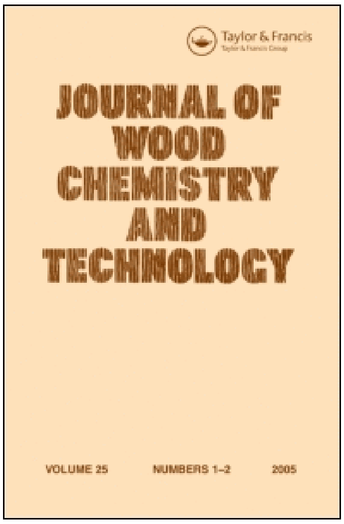

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NON-DESTRUCTIVE DETERMINATION OF LIGNIN SYRINGYL/GUAIACYL MONOMERIC COMPOSITION IN NATIVE WOOD BY FOURIER TRANSFORM RAMAN SPECTROSCOPY

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ABSTRACT

The feasibility of using FT-Raman spectroscopy for rapid non-destructive determination of lignin syringyl/guaiacyl (S/G) monomeric composition was examined using *Eucalyptus camaldulensis* and *E. globulus*, including samples of various ages and colors, which are of importance as a plantation source. The application of 2nd derivatives transformation of Raman spectroscopic data revealed highly significant correlations between wet chemical and Raman predicted values with correlation coefficient (r) = 0.998 and standard error of prediction (SEP) < 0.07 points in the calibration (for known samples), and r = 0.935 and SEP < 0.32 points in the prediction (for unknown samples), respectively. Consequently, this non-destructive method has proved its validity for analyzing *Eucalyptus* native wood meal samples, regardless of their age and color to determine lignin S/G monomeric composition. Using FT-Raman spectroscopy, elite tree selection based on quality aspects for pulp and paper production can be performed.

INTRODUCTION

Forest resources are important renewable resources of raw materials. To reduce our reliance on natural forests and manufacturing costs of pulp and paper products using plantation trees, tree breeding should be performed based on quality aspects for pulp and paper production.

For this objectives, we have examined the feasibility of Fourier transform Raman (FT-Raman) spectroscopy as a rapid non-destructive means of determining the content of various wood constituents.[1] However, the structure of wood constituents, such as lignin monomeric composition, which relate to some pulp properties, namely sheet density and breaking length.[2]

In a rapid means of spectroscopical analysis of lignin monomeric composition in the solid state, Fourier transform infrared (FTIR) spectroscopy and near-infrared (NIR) spectroscopy are frequently used.[3] On the other hand, structural analysis of lignin by Raman spectroscopy is reported.[4] However, little has been investigated on the quantification of lignin monomeric composition using Raman spectroscopy.

Here, we report on the feasibility of FT-Raman spectroscopy as a rapid non-destructive means of determining lignin monomeric composition of wood using two *Eucalyptus* species, which are important as a plantation source. We also report important frequencies used in the analysis, compared with the spectra of dehydrogenation polymers synthesized from each monolignol, individually.

RESULTS AND DISCUSSION

Wet chemical data of lignin monomeric composition expressed as syringyl/guaiacyl (S/G) ratio in calibration and in prediction were 2.76 ± 0.95 (n = 55) and 2.66 ± 0.88 (n = 25), respectively and are no significant differences between members of two sets.

