined absorption bands. These included aromatic absorptions due to lignin and weak carbohydrate bands which were not completely eliminated by the spectral subtraction. Although the diffuse reflectance difference spectra did not match closely the familiar absorption spectrum of lignin, they did exhibit a strong aromatic band at 1510 cm^{-1}, as shown in Fig. 1. This band was barely discernible in the spectrum of the unbleached pulp before subtraction. From earlier work (11), it was anticipated that the intensity of the 1510 cm^{-1} band in the difference spectrum would be proportional to the pulp's lignin content. Thus this band was tentatively

chosen as the basis for a quantitative method of lignin determination by diffuse reflectance.

<center>(Fig. 1 here)</center>

The quality of the difference spectra run on samples which had been ground and mixed with KCl was not appreciably different from that of spectra on samples which were not ground or mixed with KCl. Sample grinding and mixing with KCl was therefore omitted from subsequent work. As a result, the lignin determination became a nondestructive test.

Diffuse reflectance FTIR spectra of three white oak pulps with kappa numbers ranging from 10.8 to 19.7 were obtained without KCl dilution. A linters spectrum was subtracted from the pulp spectra expressed in absorbance and in K-M values. The integrated absorbance values of the 1510 cm^{-1} band correlated with kappa number; the integrated K-M values did not. Consequently, absorbances rather than K-M values were used in subsequent correlation studies. Reasons for the choice were that the process was successful and that sample preparation (no KCl) and data manipulation were simplified.

The K-M theory applies most rigorously to dilute samples in nonabsorbing matrices such as KCl. Apparently, lignin in a cellulose matrix does not meet that requirement.

Correlations with kappa number and Klason lignin

Plots of infrared band areas from diffuse reflectance difference spectra vs. kappa numbers and Klason lignin values are shown in Fig. 2 and 3. Band areas are in arbitrary units. Data were obtained on kraft pulps prepared over a wide yield range from three hardwoods and two softwood species. Also included are

data on several loblolly pine alkaline sulfite anthraquinone (ASAQ) pulps; for these pulps the plotted "Klason lignin" values are actually Klason plus acid-soluble lignin. Solid lines on the figures are calculated regression lines. Dashed lines represent 95% confidence contours. F tests for both regressions were significant at the 0.01 level.

(Fig. 2 and 3 here)

The figures reveal, in general, the existence of linear relations between IR band area and lignin content expressed as kappa number and Klason lignin. Although the lines would be expected to go through the origin, both have finite intercepts (95% confidence limits do not include zero). The reason for the intercepts was not evident. Use of the lines below about 1% lignin and a kappa number of 10 is therefore not recommended. Points for hardwood pulps with high lignin contents tend to be farthest from the regression lines. These high-yield pulps had undergone very little delignification, and they perhaps were not homogeneous.

Infrared band areas were not strongly affected by generic differences between hardwoods and softwoods. Separate plots of the hardwood and softwood data contained in Fig. 2 were found to have essentially identical slopes.

The regression lines on Fig. 2 and 3 may be regarded as representing functional relationships between band areas and lignin contents, and as such, they assume the role of calibration lines. Thus, the final step in measuring "FTIR lignin" involves referring a sample's IR band area to such a calibration line to estimate the lignin content of the pulp. Duplicate measurements of IR band area in the midrange of the data of this study permit estimation of kappa number within about ± 10 kappa (95% confidence limits) and Klason lignin within about

± 1.8%. These ranges are wide and might be improved by further study, perhaps by use of a calibration line based on a greater number of points and prepared from the wood and pulping process of interest. Other published infrared studies have not reported confidence limits for estimated lignin contents (11,13); however, the scatter in the plotted data of these studies suggests that the limits would be similar to those reported here.

Kappa number was originally validated for lignin determination as a result of its correlation with Klason lignin. Figure 4 is a plot of the kappa number and Klason lignin data obtained in this study. Substantial scatter about the regression line is evident. These data suggest that Klason lignin can be predicted almost as accurately from IR band area (± 1.8%) as from kappa number (± 1.4%). In view of the apparent variations in structure within and between lignins from different sources, perfect correlations between tests based on aromatic content (IR band area), reducing power (kappa number), and acid insolubility (Klason lignin) would seem to be an unrealistic expectation. Amounts of lignin must always be defined by the methodology employed in the determination.

