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**NON-DESTRUCTIVE DETERMINATION OF HEMICELLULOSIC
NEUTRAL SUGAR 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 hemicellulosic neutral sugar composition, important factors for pulp properties, in native wood was examined using two *Eucalyptus* species, including samples of various ages and colors, which are important sources of plantation pulpwood. The sugars, glucose, xylose, galactose, rhamnose, arabinose and mannose were utilized. The application of 2nd derivatives transformation of Raman spectroscopic data revealed highly significant correlations between wet chemical and Raman predicted values in the calibration (known samples) with correlation coefficients > 0.99 , and in the prediction (unknown samples) with correlation coefficients > 0.80 with the exception of rhamnose and mannose. Consequently, this non-destructive method will be valid for analyzing *Eucalyptus* native wood meal samples, regardless of their age and color to determine hemicellulosic neutral sugar composition except rhamnose and mannose. Elite tree selection based on quality aspects for pulp and paper production can be performed using FT-Raman spectroscopy.

INTRODUCTION

Trees are an important renewable source of raw materials. Tree breeding programs, with selection for quality aspects of pulp and paper production, promise to reduce our reliance on natural forests and reduce the manufacturing costs of pulp and paper products.

To achieve this, we have examined the feasibility of using Fourier transform Raman (FT-Raman) spectroscopy as a rapid non-destructive means of determining the content of various wood constituents including lignin monomeric composition.¹ However, we have not examined the hemicellulosic neutral sugar composition which relates to pulp yield and sheet density.³

Fourier transform infrared (FTIR) and near infrared (NIR) spectroscopy have been used for the rapid non-destructive spectroscopic analysis of neutral sugars in pulp.^{4,5} However, little has been performed on the hemicellulosic neutral sugar composition of wood.

Here, we report on the feasibility of using FT-Raman spectroscopy as a rapid non-destructive means of determining hemicellulosic neutral sugar composition of wood using two *Eucalyptus* species, which are important as a plantation source. We also report important frequencies used in the analysis.

RESULTS AND DISCUSSION

Wet chemical data of hemicellulosic neutral sugar composition are summarized in Table 1. There were no significant differences between members of the calibration and the prediction sets.

Plots of the calibration (known samples) by partial least squares (PLS) regression are shown in Figure 1, and the statistical results summarized in Table 2. The number of principal components (PCs) used in the PLS regression model for

TABLE 1
Wet Chemical Data of Hemicellulosic Neutral Sugar Composition

Sugar	% in Calibration (n=55)	% in Prediction (n=20)
Glucose	11.1 ± 3.1	10.9 ± 2.7
Xylose	66.0 ± 10.8	64.9 ± 10.1
Galactose	13.9 ± 8.6	14.9 ± 6.2
Rhamnose	0.8 ± 0.3	0.9 ± 0.2
Arabinose	4.0 ± 2.2	3.9 ± 1.9
Mannose	4.1 ● 2.5	4.5 ± 1.1

each sugar was decided by the residual variance, which was defined as the mean squared residual corrected for degrees of freedom. As shown in Figure 1 and Table 2, we have successfully obtained highly significant correlation coefficients over 0.99 between wet chemical and Raman predicted values for all sugars. The calibration for each sugar was highly significant with standard error of prediction (SEP) less than 0.98 points. This is the first successful calibration of the hemicellulosic neutral sugar composition of native wood meals with FT-Raman.

This method will be valid for samples of various ages, because each calibration model was created using samples of different ages taken from various parts within tree stems. This method will also be valid for colored samples, which fluorescence causing base line change in the spectra, since some of utilized samples of *Eucalyptus camaldulensis* No. 1 and 2 were colored red due to heartwood formation.⁶ Consequently, each 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 FT-Raman and NIR.

Tables 3-5 show important frequencies selected by regression coefficients used in the calibration model for all sugars. In Tables 3-5, the possible assignment of each frequency is also summarized according to the references and Raman spectra of standards as shown in Figures 2 and 3 although the assignment is tentative. The standards utilized included, commercially available monosaccharides and polysaccharides (hemicellulose), namely glucose, xylose, galactose, rhamnose,

