THE APPLICATION OF NEAR INFRARED (NIR) SPECTROSCOPY TO INORGANIC PRESERVATIVE-TREATED WOOD

Chi-Leung So†

Postdoctoral Researcher
School of Renewable Natural Resources
LSU Agricultural Center
Baton Rouge, LA 70803

Stan T. Lebow†

Research Forest Products Technologist
USDA-Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, WI 53562

Leslie H. Groom†

Project Leader
USDA-Forest Service
Southern Research Station
2500 Shreveport Highway
Pineville, LA 71360

and

Timothy G. Rials†

Director
Tennessee Forest Products Center
University of Tennessee
2506 Jacob Drive
Knoxville, TN 37996

(Received July 2003)

ABSTRACT

There is a growing need to find a rapid, inexpensive, and reliable method to distinguish between treated and untreated waste wood. This paper evaluates the ability of near infrared (NIR) spectroscopy with multivariate analysis (MVA) to distinguish preservative types and retentions. It is demonstrated that principal component analysis (PCA) can differentiate lumber treated with CCA, ACZA, or ACQ preservatives. Furthermore, separation according to wood species and assay zone was also observed. Within the range of preservative concentrations available, partial least squares (PLS) regression was also performed on the NIR data, from which retention levels were predicted. The results highlight the potential for this technique to predict the concentration, as well as identify the type, of inorganic preservatives present.

Keywords: Near infrared spectroscopy, multivariate analysis, preservative-treated wood.

† Member of SWST.

Wood and Fiber Science, 36(3), 2004, pp. 329–336
© 2004 by the Society of Wood Science and Technology

INTRODUCTION

The use of preservative-treated wood for the construction of decks, fences, and other residential applications has greatly increased during the last two decades. The primary preservative for residential applications has been chromated copper arsenate (CCA), but other preservatives such as ammoniacal copper zinc arsenate (ACZA), alkaline copper quat (ACQ), and copper boron azole (CBA) have also been used. In February 2002, the EPA announced a decision by wood preservative manufacturers to voluntarily phase out the use of CCA for virtually all residential applications by the end of 2003 (EPA 2002). This has led to the copper: organic mixtures such as ACQ and CBA becoming the favored replacements in residential applications. When treated wood is removed from service, it is often mixed with construction and demolition (C&D) waste that also contains untreated wood. Once it has weathered or been painted, it is difficult for the homeowner, contractor, or local solid waste facility to visually differentiate the treated from the untreated wood. This causes problems in the waste stream, because wood that contains preservatives often cannot be processed in the same manner as untreated wood. The obvious example is the disposal of CCA-treated wood with strict guidelines to minimize the presence of arsenic in the waste stream.

The need for sorting technologies to distinguish between CCA- and non-CCA-treated waste wood has only become greater after the recent CCA announcement. Blassino undertook a large feasibility study in Florida into on-line sorting technology for CCA-treated wood (Blassino et al. 2002). Detectors based on laser-induced breakdown spectroscopy (LIBS) and X-ray fluorescence (XRF) spectroscopy were able to quickly and accurately differentiate CCA-treated wood from untreated wood in the C&D wood waste stream. This has led to the proposed installation of such a system at a C&D recycling facility for full-scale testing. However, these methods have limited potential for detecting organic wood preservatives. Rapid detection methods for organic preservatives have also been studied. One such study (Schroder et al. 1998) involved the use of ion mobility spectrometry (IMS) in which a battery-powered IMS device coupled with a thermal desorption chamber analyzed small pieces of treated wood. The technique was cheaper and faster than portable gas chromatography (GC) systems equipped with thermal desorption injection devices. However, all the aforementioned techniques are destructive.