(Fig. 4 here)

Conclusions

Linear relationships exist between the area of the 1510 cm^{-1} infrared band, measured by diffuse reflectance FTIR, and kappa number and Klason lignin. Species differences and generic differences between hardwoods and softwoods have little effect on these relationships. This finding applies to kraft pulps prepared over a wide yield range (1-20% lignin, 10-120 kappa) and to ASAQ pulps.

Plots of infrared band area <u>vs.</u> lignin content may be used as calibration lines for the estimation of "FTIR lignin" in unbleached pulps. Because no sample preparation other than drying is required and only a single IR band is employed, this method is nondestructive and is quicker and easier than other infrared techniques. The analysis can be completed in about 15-20 minutes. No calculations are needed to obtain the result of the analysis. This procedure is insensitive to sample size; FTIR lignin may be determined in pulp samples as small as 0.5 mg.

Experimental

Spectra were collected on a Nicolet 7199 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Harrick Praying Mantis diffuse reflectance attachment. Maximum spectral resolution was 2 cm^{-1}. Five hundred scans for each sample were accumulated in approximately nine minutes.

Air-dried pulp fiber clumps were placed in the diffuse reflectance attachment where the IR beam was focused for maximum signal output. Infrared spectra were recorded for various pulps and cotton linters. Each spectrum was ratioed against a background of potassium chloride before baseline correction. The reference cotton linters was subtracted from each pulp sample by manually obtaining the best baseline subtraction in the aliphatic C-H stretch region (2800-3000 cm^{-1}). To determine the best subtraction factor, the spectrum of the cotton linters was overlaid on the pulp spectrum on the computer screen. The area of the lignin band at 1510 cm^{-1} was integrated and recorded for data analysis.

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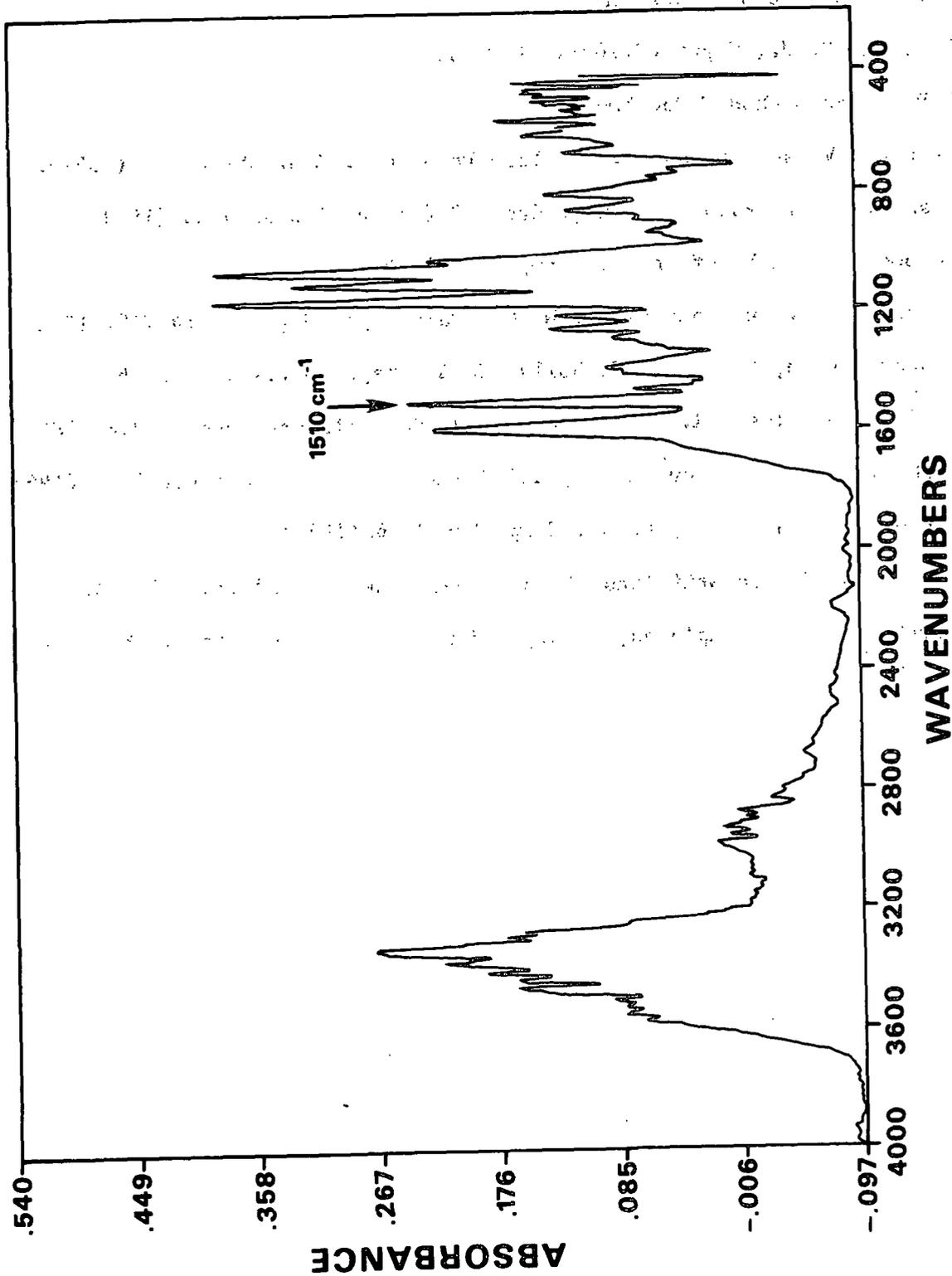13. Schultz, T. P., Templeton, M. C., and McGinnis, G. D., Anal. Chem. 57(14):2867(1985).

