A Preliminary Study of Preservative Retention and Penetration in ACQ-Treated Timbers Using Near Infrared Spectroscopy

Chi-Leung So, Thomas L. Eberhardt, Stan T. Lebow, and Leslie H. Groom

Abstract

Near infrared (NIR) spectroscopy has been previously used in our laboratory to predict copper, chromium, and arsenic levels in samples of chromated copper arsenate (CCA)-treated wood. In the present study, we utilized our custom-made NIR scanning system, NIRVANA (near infrared visual and automated numerical analysis), to scan cross sections of ACQ (alkaline copper quat)-treated timbers to assess whether this technology can be used as a quality control tool for wood treaters. Models for CuO retention were created using ACQ-treated and untreated southern yellow pine (SYP) wood blocks. Strong correlations were obtained between the CuO retentions predicted by NIR and those based on elemental analysis. NIRVANA was then utilized for automated spectra collection from ACQ-treated SYP timbers. The resultant plots showed both the variation of CuO retention and the preservative penetration depth along the specimens from the pith to the timber surface. NIRVANA appears to be ideally suited to the assessment of ACQ-treated timber providing both rapid and detailed analysis of the preservative treatment applied to the timber. This preliminary study will be extended to other preservative components (e.g., organic co-biocides), in which the preservative penetration and concentration cannot be readily assessed.

Introduction

When wood is treated with preservatives, there are minimum standards that the wood treater must adhere to for quality control. In the United States, these are provided by the American Wood-Preservers' Association (AWPA). The standard method for determining copper retention in ACQ (alkaline copper quat)-treated timber consists of grinding up core samples taken from each charge and analyzing them using elemental analysis (AWPA 2005a). In addition to determining the retention, the depth of penetration is also of great importance. This traditionally involves spraying wood cores with a chrome azurol-S solution and visually assessing for a deep blue coloration indicative of the presence of copper (AWPA 2005b).

Near infrared spectroscopy (NIR), in particular, NIRVANA (near infrared visual and automated numerical analysis), may be ideally suited to the determination of preservative retention across a sample of treated timber. It has been previously used in our laboratory to predict copper. chromium, and arsenic levels in samples of chromated copper arsenate (CCA)-treated wood (So et al. 2004). In the same study, it was possible to distinguish between various preservative treatments applied to wood, including CCA and ACQ (So et al. 2004). NIRVANA was originally developed to be used as a rapid assessment tool in tree improvement programs. Genetic and silvicultural

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studies often require large-scale sampling of trees, in which an increment core is extracted and measurements of density and growth rate are determined. NIRVANA is designed for the automated property assessment of increment cores, in which the variation of a range of properties can be predicted along a core based on the NIR spectra (So et al. 2006). We were interested in determining whether this technology could be extended to examine the radial variation of preservative retention in a timber cross section.

Experimental Procedure

Fourteen small blocks of ACQ-treated and untreated southern yellow pine (SYP) wood were provided for the calibration samples. The CuO retention values for these samples were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Commercial (6 in. by 6 in. by 8 ft) ACQ-treated SYP timbers were selected at a local lumberyard for spectral mapping. Slices of 1 in. were cut from the center of each timber. Cross sections exposing the radial penetration of the preservative were selected for NIR analysis.

NIR

NIR spectra were collected using an ASD FieldSpec Pro FR spectrometer (Analytical Spectral Devices, Boulder, CO). The sampling area at the sample surface was approximately a 4 mm spot. Spectra collected at wavelengths between 400 nm and 2500 nm. This was achieved using a fiber optic probe oriented perpendicular to the sample surface that was illuminated with a DC lamp oriented at 30° to the sample surface. Two spectra were recorded for each of the wood blocks used for calibration. Spectral mapping of the treated timber was performed using the NIRVANA system. Timber specimens were positioned using a Newport motorized stage (Newport, Irvine, CA) while the spectra were collected at 2-mm intervals along the length of each specimen.

Multivariate Analysis

Multivariate analysis of the data was performed using the Unscrambler (version 8) software (CAMO, Corvallis, OR). Multiplicative scatter correction (MSC) was applied to the NIR spectra, followed by wavelength reduction to 10-nm spacing. The NIR spectra for the calibration specimens were also averaged to one spectrum per sample. Partial least squares (PLS) analysis was performed on the calibration spectra and calibration models were generated using full cross validation (Martens and Naes 1991). The number of principal components (or factors) employed was limited to three due to the low number of samples in the calibration set. Models were assessed using several common measures of calibration performance. The correlation coefficient (R^2) is a measure of the strength of the fit to the data, and the root mean square error of calibration (RMSEC) is a measure of the calibration error in the fit, and is often expressed as a percentage of the mean value of interest (%RMSEC of mean). MSC and wavelength reduction was also applied to the spectra from the timber cross sections. The CuO retention values were predicted for the spectra using the models built from the calibration specimens.

