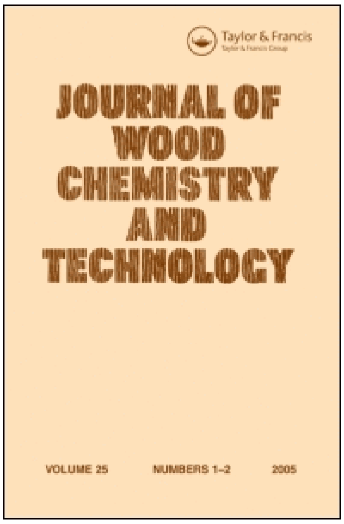

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DETERMINATION OF WOOD BASIC DENSITY BY FOURIER TRANSFORM RAMAN SPECTROSCOPY

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ABSTRACT

The feasibility of using FT-Raman spectroscopy for rapid determination of wood basic density was examined for two *Eucalyptus* species, including samples of various ages and colors, which are of importance as a plantation source. Wood basic density is an important indicator of wood physical properties, pulp properties and pulpwood productivity. Measurement included basic density (BD), extractives-free (EF) BD, alkali-extractives-free (AF) BD, total-extractives-free (TF) BD and extraneous compounds-free (ECF) BD were measured. The application of 2nd derivatives transformation to Raman spectroscopic data revealed highly significant correlations between measured and Raman predicted values for BD, EF-BD, AF-BD, TF-BD and ECF-BD with standard error of prediction (SEP) ≒ 8, 45, 22, 37 and 49 kg/m^3 in the calibration (for known samples) and SEP ≒ 28, 38, 40, 29 and 40 kg/m^3 in the prediction (for unknown samples), respectively. Consequently, this method has proved its validity for analyzing *Eucalyptus* native wood meal samples, regardless of their age and color, to determine basic density. FT-Raman spectroscopy can be used for (1) the measurement of physical properties of forest products, and (2) elite tree selection to improve both quality and productivity, reducing the cost of pulp and paper products and our reliance on natural forests.

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INTRODUCTION

Wood density is an important property for wood utilization and conversion.[1, 2] The presence of extraneous compounds[3, 4] can lead to errors in the measurement of wood density and its effect on the mechanical and pulp properties of wood. Extracted wood density is therefore used in studies of the variation in wood density between trees[3, 5] and within trees.[6, 7]

Basic density is an essential factor in the forest management of plantation pulpwood productivity [t/ha/year],[8] but the conventional measurement of basic density is not so easy because of the need to prevent wood shrink during storage. Indirect measurement of wood density using the Pilodyn, which drives a hardened-steel flat-nosed pin into wood with a known force,[9] works very well for *E. globulus*[10] and *E. nitens*,[11] but not for *E. camaldulensis*[12] probably because of extractives in the heartwood. The method would not be suitable for mixed heartwood and sapwood samples. The conventional method of determining extracted wood density is complicated by the need to use wet chemical treatments to quantify extractives content. A rapid means of determining the extracted wood basic density is needed.

Wood basic density can be predicted from the relationship between density and the wood chemical components.[6, 7] In addition, we have proved the feasibility of using Fourier transform Raman (FT-Raman) spectroscopy as a rapid non-destructive means of determining various wood constituents.[13-15]

Here, we report on the feasibility of using FT-Raman spectroscopy as a rapid means of determining the unextracted and extracted basic density for two *Eucalyptus* species. We also report important frequencies used in the analysis.

RESULTS AND DISCUSSION

Conventional measurements of unextracted and extracted basic density are summarized in Table 1. There were no significant differences between the calibration and the prediction sets.

TABLE 1

Values of Unextracted and Extracted Wood Basic Densities Measured by Conventional Method

Trait	Calibration Set (n=55)	Prediction Set (n=25)
BD (kg/m^3)	572 ± 93	569 ± 67
EF-BD (kg/m^3)	531 ± 95	528 ± 81
AF-BD (kg/m^3)	506 ± 82	503 ± 52
TF-BD (kg/m^3)	465 ± 83	462 ± 66
ECF-BD (kg/m^3)	565 ± 104	561 ± 86

BD - basic density; EF - extractives-free; AF - alkali-extractives-free; TF - total-extractives-free; ECF - extraneous compounds-free

Plots of the calibration by the partial least squares (PLS) regression are shown in Figure 1, and the statistical results are summarized in Table 2. The number of principal components used in the PLS regression model for each basic density was determined by the minimum standard error of prediction.