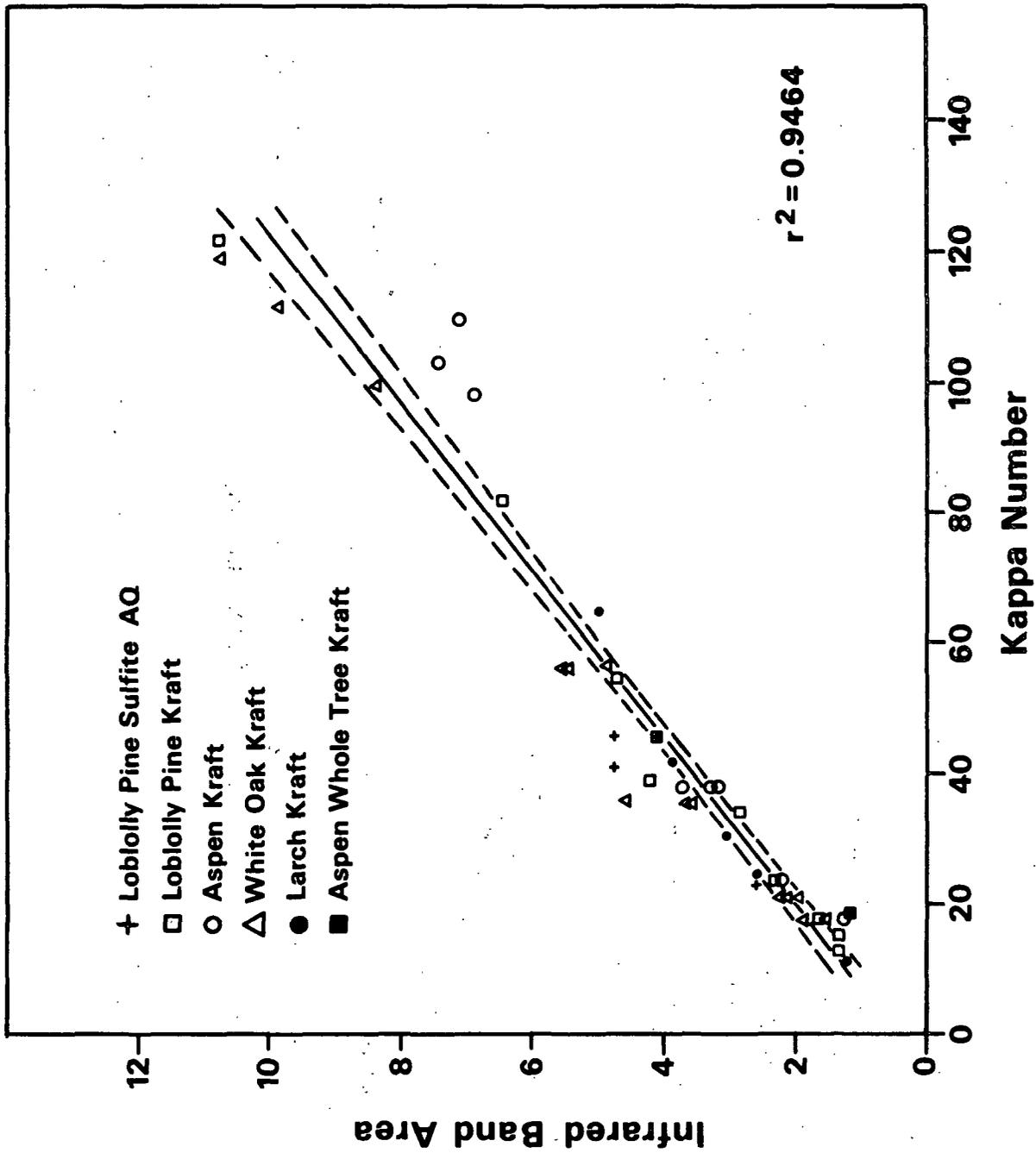Fig. 1. Subtraction spectrum. Unbleached pulp minus cotton linters.