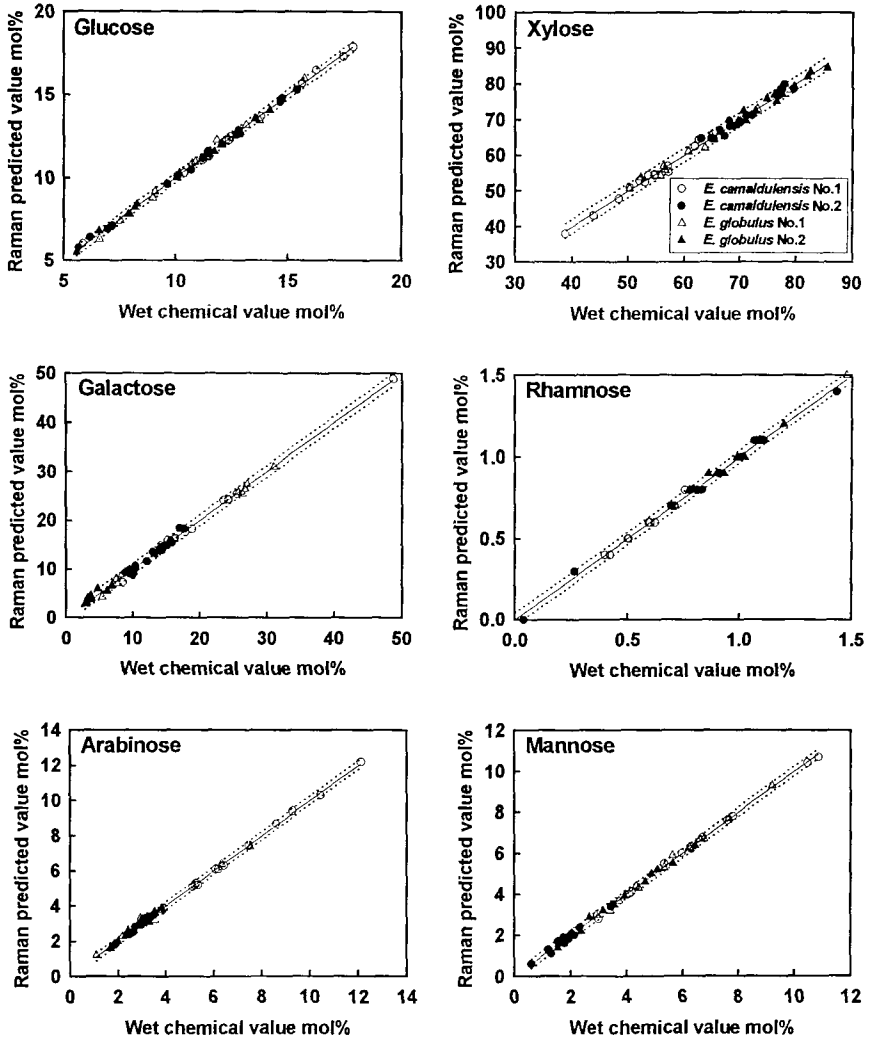


FIGURE 1. Plots of FT-Raman calibration (for known samples) against the hemicellulosic neutral sugar composition. The 95% confidence contours are represented by dashed lines.

TABLE 2
Statistical Result in Calibration

Trait	r	SEP	No. of used PCs
Glucose	0.999	0.15	9
Xylose	0.996	0.98	8
Galactose	0.998	0.57	9
Rhamnose	0.998	0.02	9
Arabinose	0.999	0.11	9
Mannose	0.999	0.11	9

r; correlation coefficients, SEP; standard error of prediction, PC; principal component

TABLE 3
Possible Assignment of Important Frequencies in the Calibration Models and Their Presence in Standards for Glucose and Xylose

Sugar	Raman Shift cm^{-1}	Glucose	Glucos-mannan	Assignment	Ref.
Glucose	172	-	-	• C-O-C bending (in LCC)	8
	438	×	×	• Skeletal deformation	8
	769	×	×	• Hydrogen bonded OH out of plane bending	9
	1360	×	×	• C-OH, C-H bending	8
	1363	×	×	• C-OH, C-H bending	8
	1560	-	×	• Carbanion	9
	1564	-	-	• C=C stretching (in lignin)	8
	1603	-	-	• C=O stretching in cinnamic acids (in LCC)	10
	1680	-	×	• C=O stretching (in Ac)	8
	1687	-	×	• C=O stretching (in Ac)	8
Sugar	Raman Shift cm^{-1}	Xylose	Xylan	Assignment	Ref.
Xylose	785	-	×	• Ring vibration	8
	1309	×	×	• CH_2 twist and rock	8
	1317	-	×	• C-H bond deformation	11
	1444	-	×	• CH_2 wagging mode	12
	1576	-	×	• CH_2 deformation	8
	1591	-	×	• C=O stretching (in Ac)	8
	1599	-	×	• C=O stretching (in Ac)	8
	1599	-	×	• COO^- ion asymmetric stretching	12
	1641	-	×	• C=O stretching (in Ac)	13
	1695	-	×	• C=O stretching (in Ac)	8
1741	-	-	• C=O stretching (in lignin)	8	