Results and Discussion

Determining the variation of preservative retention along cross sections of a treated timber requires the generation of calibration models for preservative components of interest (e.g., CuO retention). Models for CuO retention were built using small, laboratory-generated ACQ-treated and untreated SYP wood blocks. PLS regression was performed on the NIR data obtained from these blocks using the ICP-OES results. The calibration set consisted of only 14 specimens, and thus modeling was limited to only three factors or less. The effect of wavelength region was investigated utilizing the full range (400 to 2500 nm), visible region (400 to 700 nm), and the NIR region (1000 to 2500 nm). The correlations appeared to be strong between the preservative retentions predicted by this technique and those based on the ICP-OES results. **Figure 1** shows the calibration for the 400 to 2500 nm region, resulting in a R^2 value of 0.93. The visible and NIR regions gave similar R^2 values of 0.81 and 0.94, respectively **(Table 1).** The values of %RMSEC of mean provide an indication of the calibration error in the fit, with higher values indicative of greater calibration error. These values were similar to those obtained for CuO, CrO_3, and As_2O_5 retentions in an earlier paper (So et al. 2004) even considering the low number of calibration specimens. The higher value for the visible region was due to the low number of factors employed.

NIRVANA was utilized for the automated spectral mapping of ACQ-treated SYP timber cross sections. Two

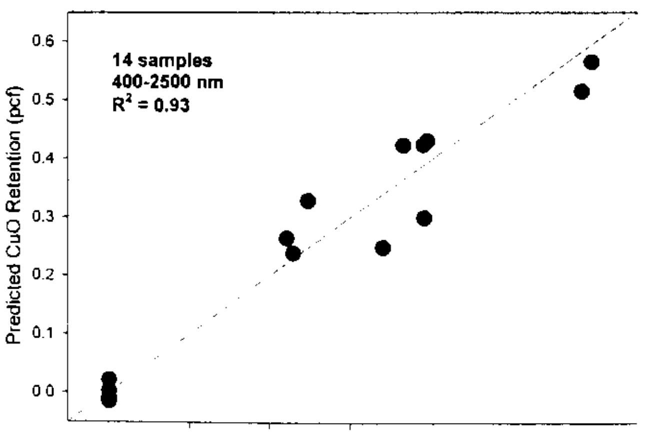

Figure 1. – *Relationship between predicted vs. measured CuO retention in the 400 to 2500 nm region.*

Table 1. – *Regression statistics for predictions of CuO retention from PLS modeling.*

Wavelength range	No. of factors	R^2	RMSEC	%RMSEC of mean
(nm)				(%)
Full (400 to 2500)	3	0.93	0.051	19
Visible (400 to 700)	1	0.81	0.086	32
NIR (1000 to 2500)	3	0.94	0.048	18

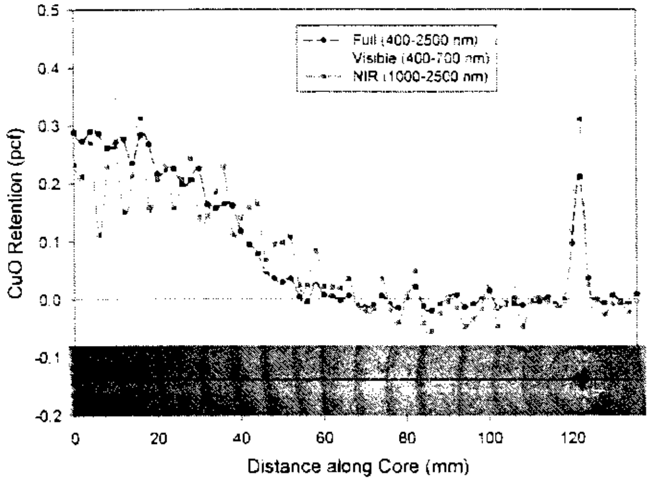

Figure 2. – *Variation of CuO retention and preservative penetration depth in a timber from a fast-growth SYP tree with no obvious heartwood formation.*

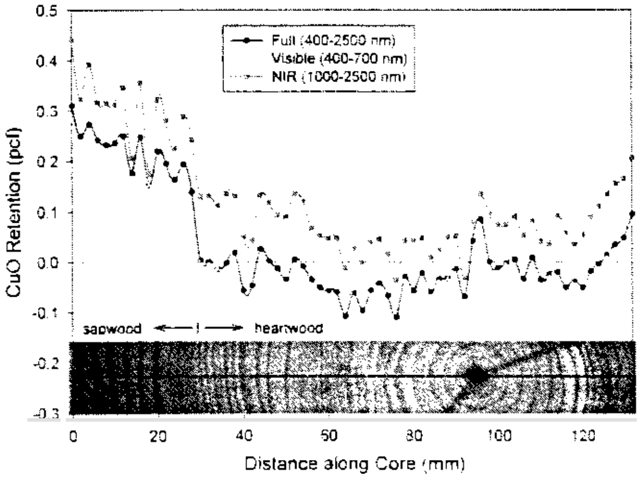

Figure 3. – *Variation of CuO retention and preservative penetration depth in a timber from a slow-growth SYP tree showing an abrupt heartwood/sapwood transition.*