As shown in Figure 1 and Table 2, we successfully obtained highly significant correlation coefficients over 0.88 between measured and Raman predicted values for all basic densities. This is the first successful calibration of basic density using native wood meals and FT-Raman spectroscopy. The samples utilized in the calibration have important implications as each calibration model was created using two *Eucalyptus* species, including samples of different ages and color taken from various parts within the tree stems. It should be difficult to obtain calibrations using different species in FT-Raman because the presence of colored materials will change the base line spectra due to the differences in fluorescence intensity.[16] However, successful calibrations were obtained with red colored heartwood present in *E. camaldulensis*.[17] Consequently, each calibration will be valid for *Eucalyptus* native wood meal samples, regardless of their age and heartwood color. These results are unique among the few reports on FT-Raman and NIR for basic density determination.

Tables 3 shows important frequencies selected for each basic density using the magnitude of regression coefficients used in the calibration model. The frequencies in the calibration models were assigned according to the references and are tentative

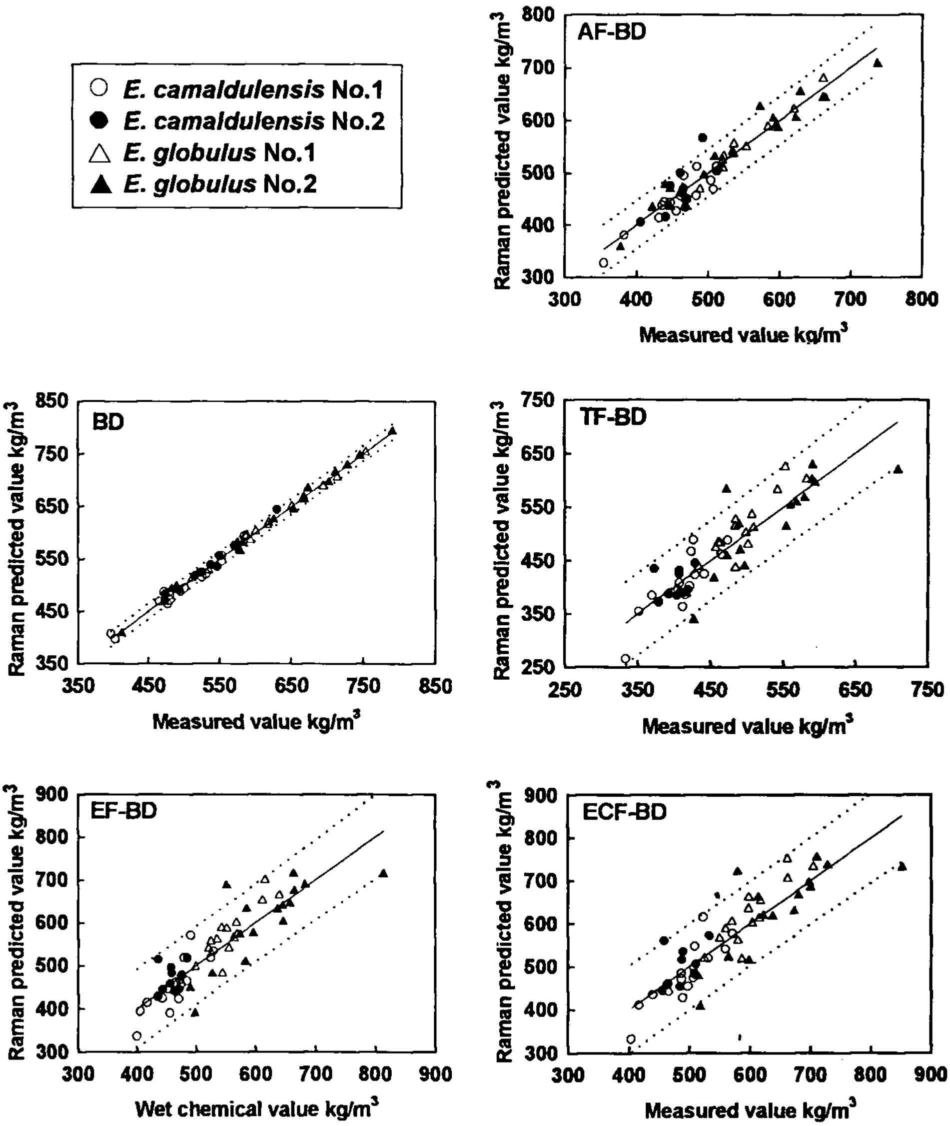

FIGURE 1. Plots of FT-Raman calibration (for known samples) against basic densities. BD - basic density; EF - extractives-free; AF - alkali-extractives-free; TF - total-extractives-free; ECF - extraneous compounds-free. The 95% confidence contours are represented by dashed lines.

TABLE 2

Statistical Results in Calibration

Trait	r	SEP	No. of used PCs
BD	0.996	8.2	5
EF-BD	0.883	44.6	2
AF-BD	0.962	22.3	3
TF-BD	0.894	37.3	2
ECF-BD	0.882	49.0	2

BD - basic density; EF - extractives-free; AF - alkali-extractives-free;
TF - total-extractives-free; ECF - extraneous compounds-free;
r - correlation coefficients; SEP - standard error of prediction;
PC - principal component

only. Many of the frequencies were important for more than one of the basic densities. Many frequencies could be assigned as wood constituents from our results or those of others. As shown in Table 4, they could be derived from the correlations between basic densities and wood constituents. The α - cellulose, lignin, extractives, lignin and lignin S/G ratio were found