LCC; lignin carbohydrate complex, Ac; acetyl group, ×; present, -; not present

TABLE 4
Possible Assignment of Important Frequencies in the Calibration Models and Their Presence in Standards for Galactose and Rhamnose

Sugar	Raman Shift cm^{-1}	Galactose	Arabino-galactan	Assignment	Ref.
Galactose	118	-	×	• C-O-C bending	8
	796	-	×	• Keto furanose derivatives	8
	1132	-	-	• Asymmetric in-phase ring stretching (in lignin)	12
	1309	×	-	• CH_2 twist and rock	8
	1533	-	-	• C=C skeletal in-plane (in lignin)	8
	1591	-	-	• C=O stretching (in lignin)	8
	1633	-	-	• C=O stretching in cinnamic acids (in LCC)	10
	1641	-	×	• See xylose	
	1680	-	-	• C=O stretching (in lignin)	8
	1695	-	-	• See xylose	
Sugar	Raman Shift cm^{-1}	Rhamnose	Xylan	Assignment	Ref.
Rhamnose	418	-	-	• C-O-C bending (in LCC or lignin)	8
	1063	×	-	• C-O stretching	11
	1198	-	×	• O-C-H, C-C-H, C-O-H bending	8
	1225	×	×	• in-plane deformation of OH and COOH	14
	1240	×	×	• Ring stretching	8
	1614	-	×	• C=O stretching (in Ac)	14
	1633	-	×	• See galactose	
	1691	-	×	• C=O stretching (in Ac)	8
	1753	-	-	• C=O stretching (in lignin)	8
	1784	-	-	• C=O stretching (in Ac)	8

LCC; lignin carbohydrate complex, Ac, acetyl group, ×; present, -; not present

TABLE 5
Possible Assignment of Important Frequencies in the Calibration Models and Their Presence in Standards for Arabinose and Mannose

Sugar	Raman Shift cm^{-1}	Arabinose	Arabino-galactan	Assignment	Ref.
Arabinose	118	-	×	• See galactose	
	758	-	-	• Ring vibration (in lignin)	8
	935	×	×	• C-O stretching	11
	962	-	×	• C-H bending	8
	1128	×	×	• Asymmetric in-phase ring stretching	12
	1140	×	×	• C-O stretching	11
	1317	-	×	• In-plane C-H deformation	8
				• CH_2 wagging	11
	1329	×	×	• CH deformation	8
	1583	-	×	• Asymmetric C-O stretching	8
1630	-	-	• C=O stretching in cinnamic acids (in LCC)	10	
Sugar	Raman Shift cm^{-1}	Mannose	Glucoman-nan	Assignment	Ref.
Mannose	785	-	×	• See xylose	
	935	-	-	• See arabinose	
	955	×	×	• C-H bending	8
	962	×	-	• C-H bending	8
	1063	-	×	• See rhamnose	
	1066	-	×	• C-O stretching	11
	1171	-	×	• Acetylated C-O stretching	8
	1522	-	×	• C=C skeletal in-plane (in LCC)	8
	1599	-	×	• See xylose	
	1630	-	×	• See rhamnose	

LCC; lignin carbohydrate complex, ×; present, -; not present

arabinose and mannose, and glucomanan, arabinogalactan and xylan. Since rhamnose is a part of the xylan in the species utilized,⁷ xylan was used as its standard. Table 6 shows the correlations between sugars in the calibration data sets.

Many of the important frequencies obtained for each sugar were also present in the standards as shown in Tables 3-5. The 2nd derivatives form of the spectra was

