Estimation of lignin in jute fibres using FT-IR spectroscopy

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A new method for lignin estimation using Fourier Transform-Infra Red (FT-IR) spectroscopy has been developed. The infrared absorbance due to specific lignin peak is used for lignin estimation. The new method is quick, reproducible and does not require handling of hazardous chemical like conc. sulphuric acid as in the chemical method.

Keywords: FT-IR spectroscopy, Jute, Lignin, Phloroglucinol-HCl

1 Introduction
Jute fibres generally consist of 58-63% cellulose, 20-24% hemi-cellulose and 12-15% lignin as major constituents and oil, waxes, etc. as minor quantities. Lignin, which is a random three-dimensional network polymer composed primarily of phenylpropane units, has a significant presence in jute fibres.

During the pretreatment of jute fibres for preparatory processes, a part of the lignin and hemi-cellulose get removed, and therefore the fibres deteriorate in their tensile properties. To reinforce the structure, BTRA has developed tailor-made polymers with various functional groups to replace the part of hemi-cellulose and lignin. These polymers either bind the cellulose, hemi-cellulose and lignin or fill-up the voids created by their removal. Hence, it is necessary to know the amount of lignin present in jute fibres/fabrics after pretreatment before reinforcing with the suitable amount of polymers.

Generally, in paper industry, lignin is estimated gravimetrically by TAPPI standard method. But this method is tedious, time-consuming and requires handling of conc. sulphuric acid. Hence, it was thought worthwhile to develop a method for estimation of lignin in jute fibres using Fourier Transform-Infra Red (FT-IR) spectroscopy and the same is discussed in this paper.

2 Materials and Methods
2.1 Materials
2.1.1 Preparation of Pure Lignin and Cellulose for Calibration
The pure lignin from dewaxed jute hessian fibre was prepared by controlled carbonisation of cellulosic materials at deep frozen conditions using 72% sulphuric acid. Lignin residue was filtered and thoroughly washed with dilute ammonia and then with water till free from acid.

For preparing pure cellulose, jute hessian fibre was treated with 0.7% sodium chloride (NaClO₂) solution at boil for 2h. The treatment was repeated again for full removal of lignin. This cellulose after antichlorine treatment was thoroughly washed and dried.

2.1.2 Preparation of Jute Lignin Blends for Calibration Standards
A series of calibration standards was prepared in the laboratory by mixing the fine powders of jute lignin and jute cellulose and passed through 200 mesh sieve. The blend composition (cellulose/lignin) varied from 94:6 to 85:15.

2.1.3 Preparation of Jute Fibre Samples
Jute hessian grey fibre was treated with 0.7% sodium chlorite solution at boil for different durations (5, 10, 20, 40 and 90 min) to obtain jute fibre samples having different lignin content. The material-to-liquor ratio and pH were maintained at 1:50 and 4 respectively.

2.2 Methods
2.2.1 FT-IR Analysis
The FT-IR spectra of all the samples were recorded on a Perkin Elmer FT-IR spectrophotometer (Model System 2000) between 4000 cm⁻¹ and 400 cm⁻¹, using potassium bromide pellet technique. An average of 25 scans was taken. Peak areas were calculated using the instrument software.

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The calibration graphs were prepared by analysing a series of known standard delignified jute/lignin blends prepared in the laboratory. Calibration constants like slope and intercept were obtained by linear regression analysis using the instrument software.

2.2.2 Chemical Method for Lignin Estimation
To verify the results obtained by FT-IR method, the estimation of lignin was carried out as per the TAPPI standard test method\(^2\) with little modification. About 2-3 g of accurately weighed sample was cut into small pieces and placed in a 100 ml conical flask, to which 40 ml of 72% ice cold conc. sulphuric acid was added and the sample was kept in freezer for 8 h. The sample was then removed, diluted with distilled water up to 800ml and digested for 5 h to precipitate the lignin. The solution was allowed to settle down overnight and the precipitate was filtered, washed with hot water and subsequently with cold water, and then dried in an oven. Residual lignin content was estimated based on original sample weight.

2.2.3 Phloroglucinol-HCl Reagent Staining Test
The qualitative identification and finding out the location of the lignin was done by staining the cross-sections of fibres by phloroglucinol-HCl reagent\(^3\). The stained cross-section shows magenta colour in the areas where lignin is present.

3 Results and Discussion
FT-IR spectra of grey and delignified jute fibres

![Figure 1](image)

**Table 1—Calibration data for lignin estimation using FT-IR spectra**

<table>
<thead>
<tr>
<th>Actual lignin in blend (%)</th>
<th>R1: Peak area ratio</th>
<th>R2: Peak area ratio</th>
<th>R3: Peak area ratio</th>
<th>Estimated lignin based on peak area ratio (%)</th>
<th>Mean of estimated lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.024</td>
<td>0.275</td>
<td>4.647</td>
<td>6.19</td>
<td>5.98</td>
</tr>
<tr>
<td>9</td>
<td>0.030</td>
<td>0.348</td>
<td>6.483</td>
<td>8.66</td>
<td>8.98</td>
</tr>
<tr>
<td>12</td>
<td>0.038</td>
<td>0.409</td>
<td>8.336</td>
<td>12.16</td>
<td>12.16</td>
</tr>
<tr>
<td>15</td>
<td>0.044</td>
<td>0.466</td>
<td>9.953</td>
<td>14.99</td>
<td>14.89</td>
</tr>
</tbody>
</table>

Regression constants:
- Slope: 437.2
- Intercept: -4.429
- Correlation coefficient: 0.998
- Standard deviation: 0.2458

Base line points for peak: (1506, 1471); 1550, 1400 cm\(^{-1}\)
peak (3405); 3660, 3000 cm\(^{-1}\)
peak (2907); 3000, 2800 cm\(^{-1}\)
peak (8081); 920, 860 cm\(^{-1}\).