in the important frequencies, but not the hemicellulosic neutral sugars arabinose and glucose which were also highly correlated with basic densities. From our previous studies,[6, 7, 18] the basic densities were expected to be expressed by wood constituents. In this study, we have successfully achieved this using FT-Raman spectroscopy to detect structural features.[19] In particular, many important frequencies probably derived from lignin and extraneous compounds were extracted as ring breathing, C=C stretching, and so on, with further assignments expected. However, a frequency directly relating to density could not be detected although 233 and 499 cm^{-1} have not been assigned.

Figure 2 and Table 5 show the prediction of basic densities by Raman spectroscopy using the calibration models.

Highly significant correlations were obtained between measured and Raman predicted values of basic density using samples of different species, age and color, that included different positions within the stems. FT-Raman spectroscopy has proved its validity for determining basic densities for mixed *Eucalyptus* native wood

TABLE 3
Possible Assignment of Important Frequencies in the Calibration Models and Their Presence

Raman shift cm^{-1}	BD	EF-BD	AF-BD	TF-BD	ECF-BD	Assignment	Ref.
114	×	—	—	—	—	• Skeletal deformation • Extractives	- 13
121	×	—	—	—	—	• Skeletal deformation • Syringyl lignin	- 14
160	—	—	×	—	—	• Skeletal deformation	-
164	—	×	—	×	×	• Skeletal deformation	-
168	—	×	—	—	×	• Hemicellulose	13
202	—	—	—	×	—	• Skeletal deformation	-
226	—	×	—	—	—	• Torsional mode	20
233	×	—	—	—	—	• ?	
341	×	—	—	—	×	• C-O-C with β configuration in cellulose • Cellulose	20 13
345	×	—	—	—	—	• See 341 cm^{-1}	-
499	—	—	×	×	—	• ?	
731	×	—	×	—	—	• Ring breathing	20
781	—	×	—	×	—	• Ring vibration • Extractives • Syringyl lignin	20 13 14
785	—	—	—	×	—	• Ring vibration	20
943	—	—	×	—	—	• Ring breathing	20
1039	—	—	—	×	×	• Ring vibration • Hot water solubles	21 20
1379	—	—	—	—	×	• C-H deformation or C-C-H bending (syringyl lignin)	14
1414	×	×	×	×	×	• Ring stretching	20
1448	×	×	×	×	×	• CH_3, CH_2 deformation • Ring stretching (guaiacyl lignin)	22 14
1537	—	—	×	—	—	• C=C stretching	20
1595	×	×	×	×	×	• Ring stretching (guaiacyl lignin)	14
1610	—	×	—	—	×	• C=C stretching • Extractives	13 20
1622	—	×	—	×	×	• C=C stretching • Lignin	20 13
1626	—	—	×	—	—	• Ring stretching	20
1788	×	—	×	—	—	• C=C stretching	20