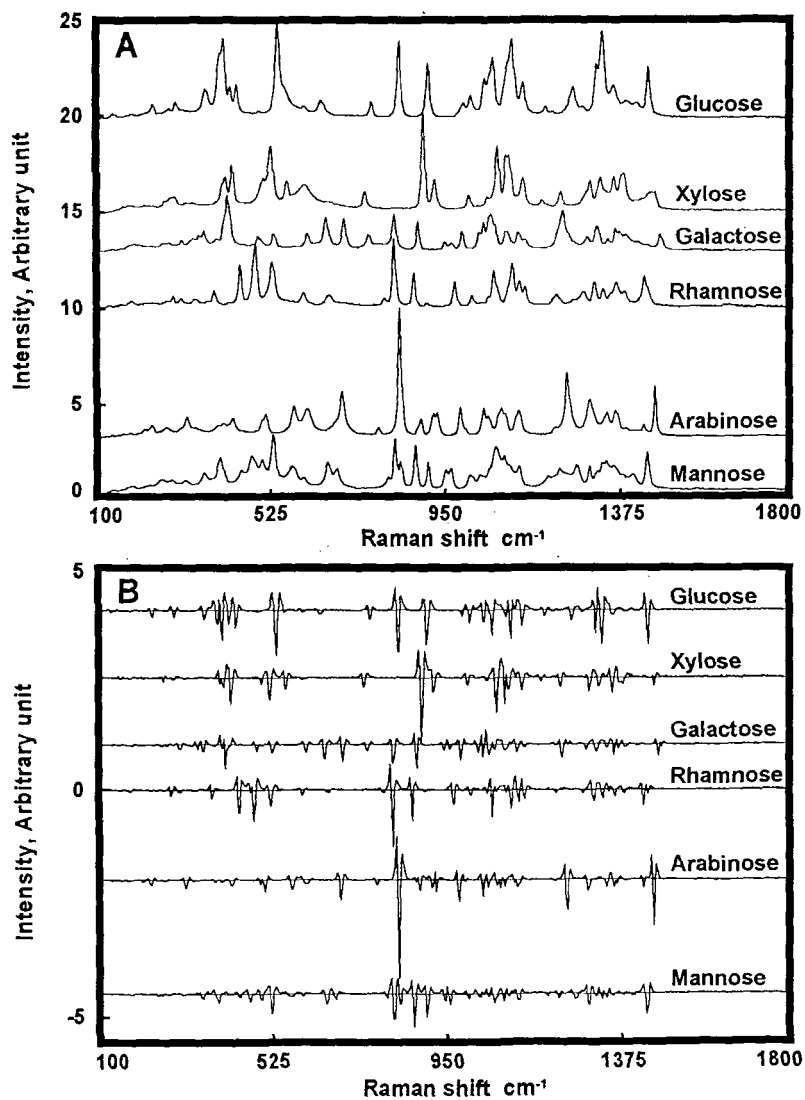


FIGURE 2. Normal FT-Raman spectra (A) and its 2nd derivatives form (B) of monosaccharide standards.