A method is needed for the rapid, inexpensive, and reliable identification of wood that has been treated with inorganic and/or organic preservatives. One possible method is near infrared (NIR) spectroscopy with multivariate analysis (MVA). This has the potential for detecting and distinguishing wood treated with both organic and inorganic preservatives, and can be installed on-line at a waste wood sorting facility or used in the field with a hand-held spectrometer. This is becoming a popular technique for the study of the properties of wood and its fibers ranging from investigating clearwood properties (Hoffmeyer and Pedersen 1995; Thumm and Meder 2001; Schimleck et al. 2001) to wood composites such as medium density fiberboard (Rials et al. 2002) and on-line particleboard manufacture (Engstrom et al. 1998). It is already established in the pulp and paper field and used to predict pulp yield and cellulose content (Wright et al. 1990; Wallbacks et al. 1991a; Michell 1995). Principal component analysis (PCA) of NIR spectra has been successfully applied to the study of pulp characteristics and processes (Wallbacks et al. 1991b) as well as the classification of various wood species (Schimleck et al. 1996). In the latter study, PCA was used to discriminate between pines and eucalypts, and different classes of eucalypts, based on the NIR spectra of the ground woods. Although there has been much research into the classification and prediction of chemical properties, little has been published with regards to wood preservatives. One paper (Feldhoff et al. 1998) used NIR for the detection of inorganic preservatives in timber. However, no multivariate analytical methods were applied, and preservative identification was based purely on differences in absorption from certain peaks in the spectra.

MATERIALS AND METHODS

Several commercially treated deck boards of the Hemlock-Fir (Hem-Fir) species group; Eastern Hemlock (*Tsuga canadensis*), and Douglas-fir (*Pseudotsuga menziesii*) were obtained for this study with the following preservative/wood species combinations: CCA/Hem-Fir (CCAHF); CCA/Eastern Hemlock (CCAEH); ACZA/Douglas-fir (ACZA) and ACQ/Hem-Fir (ACQ). Although southern pine is the species group most often treated with preservatives, we chose to utilize species that are more difficult to treat with the assumption that they would provide a greater range of preservative concentrations within the wood. The CCA treatment solution was Type C, which is composed of 47.5% CrO_3, 34.0% As_2O_5, and 18.5% CuO. The ACZA treatment solution contained 50.0% CuO, 25% ZnO, and 25.0% As_2O_5. The ACQ was a Type B formulation containing 66% CuO and 33% quaternary ammonium compound (didecyldimethylammonium chloride). CCA treatment solutions are acidic, while ACQ and ACZA solutions are alkaline. The ACQ and ACZA solutions also contained ammonia and ammonium bicarbonate. The deck boards were not exposed to weathering. Each treated deck board was cut into shorter boards of approximately 4- × 14- × 12.5-mm dimensions, which were allowed to equilibrate to constant moisture content in a room maintained at 22°C and 65% relative humidity. Sections of wood were then removed from the outer (0–5-mm) and inner (5–15-mm) assay zones and milled to pass through a Wiley mill 30-mesh screen. The number of samples in each set is shown in Table 1. All samples were analyzed for copper, chromium, zinc, and arsenic using a standard laboratory method of digestion followed by atomic absorption spectroscopy analysis of the resulting liquid (AWPA 1995).

TABLE 1. *Summary description of sample sets.*

Sample Set	No. of Samples	Constituents and Wood Species
	165	CCAHF, ACQ, ACZA, CCAEH
CCA	85	CCAHF, CCAEH
Hem-Fir	80	CCAHF, ACQ
CCA Hem-Fir	40	CCAHF
ACQ Hem-Fir	40	ACQ
ACZA Doug Fir	40	ACZA
CCA East Hemlock	45	CCAEH

Near infrared spectroscopy.—The NIR measurements were made using a Nexus model 670 FTIR spectrometer (Thermo Nicolet Instruments, Madison, WI) at 1-nm intervals between 1000–2500 nm. The NIR spectra were collected by embedding a fiber optic probe into a bag of the milled sample. Forty scans were collected and averaged into a single spectrum. Two spectra were recorded for each sample at different locations within the mixture.