BD - basic density; EF - extractives-free; AF - alkali-extractives-free;
TF - total-extractives-free; ECF - extraneous compounds-free;
× present; — not present

TABLE 4
Correlations between Basic Densities and Wood Chemical Components in the Calibration Sets

	BD	EF-BD	AF-BD	TF-BD	ECF-BD
Holocellulose	*** 0.395	*** 0.602	** 0.328	*** 0.573	*** 0.638
α-cellulose	*** 0.481	*** 0.641	*** 0.440	*** 0.631	*** 0.678
Hemicellulose	-0.085	0.064	-0.155	0.017	0.070
Lignin	*** -0.564	*** -0.575	*** -0.483	*** -0.501	*** 0.536
Extractives	-0.147	*** -0.414	-0.085	*** -0.396	*** -0.422
Alkali-extractives	0.212	** 0.285	0.019	0.106	* 0.249
Total-extractives	-0.016	* -0.240	-0.073	** -0.333	** -0.271
Lignin S/G ratio	*** 0.595	*** 0.684	*** 0.543	*** 0.654	*** 0.672
Glucose	** -0.278	** -0.307	-0.213	* -0.250	** -0.282
Xylose	* 0.231	0.221	0.115	0.106	0.169
Galactose	-0.058	-0.052	0.054	0.061	0.003
Rhamnose	0.153	0.205	0.073	0.135	0.160
Arabinose	*** -0.402	*** -0.378	** -0.341	** -0.317	*** -0.356
Mannose	-0.168	-0.123	-0.133	0.083	-0.118

*** Significant at 1% level, ** Significant at 5% level, * Significant at 10% level
BD - basic density; EF - extractives-free; AF - alkali-extractives-free;
TF - total-extractives-free; ECF - extraneous compounds-free;
Various BDs - kg/m^3; Wood constituents - % in original wood;
Lignin S/G ratio - molar ratio; Sugars - mol% in hemicellulose