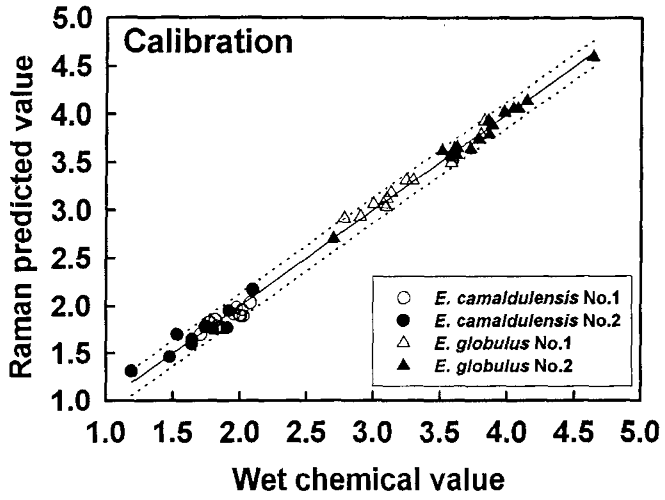

FIGURE 1. Plot of FT-Raman calibration (for known samples) against lignin syringyl/guaiacyl ratio. The 95% confidence contours are represented by dashed lines.

Plot of the calibration by partial least squares (PLS) regression is shown in Figure 1. The number of principal components (PCs) used in the model was decided by the residual variance, which was defined as the mean squared residual corrected for degrees of freedom. As shown in Figure 1, we have successfully obtained statistically significant correlation with correlation coefficient (r); 0.998 and standard error of prediction (SEP); 0.07 points using 5 PCs between wet chemical and Raman predicted values. This is the first successful calibration of lignin S/G ratio of native wood meals with FT-Raman spectroscopy.

This method will be valid for samples of various ages, since the calibration model was created using samples of different ages taken from various parts within the tree stems. This will be also valid for different species and for colored samples, which fluorescence causing base line change in the spectra due to colored materials.[7] In fact, some of utilized samples were colored red due to heartwood formation.[8]

TABLE 1

Possible Assignment of Important Frequencies in the Calibration Model

Raman Shift cm^{-1}	Assignment	Reference
121	• Skeletal deformation (syringyl)	–
195	• Skeletal deformation (syringyl)	5
781	• Ring vibration (syringyl)	5
793	• C-H out of plane bending (syringyl)	5
1093	• C-O deformation in aliphatic ethers (syringyl)	6
1379	• C-H deformation or C-C-H bending (syringyl)	3
1583	• Ring stretching (guaiacyl)	3
1591	• Ring stretching (syringyl)	3
1595	• Ring stretching (guaiacyl)	3
1657	• C=O stretching (guaiacyl)	9

Syringyl or guaiacyl assignment was decided by the spectra of 2nd derivatives form of corresponding dehydrogenation polymer shown in Figure 2B.

Consequently, the calibration will be valid for *Eucalyptus* native wood meal samples, regardless of their age and heartwood color. The results are unique among the few reports of FT-Raman.

Table 1 shows important frequencies selected by regression coefficients used in the calibration model. To assign them, three types of synthesized dehydrogenation polymer (DHP), namely p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) DHPs were utilized as lignin standards, and the Raman spectra are shown in Figure 2A. The spectra of DHPs are very similar and the quantitative determination will be quit difficult although peaks around 1600 cm^{-1} might have the characteristic Raman shift for each DHP. Consequently, we have applied 2nd derivation to the spectra of G-and S-DHPs because H moiety was not detected in the wet chemical analysis, and showed them in Figure 2B. Important frequencies extracted in the calibration model agree with the characteristic peaks in either DHP significantly and the possible assignment of each frequency has been achieved and summarized in Table 1.

From Table 1 and Figure 2B, important frequencies including around 1600 cm^{-1} were distinguished to each moiety very clearly and the validity of 2nd derivation of the spectra has been proved. In addition to this, frequencies less than 200 cm^{-1} were