Multivariate analysis.—Multivariate analysis of the data was performed using the Unscrambler (vsn. 7.5) software, CAMO, Corvallis, OR. The NIR data were first averaged to one spectrum per sample and reduced to 10-nm wavelength spacing. Multiplicative scatter correction (MSC) was applied to the data prior to analysis. Principal component analysis (PCA) was used to observe any clustering and/or separation in the sample sets. For partial least squares (PLS) analysis, two thirds of each sample set was used for calibration to create the model and the rest used to validate the model. The number of principal components (factors) used for the models was selected by observing the response of the residual Y-variance to added factors as described earlier (Rials et al. 2002). Models were gener-

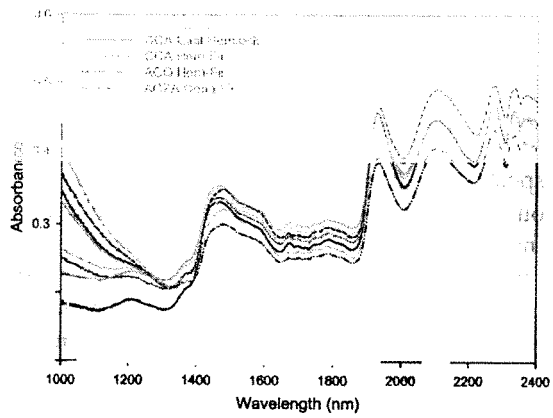


FIG. 1. Comparison of near infrared spectra collected from treated samples; MSC-corrected spectra appear in gray.

ated using full cross validation, in which one sample is systematically removed from the data set, a model is created from the remaining samples, and this model is used to predict a value for the extracted sample. This process is subsequently repeated for all remaining samples (Martens and Naes 1991). A summary description of the PLS technique can be found in an earlier paper (Rials et al. 2002) while a complete description of MVA can be found elsewhere (Martens and Naes 1991; Massart et al. 1998).

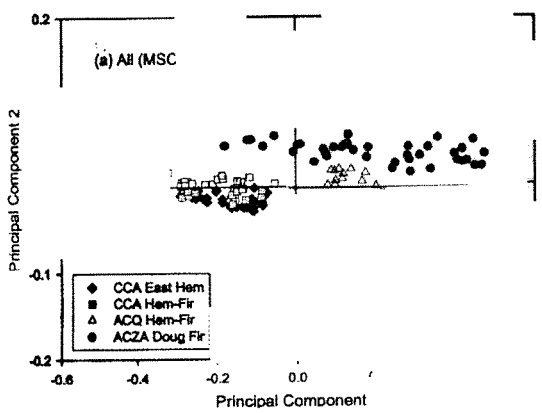
RESULTS AND DISCUSSION

The samples exhibited a range of colors both between and within sample sets, relating to their preservative type, wood species, and preservative concentration. However, the wavelength range for the NIR spectra collection was 1000–2400 nm to avoid the low wavelength visible region, thus minimizing masking of information within the NIR region. Two NIR spectra were collected for each sample in the NIR region, Figure 1 shows a typical spectrum from each of the sample sets. The spectra appear to be very similar except at lower wavelengths (closer to the visible region). A few major peaks to note include the first overtone of the cellulose hydroxyls (1400–1660 nm) overlapping with the first overtone of the lignin hydroxyl vibrations (1400–1520 nm), and the peak range between 1890–2020 nm assigned to the interactions with cellulose hydroxyls and water. A detailed assignment of the various vibrations can be found in the literature (Martens and Naes 1991; Fourty et al. 1996; Curran et al. 1992).

Multiplicative scatter correction (MSC) was applied to the spectra, and these corresponding spectra are shown in gray. MSC has been previously used to remove the effects of light scattering variation in the NIR spectra of milled Scots pine needles (Hiukka 1998). The report indicated that the MSC-corrected models generally gave better results, and required fewer principal components, than the non-scatter-corrected models. The MSC-corrected spectra reduce the scatter by removing the additive and multiplicative effects (Martens and Naes 1991); this is particularly evident in the region above 1900 nm.