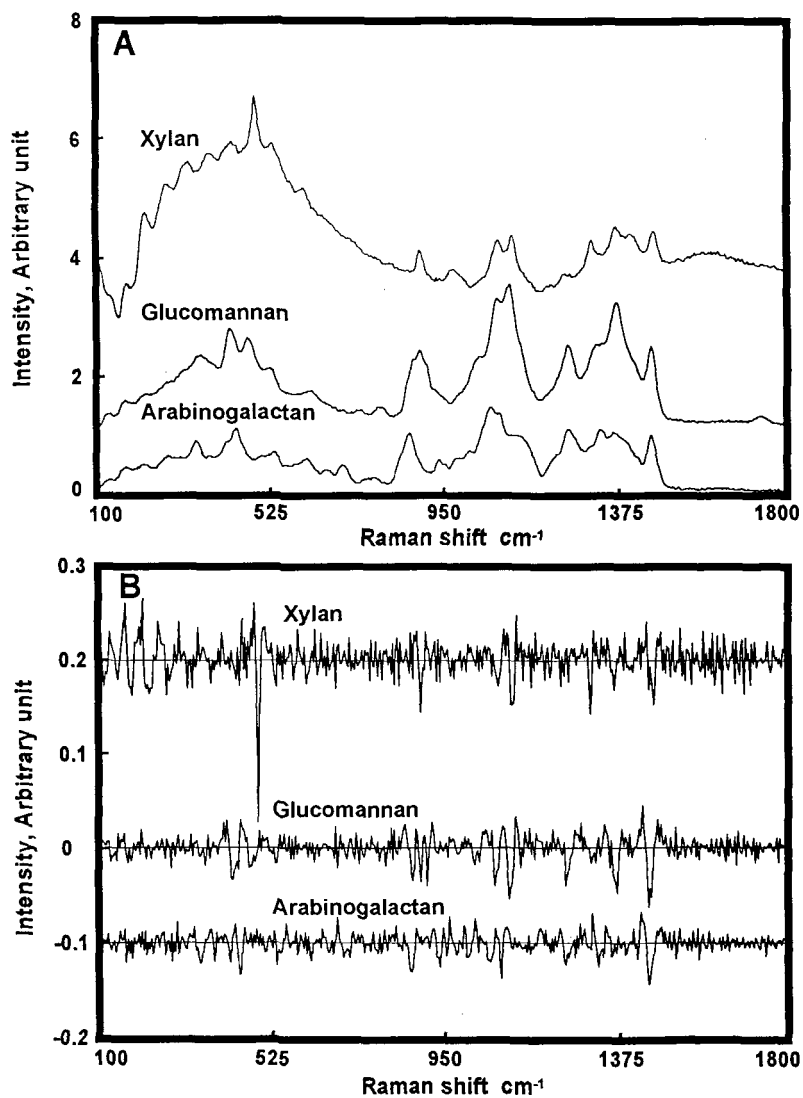


FIGURE 3. Normal FT-Raman spectra and its 2nd derivatives form (B) of polysaccharides (hemicellulose) standards.

TABLE 6
Correlations between Sugars in the Calibration Data Sets

	Glucose mol%	Xylose mol%	Galactose mol%	Rhamnose mol%	Arabinose mol%	Mannose mol%
Glucose mol%	—					
Xylose mol%	*** -0.492	—				
Galactose mol%	0.065	*** -0.827	—			
Rhamnose mol%	-0.104	*** 0.467	*** -0.518	—		
Arabinose mol%	*** 0.468	*** -0.601	0.172	** -0.275	—	
Mannose mol%	** 0.273	*** -0.377	-0.061	0.030	*** 0.571	—
Holocellulose %	0.016	0.110	-0.111	** 0.274	-0.196	0.032
α -Cellulose %	0.065	0.121	-0.114	** 0.272	-0.218	-0.047
Hemicellulose %	-0.105	-0.014	-0.004	0.033	0.027	0.174
Lignin %	* 0.262	*** -0.597	*** 0.564	*** -0.410	*** 0.484	*** -0.081
Extractives %	-0.098	0.087	-0.066	-0.204	0.027	-0.025
Alkali- extractives%	* -0.231	*** 0.509	*** -0.464	*** 0.363	** -0.332	-0.057
Total- extractives%	-0.213	*** 0.347	** -0.303	-0.004	-0.147	-0.054

*** Significant at 1% level of analysis of variance (ANOVA), ** Significant at 5% level of ANOVA, * Significant at 10% level of ANOVA

used to assign them. However, some frequencies such as 1695 cm^{-1} (galactose) and 758 cm^{-1} (arabinose) were derived from the correlations between the sugars (Table 6), and those frequencies not observed in the standards such as 1603 cm^{-1} (glucose) and 1633 cm^{-1} (galactose) are possibly from the lignin carbohydrate complex (LCC). For all sugars, there were many frequencies present in the corresponding polysaccharides (hemicellulose) spectrum that were not present in the monosaccharide spectrum. This may be due to the disappearance in the monosaccharide spectrum of many intrinsic peaks caused by the vibrational restriction inside and outside the pyranose unit, such as C-H bending and C-O stretching, in corresponding polysaccharides (Figures 2 and 3).

Figure 4 and Table 7 show the prediction (validation) of each sugar for unknown samples using Raman spectroscopy calibration models obtained with known samples.

For all sugars, except rhamnose and mannose, highly significant correlations were obtained between wet chemical and Raman predicted values using samples of two *Eucalyptus* species, including various ages and colors. Since the rhamnose of hemicellulose is generally less than 1%, it has a negligible effect on pulp and paper properties.³ The mannose content can also be calculated from the predicted data of all the other sugars. Consequently, the non-destructive FT-Raman spectroscopic method has proved its validity for determining the hemicellulosic neutral sugar composition of *Eucalyptus* native wood meal samples, regardless of their age and color.