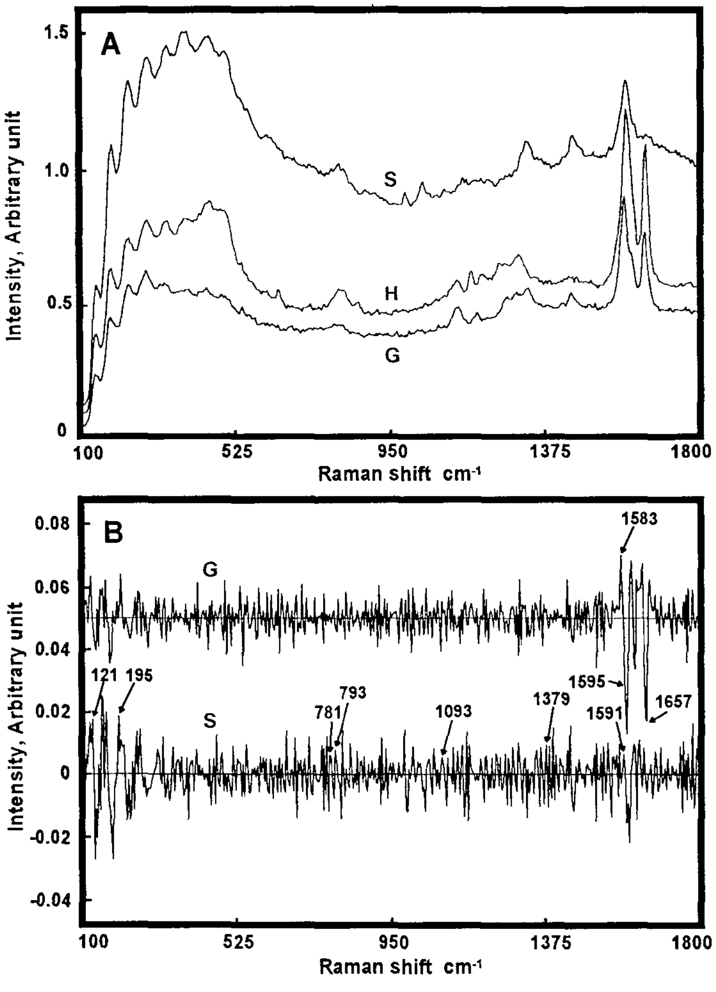

FIGURE 2. Normal FT-Raman spectra (A), and their 2nd derivative forms (B) of Standards. H; p-hydroxyphenyl dehydrogenation polymer (DHP), G; guaiacyl DHP, and S; syringyl DHP.

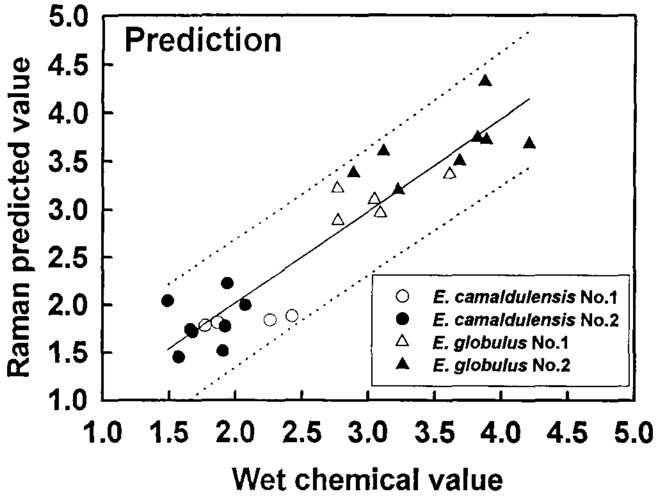

FIGURE 3. Plot of FT-Raman prediction (for unknown samples) against lignin syringyl/guaiacyl ratio. The 95% confidence contours are represented by dashed lines.

included and utilized as important variables in this study as same as in the previous study.[1] The result suggests the possible utilization of those short frequencies in the chemical study of wood, especially with 2nd derivation of the spectra although the Raman intensity is rather low.

Figure 3 shows the prediction of lignin S/G ratio by Raman spectroscopy using the obtained calibration model. As a result, highly significant correlation between wet chemical and Raman predicted values was successfully obtained with r; 0.935 and SEP; 0.32 points.

The non-destructive FT-Raman spectroscopic method has proved its validity for determining lignin monomeric composition for *Eucalyptus* native wood meal samples, regardless of their age and color.