Differences between the spectra in Fig. 1 cannot be readily quantified; however, the application of multivariate analysis to the spectral data allows hidden relationships and/or differences to be revealed. Principal component analysis (PCA) was performed on the combinations of sample sets shown in Table 1. Figure 2a shows the scores plot resulting from the complete sample set. Although there is some overlap, clusters are clearly evident, showing that the three preservative treatments were readily identifiable. The spectra were then broken down into a CCA sample set (East Hemlock and Hem-Fir species) and a Hem-Fir sample set (CCA- and ACQ-treatments) to enhance the differences observed in Fig. 2a. The scores plot for the CCA samples showed separation between the CCA Eastern Hemlock and CCA Hem-Fir samples, which was obscured in Fig. 2a. This shows that PCA can still distinguish between these species even when the same preservative treatments have been applied to them. In the case of the Hem-Fir samples, the magnitude of the separation between the ACQ and CCA treatments was much larger than that observed with the two CCA sample sets, indicating that the type of treatment has a greater influence than the species in the sample separation. The same PCA scores plot is shown in Fig. 2b when no multiplicative scatter correction (MSC) has been applied. Although clusters can be observed, there is clear overlap between the sample sets.

Further analyses were performed on the four individual sample sets with MSC. Clustering was again evident, but this time, based on assay zone location. Figure 3 is a PCA scores map for CCA Eastern Hemlock, in which the samples separated according to assay zone location; core, inner, and outer assay zone. This trend was also noted in the other sample sets. The inner and outer assay zones differ in terms of their treatment level; the inner assay zones generally have lower levels of preservative due to the depth of penetration. This was observed in the atomic absorption spectroscopy results, in which there was a range of high retentions associated with the outer assay zone and a range of lower ones with



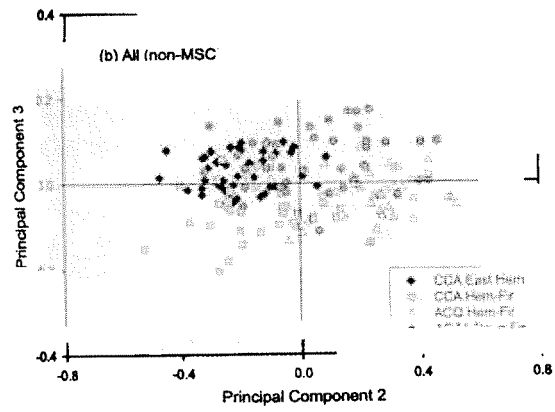


FIG. 2. Principal component analysis from NIR spectra collected for All sample set (a) MSC and (b) non-MSC.

TABLE 2. *Various preservative retention statistics for selected sample sets.*

Retention Statistic	Retention Value (pcf)			
	All (CuO)	CCA-C (CuO)	CCA-C (CrO_3)	CCA-C (As_2O_5)
Mean	0.244	0.060	0.141	0.113
Median	0.123	0.057	0.120	0.085
Mode	0.016	0.016	0.039	0.057
Minimum	0.003	0.003	0.003	0.006
Maximum	1.088	0.183	0.405	0.336
Standard Deviation	0.232	0.045	0.123	0.096

was only one retention type present. The results of the PLS-1 regression on the All sample set are shown in Fig. 4, showing a good relationship between experimentally determined CuO retentions and that predicted by NIR, with the equivalence line representing the idealized relationship. The correlation coefficient (r^2) was very high at 0.98 using only five principal components (Table 3). A PLS-2 regression on the CCA samples produced similarly high correlations, with Figs. 5a–c showing the predictions for CuO, CrO_3, and As_2O_5 retentions, respectively. The high r^2 values for the CCA regression were obtained using only 2 factors (Table 3). The non-MSC regression values in Table 3 are generally poorer than their MSC equivalents or require more factors. This is particularly evident

the inner assay zone. A summary of retention values from the atomic absorption spectroscopy is shown in Table 2 for selected sample sets and has not been further disseminated into assay zones; thus a large range of values and the high standard deviations were obtained.

Partial least squares (PLS) regression was undertaken to predict the values of preservative retention for the samples. Table 2 shows the summary statistics of the atomic absorption results for a few sample sets used in the analysis. PLS-2 regression was carried out on the CCA samples to predict the retentions of chromium, copper, and arsenic, active oxide bases, while PLS-1 was applied to the samples in which there

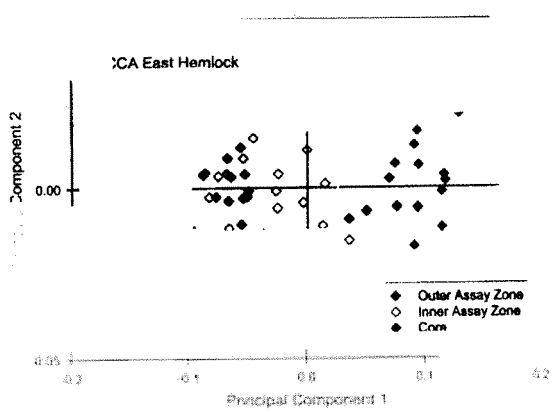


FIG. 3. Principal component analysis from NIR spectra collected for CCA East Hemlock sample set.