Elite tree selection can be performed using FT-Raman spectroscopy for the quality aspects that will reduce the cost of pulp and paper products and reduce 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 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.³ Commercially available glucose, xylose, galactose, rhamnose, arabinose and mannose, and glucomannan from Konjaku (Wako Pure Chemical Industries, Osaka, Japan or Tokyo Chemical Industry, Tokyo, Japan),

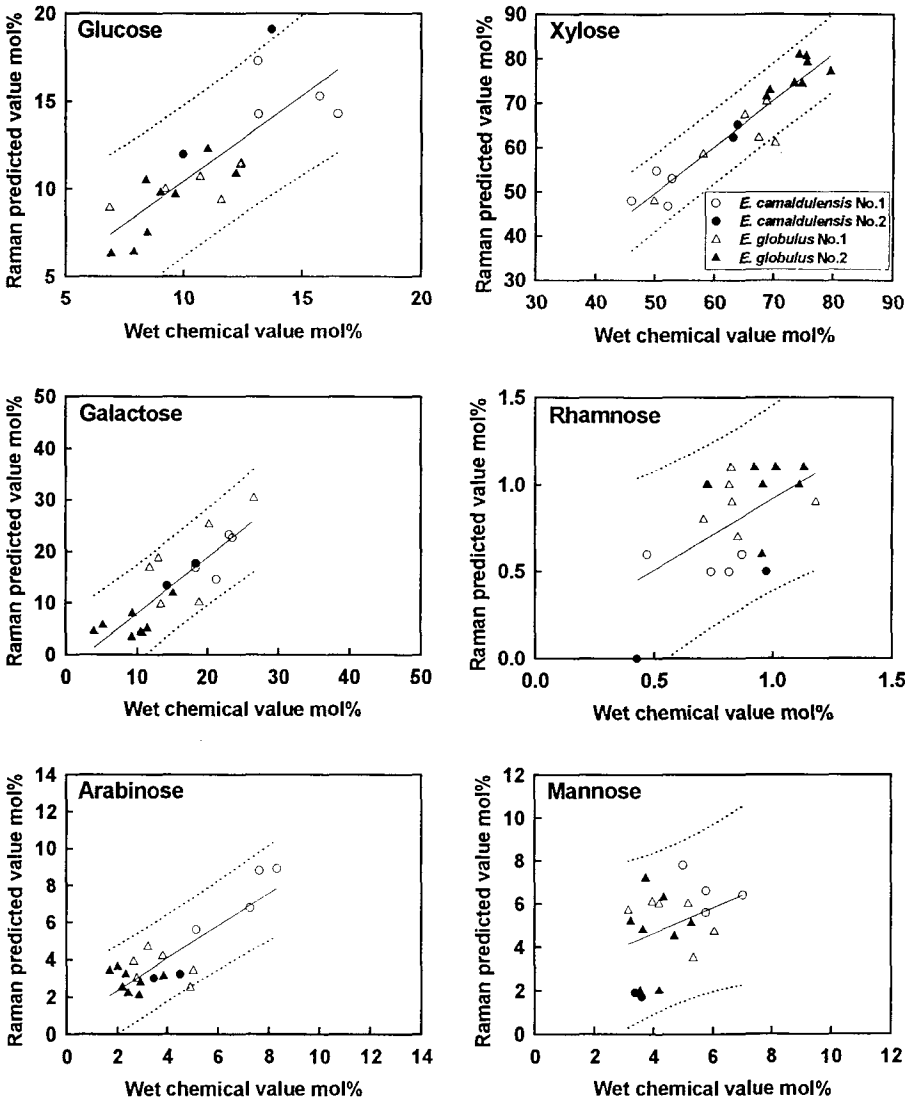


FIGURE 4. Plots of FT-Raman prediction (for unknown samples) against the hemicellulosic neutral sugar composition. The 95% confidence contours are represented by dashed lines.

TABLE 7
Statistical Result in Prediction

Sugar	r	SEP
Glucose	0.800	2.0
Xylose	0.939	3.9
Galactose	0.844	4.3
Rhamnose	0.545	0.2
Arabinose	0.840	1.1
Mannose	0.347	1.8

r; correlation coefficients, SEP; standard error of prediction

arabinogalactan from larch and xylan from birch (Sigma, St. Louis, USA) were used as standards for neutral sugar analysis.

Wet chemical method

Hemicellulosic neutral sugars, namely glucose, xylose, galactose, rhamnose, arabinose and mannose, were determined by hydrolysis of holocellulose with trifluoroacetic acid and high performance liquid chromatography.¹⁵ The sugar composition was expressed as mol%. The correlations between hemicellulosic neutral sugars and other wood constituents were calculated by ANOVA using the software SPSS (SPSS Inc., IL, USA).

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) and standards were packed into NMR tubes and spectra were collected using 180° backscattering at 500 mW, 4 cm⁻¹ resolution and 256 scans.¹ 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 hemicellulosic neutral sugar composition using the software of Unscrambler 6.0 (Camo AS, Trondheim, Norway). A total of 55 wood samples for calibration (known samples) and 20 for prediction (unknown samples) were selected randomly.

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