samples were chosen for analysis: one from a fast-growth tree with widely-spaced growth rings, exhibiting no obvious heartwood formation: and the other from a slow-growth tree with narrow rings showing a fairly abrupt heartwood/sapwood transition. The spectra were collected and CuO retention values predicted using the models previously mentioned. The resultant plots for the fast-growth and slow-growth samples are shown in **Figures 2 and 3,** respectively. These show the variation of CuO retention and preservative penetration depth along timber cross sections between the pith and timber surface. The scan lines are displayed as dashed lines on each image. The scattered nature of the plots is primarily due to the earlywood and latewood bands; this is particularly evident with the widely spaced rings in **Figure 2.** It may be preferable to apply an 'average' line for the analysis of the trends. Nevertheless, it can be clearly observed in **Figure 2** that above 80 mm, there is no preservative penetration (i.e., 0 pcf). The effect of the preservative becomes apparent below 80 mm, in which the CuO retention continues to steadily increase to a maximum at the timber surface (0 mm). The spikes in **Figures 2 and 3** clearly show the position of the pith and can be used as a reference point to verify sample alignment. An important point to note is that this technique cannot be considered a measure of color since the CuO is detected outside the visible region in the 1000 to 2500 nm plots. **Figure 3** shows the effect of a heartwood/sapwood transition on the preservative distribution. CuO retention is at a maximum value at the timber surface. It steadily decreases as it penetrates further into the sapwood, until it reaches the heartwood transition (at approximately 30 mm), at which minimal penetration occurs and the CuO retention abruptly drops to a value of 0 pcf. The variation of the data points in the heartwood region may be attributed to the presence of narrow growth rings.

Conclusions

These preliminary results show the suitability of NIR-VANA for quality control assessments of ACQ-treated lumber by providing both rapid and detailed analysis of both the preservative retention and depth of penetration. This preliminary study needs further model refinement by using additional calibration samples with a complete range of preservative retentions. This will also be extended to other preservative components (e.g., organic co-biocides), in which the preservative penetration and concentration cannot be readily assessed.

Acknowledgments

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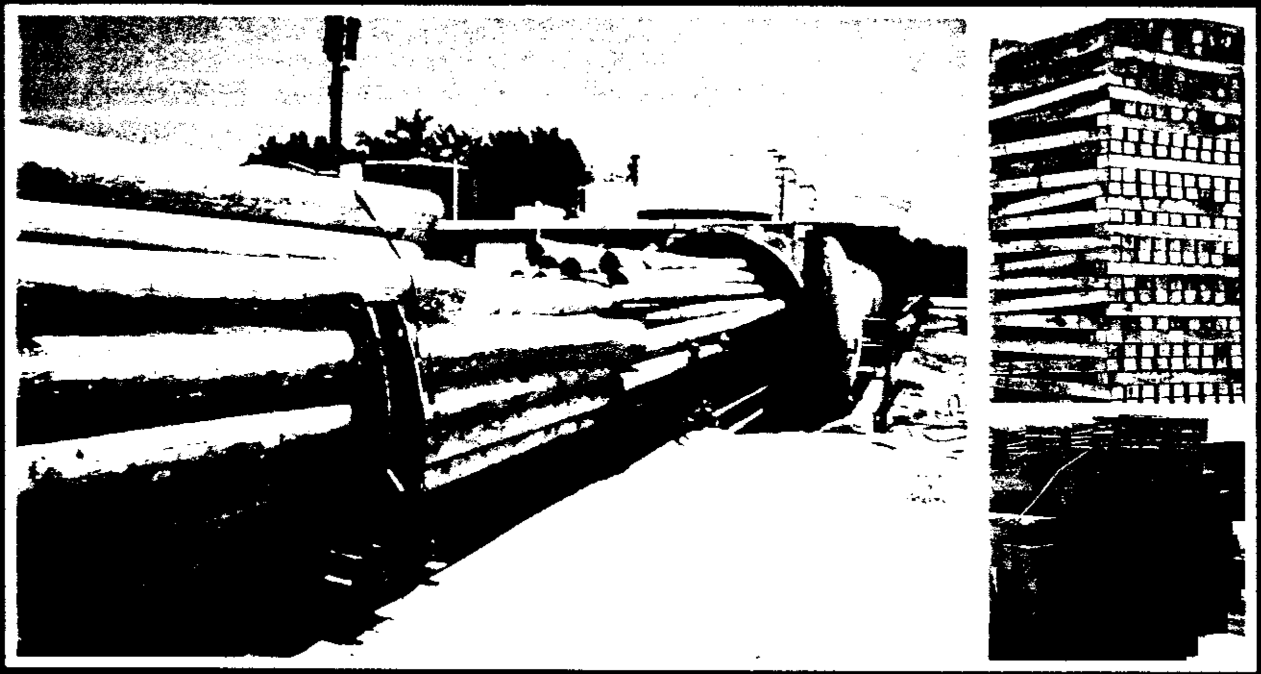

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