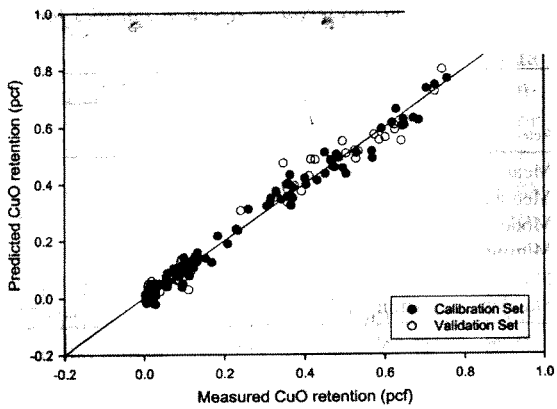


FIG. 4. Relationship between measured values of CuO retention and those predicted by PLS-1 modeling using NIR spectra for All samples.

for the All sample set in which the %RMSEP of the mean increases twofold from 15.6 to 33.2%.

A plot of the coefficients for the CCA regression is shown in Fig. 6. An interesting observation in the plot is that the peaks for the As_2O_5 and CrO_3 plots around 1950 nm correspond to a doublet trough for the CuO retention; this wavelength range (1890–2020 nm) arises from the cellulose hydroxyl–water interactions. PLS regression on the spectra has shown that the chemical features in the NIR spectra are important in the prediction of preservative content and may be related to the preservative treatment process.

TABLE 3. *Summary regression statistics for predictions of preservative retentions from PLS modeling both with and without MSC.*

			Regression Parameters			
Sample Set	MSC/ Non-MSC	Retention Type	No. of PCs		RMSEP	% RMSEP of mean
All[a]	MSC	CuO	5	0.98	0.038	15.6
CCA[b]		CuO	2	0.97	0.010	16.7
CCA[b]		CrO_3	2	0.93	0.029	20.6
CCA[b]		As_2O_5	2	0.86	0.027	23.9
All[a]	Non-MSC	CuO	5		0.081	33.2
CCA[b]		CuO	3		0.014	23.3
CCA[b]		CrO_3	3		0.034	24.1
CCA[b]		As_2O_5	3		0.030	26.5

[a]PLS-1 algorithm
[b]PLS-2 algorithm
RMSEP — Root Mean Square Error of Prediction