(Fig. 1) show the characteristic peak differences in the region of 1400-1600 cm\(^{-1}\). In lignin spectrum, the specific absorbance peak at 1506 cm\(^{-1}\) is attributed to the skeletal vibrations of aromatic ring and the peak at 1471 cm\(^{-1}\) is attributed to C-H asymmetric deformation\(^3\). Hence, the lignin estimation was calibrated based on the area of these combined peaks which is not present in the spectrum of delignified jute. For normalization purpose and to eliminate minor variations in sample preparation, three other peaks at 3405 cm\(^{-1}\), 2907 cm\(^{-1}\) and 898 cm\(^{-1}\) were used. The peak areas ratios were calculated with
respect to the total area of combined lignin peak (1506, 1471 cm⁻¹) using the instrument software. The base line points for different peaks are shown in Table 1 for area calculation.

A set of laboratory blends of delignified jute and the jute lignin was prepared as described earlier and FT-IR spectra of the same were recorded. The calibration data for lignin estimation, obtained from the FT-IR spectra of a set of laboratory blends of delignified jute and jute lignin, are shown in Table 1. It is observed that the peak area ratio R1 (A 1506, 1471/A 3405) increases gradually as the lignin content in the blend increases, indicating that the ratio is sensitive to the lignin content in the sample. A similar trend is observed in the other two peak area ratios R2 (A 1506, 1471/A 2907) and R3 (A 1506, 1471/A 898). Linear regression analysis was carried out for these three sets of data against lignin percentage in the blend, using the least square fit software of the instrument. Regression constants, like slope and intercept were obtained for every ratio (Table 1). A very good correlation coefficient was obtained in all the three cases. The calibration graphs of lignin against the three peak area ratios are shown in Fig. 2. Using the slope and intercept, lignin contents were calculated for calibration standards. The average estimated lignin values based on three peak area ratios almost match with the actual lignin contents in the blends with little experimental variations.

To verify the sensitivity of the method, FT-IR spectra of a series of samples with decreasing amount of lignin were taken and the data based on these spectra are given in Table 2. It is seen that all the peak ratios gradually reduce as the treatment duration increases. From the respective peak area ratio and the calibration constants, the lignin content is calculated. The data shows that the average lignin content, calculated on the basis of three peak area ratios, varies between 6% and 17%. The lignin content of the above samples was also estimated by the chemical method and was found to be almost matching.

To ascertain the lignin present qualitatively in the above samples, the thin cross-sections of the samples were prepared and stained with phloroglucinol-HCl reagent. Photomicrographs of the stained cross-sections (Fig. 3) show that the grey jute sample develops magenta colour quite extensively (Fig. 3a), whereas samples treated with sodium chlorite for 10 min and 40 min develop medium and light magenta colour respectively (Figs 3b & 3c). This indicates that the lignin content goes on decreasing as the duration of the sodium chlorite treatment increases. Phloroglucinol-HCl reagent staining test goes hand-in-hand with the FT-IR spectroscopy observations.

![Fig. 2—Calibration graphs for lignin estimation](image-url)

### Table 2—Lignin estimated in partially delignified jute hessian fibres using the calibration constants

<table>
<thead>
<tr>
<th>Duration of NaClO₃ treatment at boil</th>
<th>Peak area ratio</th>
<th>Estimated lignin based on peak area ratio, %</th>
<th>Mean of lignin estimated by FT-IR %</th>
<th>Lignin by chemical method %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Control)</td>
<td>R1 (A 1506, 1471/A 3405)</td>
<td>14.24, 13.67, 12.92</td>
<td>13.61</td>
<td>13.67</td>
</tr>
<tr>
<td>5</td>
<td>R2 (A 1506, 1471/A 2907)</td>
<td>11.24, 11.12, 10.85</td>
<td>11.07</td>
<td>12.13</td>
</tr>
<tr>
<td>10</td>
<td>R3 (A 1506, 1471/A 898)</td>
<td>10.81, 10.52, 9.98</td>
<td>10.44</td>
<td>10.28</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>9.95, 10.42, 9.60</td>
<td>9.97</td>
<td>9.66</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>7.80, 7.41, 6.94</td>
<td>7.38</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>6.51, 6.38, 6.36</td>
<td>6.42</td>
<td></td>
</tr>
</tbody>
</table>
Table 3—Lignin estimated in some natural fibres using FT-IR method

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Lignin, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Estimated by FT-IR method</td>
</tr>
<tr>
<td>Pineapple</td>
<td>4-6</td>
</tr>
<tr>
<td>Ramie</td>
<td>3-4</td>
</tr>
<tr>
<td>Flax</td>
<td>4-6</td>
</tr>
<tr>
<td>Sisal</td>
<td>6-8</td>
</tr>
<tr>
<td>Hemp</td>
<td>1-2</td>
</tr>
<tr>
<td>Kapok</td>
<td>10-13</td>
</tr>
<tr>
<td>Coir</td>
<td>22-25</td>
</tr>
</tbody>
</table>

Using the same calibration constants, lignin was estimated in some other natural fibres and the results are given in Table 3. It is observed that the estimated values of lignin content by this method are comparable with the values reported in the literature. However, for precise results, the calibration for lignin estimation should be done for individual fibres using the lignin extracted from the respective fibres.

4 Conclusion

Lignin estimation can be carried out using FT-IR spectroscopy. The method is comparable with the chemical method and it is less tedious, less time-consuming and does not require handling of hazardous chemical.

Acknowledgement

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References