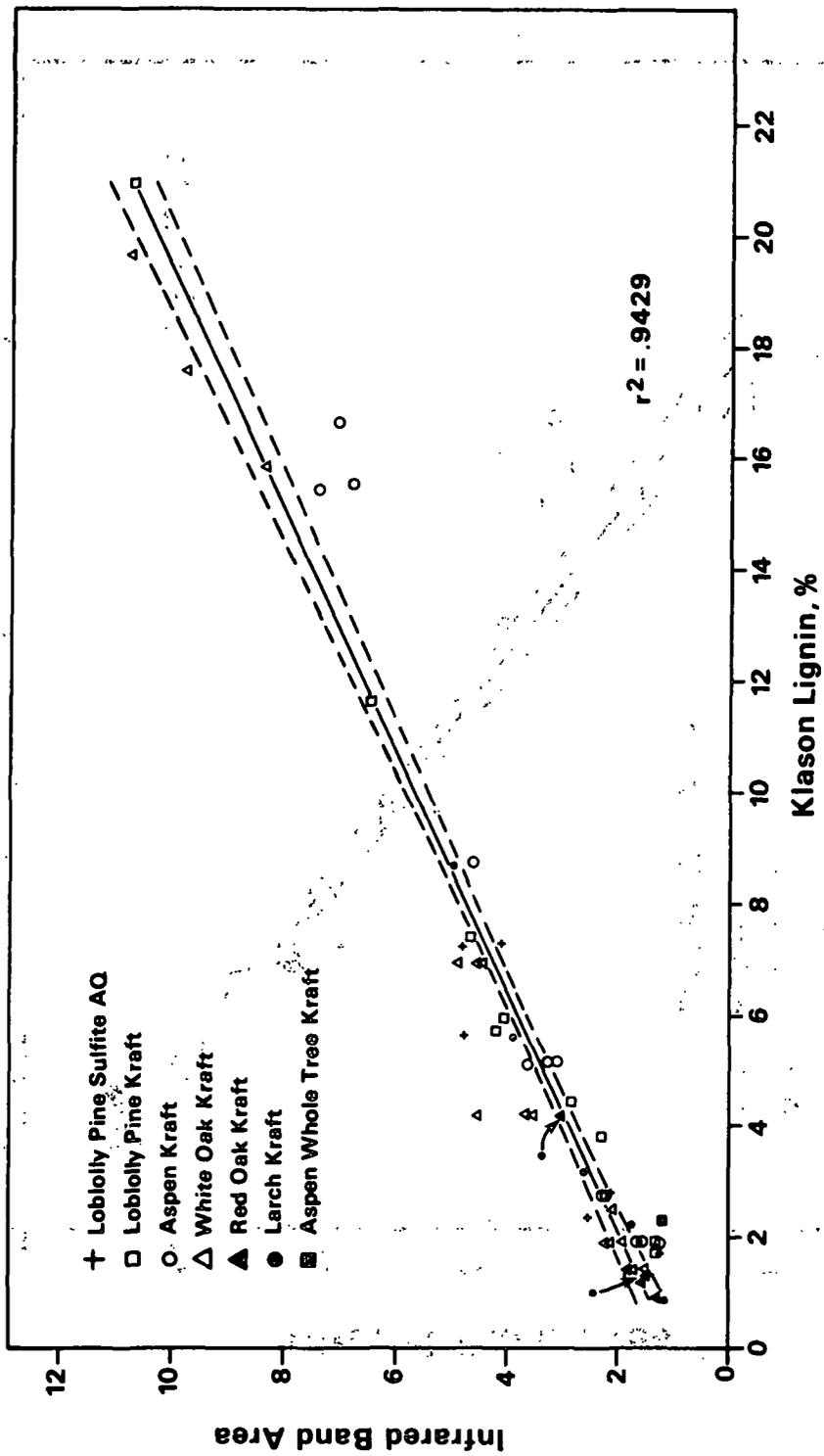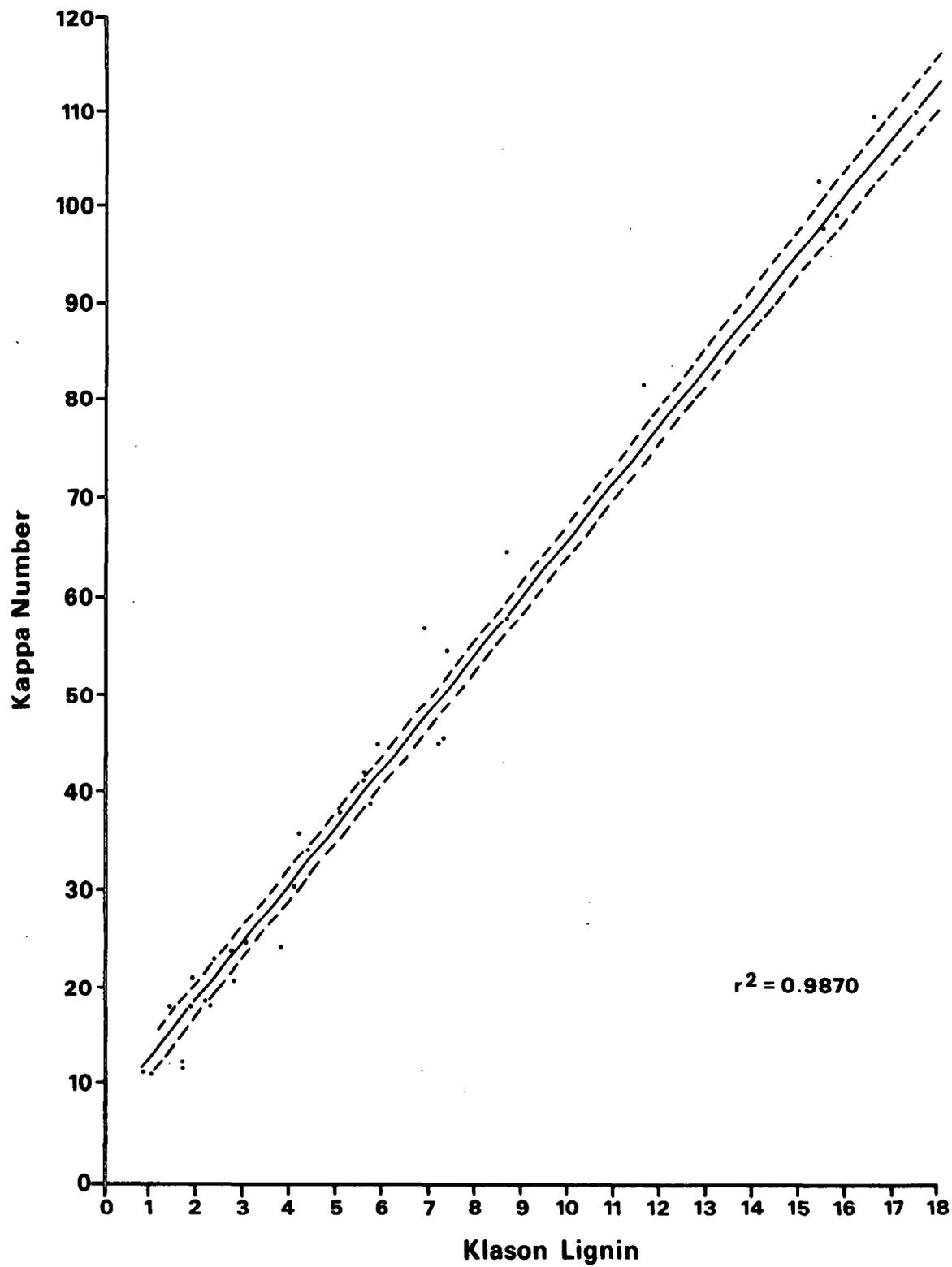Fig. 2. IR band area vs. kappa number. All species.

Fig. 3. IR band area vs. Klason lignin, %. All species.

Fig. 4.   Kappa number vs. Klason lignin.