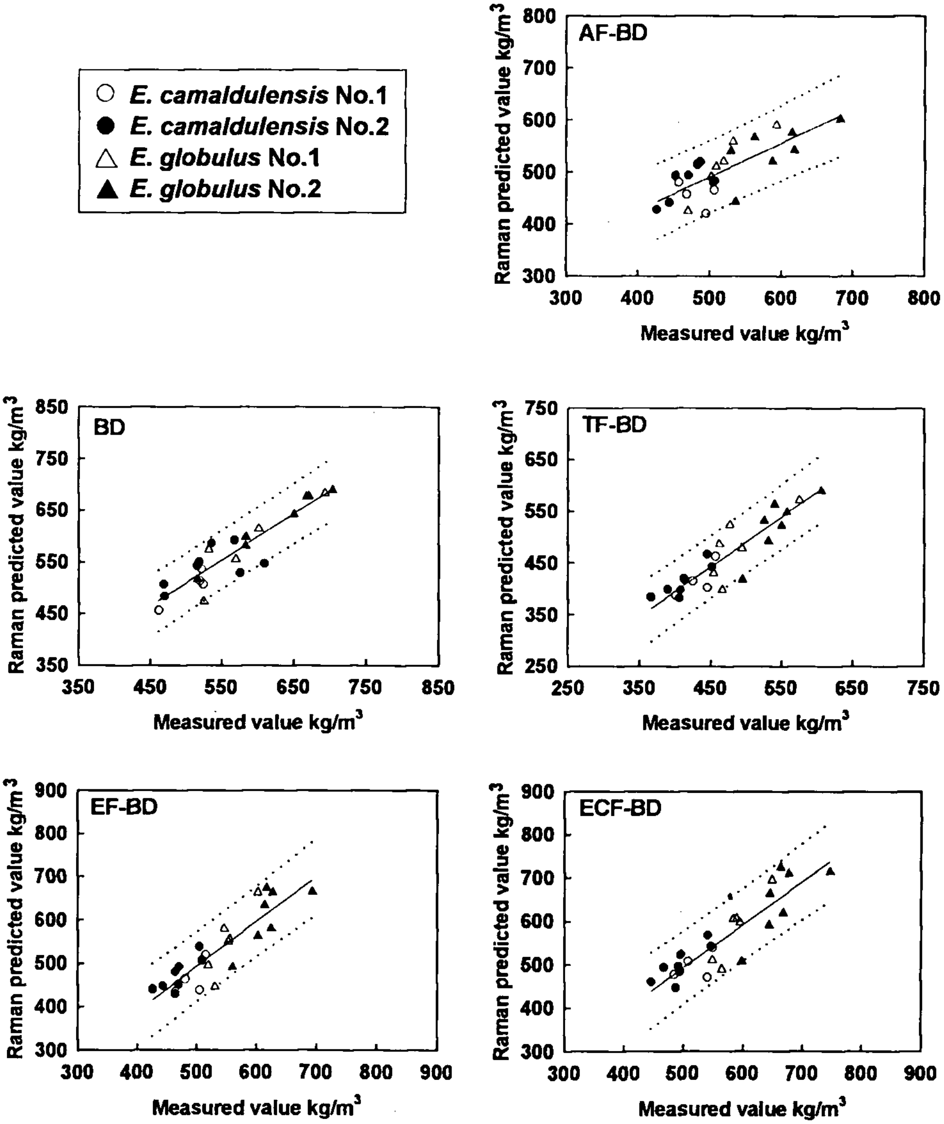

FIGURE 2. Plots of FT-Raman prediction (for unknown samples) against basic densities. BD - basic density; EF - extractives-free; AF - alkali-extractives-free; TF - total-extractives-free; ECF - extraneous compounds-free. The 95% confidence contours are represented by dashed lines.

TABLE 5
Statistical Result in Prediction

Trait	r	SEP
BD	0.917	27.8
EF-BD	0.885	37.9
AF-BD	0.774	39.5
TF-BD	0.900	28.7
ECF-BD	0.890	39.5

BD - basic density; EF - extractives-free; AF- alkali-extractives-free; TF - total-extractives-free; ECF - extraneous compounds-free
r - correlation coefficients; SEP - standard error of prediction

meal samples. This provides an advantage over the Pilodyn method which requires calibration for each species. FT-Raman spectroscopy could be used to estimate the density of particleboard from wood meals of the raw material very quickly, even online. It could also be used to determine the mixing ratio of different sources. Blow out and internal rupture of particleboard by gas pressure, caused by extractives during resin curing process, could be avoided because extractives can be predicted simultaneously with basic densities in wood meals.[23]

FT-Raman spectroscopy can be used for (1) the measurement of physical properties of forest products, and (2) elite tree selection to improve both quality and productivity, reducing the cost of pulp and paper products and our reliance on natural forests.

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

19 block samples, each about 2 x 2 x 6 cm, from tree No. 1 and 18 block samples from tree No. 2. The *E. globulus* samples included 20 block samples from tree No. 1 and 23 block samples from tree No.2. The block samples were taken randomly in the stems, and had been utilized in an earlier study.[13, 14, 24]

Basic densities

The contents of extraneous compounds were determined by a small-scale method for extractives (extraneous compounds dissolved in a Soxhlet apparatus using a sequence of toluene/ethanol, ethanol and water), alkali-extractives and total-extractives (extractives plus alkali-extractives).[13, 25] Basic density was determined by the water immersion method[26] combined with freeze-fracture and -drying, and expressed as dry weight / green volume [kg/m^3].[6]

Extractives-free basic density (EF-BD), alkali-extractives-free basic density (AF-BD), total-extractives-free basic density (TF-BD) and extraneous compounds-free basic density (ECF-BD) were defined as follows.

EF-BD = basic density x (100 - extractives content %) / 100
AF-BD = basic density x (100 - alkali-extractives content %) / 100
TF-BD = basic density x (100 - total-extractives content %) / 100
ECF-BD = basic density x (original wood basis holocellulose % + original wood basis lignin %) / 100, respectively.[6]

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.[13, 14] Raman spectra of 100-1800 cm^{-1} frequencies were transformed to the 2nd derivatives form after the multiplicative scatter correction. Then they were subjected to the PLS regression with various basic densities by using the software of Unscrambler 6.0 (Camo AS, Trondheim, Norway). A total of 55 samples for calibration and 25 for prediction were selected randomly.

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