By using FT-Raman method, elite tree selection can be performed based on quality aspects that will reduce our reliance on natural forests and reduce the cost of pulp and paper products.

EXPERIMENTAL

Materials

The *E. camaldulensis* and *E. globulus* samples (two 14 year-old trees, numbered 1 and 2) were grown at CALM (Department of Conservation and Land Management, Western Australia, Australia). The *E. camaldulensis* samples included 17 block samples, each about 2 x 2 x 6 cm, from trees No. 1 and 2. The *E. globulus* samples included 19 block samples from tree No.1 and 22 block samples from tree No.2. The block samples were taken randomly in the stems, and had been utilized in an earlier study.[1] As standard samples for lignin analysis, three types of DHPs, namely H-, G- and S-DHPs were prepared from p-hydroxyphenyl, coniferyl and sinapyl alcohols, respectively using peroxidase and hydrogen peroxide by the conventional mixing method.[10]

Wet chemical method

Lignin S/G ratio was determined by modified thioacidolysis method and expressed as molar ratio.[11]

Raman spectroscopy

Raman spectra were collected using a Nicolet Raman 950 spectrometer (Nicolet Instrument Corp., Madison, USA) equipped with a Nd: YAG laser operating at 1064 nm, and Ge detector. Wood meal samples (20 mesh pass) were packed into NMR tubes and spectra were collected using 180° backscattering at 500 mW, 4 cm^{-1} resolution and 256 scans.[1] The spectra of standard samples were collected in capillary tubes with the same manner. Raman spectra of 100-1800 cm^{-1} frequencies were transformed to the 2nd derivatives form after multiplicative scatter correction. They were then subjected to PLS regression with the lignin monomeric composition using the software of Unscrambler 6.0 (Camo AS, Trondheim, Norway). A total 55 of wood samples for calibration and 25 for prediction were selected randomly.

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REFERENCES

1. T. Ona, T. Sonoda, K. Ito, M. Shibata, T. Kato, and Y. Ootake, J. Wood Chem. Technol., *in submission.*

2. T. Ona, T. Sonoda, K. Ito, M. Shibata, Y. Tamai, and Y. Kojima, Appita, 49, 325 (1996).

3. O. Faix, In Methods in Lignin Chemistry, S.Y. Lin and C. W. Dence (eds.), p. 83-106, Springer-Verlag, Berlin, Heidelberg, 1992.

4. R. H. Atalla, U. P. Agarwal, and J. S. Bond, In Methods in Lignin Chemistry, S.Y. Lin and C. W. Dence (eds.), p. 162-176, Springer-Verlag, Berlin, Heidelberg, 1992.

5. F. S. Parker, Applications of Infrared, Raman, and Resonance Raman Spectroscopy in Biochemistry, Plenum Press, New York, London, 1991.

6. T. P. Schulz and W. G. Glasser, Holzforschung, 40, 37 (1986).

7. V. M. Hallmark, In Fourier Transform Raman Spectroscopy: From Concept to Experiment, D. B. Chase and J. F. Rabolt (eds.), p. 73-110, Academic Press, San Diego, New York, Boston, London, Sydney, Tokyo, Toronto, 1994.

8. T. Ona, T. Sonoda, K. Ito, and M. Shibata, Jpn. Tappi, 49, 861 (1995).

9. U. P. Agarwal, R. H. Atalla, and I. Forsskåhl, Holzforschung, 49, 300 (1995).

10. A. Ishizu, T. Kondo, K. Sakai, A. Sakakibara, N. Terashima, J. Nakano, T. Higuchi, and G. Meshitsuka, In Lignin Chemistry (New Ed.), J. Nakano (ed.), p. 519-545, Uni Publishers, Tokyo, 1990.

11. T. Ona, T. Sonoda, K. Ito, and M. Shibata, Holzforschung, *in press.*