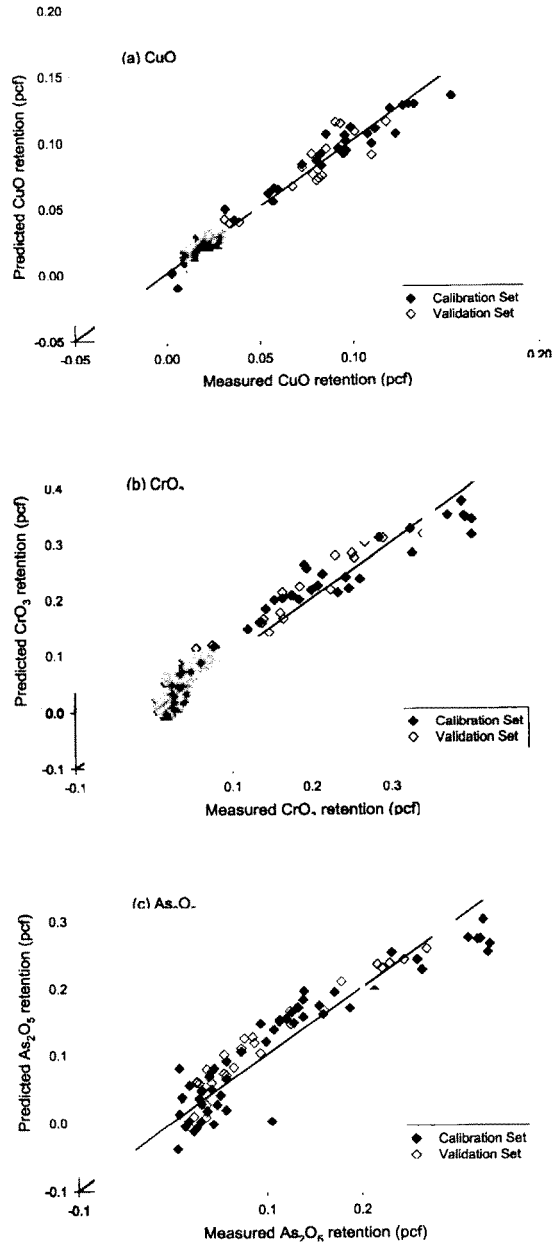


FIG. 5. Relationship between measured values of: (a) CuO, (b) CrO_3, and (c) As_2O_5 retentions and those predicted by PLS-2 modeling using NIR spectra for CCA samples.

CONCLUSIONS

The results of this evaluation clearly show that near infrared (NIR) spectroscopy, in conjunction with multivariate analysis, has great potential for

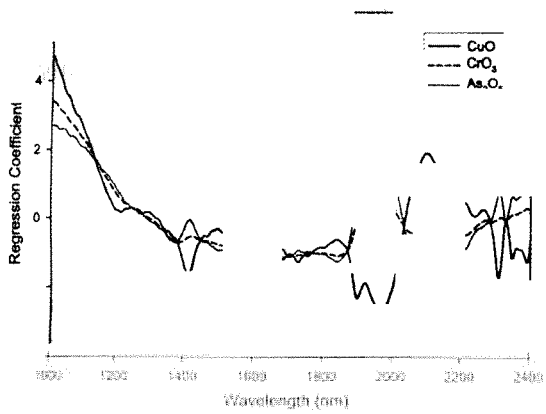


FIG. 6. Comparison of regression coefficients from PLS models for CuO, CrO_3, and As_2O_5 retentions.

identifying various inorganic preservative treatments applied to several species of wood. The results from the PLS regression provide very good correlations between the measured and NIR-predicted values such that the levels of arsenic, chromium, and copper may be estimated from an NIR scan of the sample. Early work with solvent-based organic preservatives has been equally promising, and work is continuing to evaluate the applicability of the technique to solid wood. NIR spectroscopy can be used in both field-portable and on-line applications, and appears to have potential for use in sorting and recycling of treated wood.

ACKNOWLEDGEMENT

The authors would like to thank Karen Reed for NIR spectral collection.

REFERENCES

AMERICAN WOOD PRESERVERS' ASSOCIATION (AWPA). 1995. A11-93 Standard method for the analysis of treated wood and treating solutions by atomic absorption spectroscopy. The AWPA Book of Standards. AWPA, Woodstock, MD.

BLASSINO, M., H. M. SOLO-GABRIELE, AND T. TOWNSEND. 2002. Sorting technologies for CCA-treated wood waste. Waste Management Res. 20:290–301.

CURRAN, P. J., J. L. DUNGAN, B. A. MACLER, S. E. PLUMMER, AND D. L. PETERSON. 1992. Reflectance spectroscopy of fresh whole leaves for the estimation of chemical concentration. Remot. Sens. Environ. 39:153–166.

ENGSTROM, B., B. JOHNSON, M. HEDQUIST, M. GROTHAGE, H. SUNDSTROM, AND A. ARLEBRANDT. 1998. Process modeling system for particleboard manufacturing, incorporating near infrared spectroscopy on dried wood particles. Pages 107–114 *in* Proc. Second European Panel Products Symposium, 21–22 October 1998, Llandudno, Wales.

ENVIRONMENTAL PROTECTION AGENCY (EPA). 2002. Notice of receipt of requests to cancel certain chromated copper arsenate (CCA) wood preservative products and amend to terminate certain uses of CCA products. Federal Register 67(36):8244–8246.

FELDHOFF, R., T. HUTH-FEHRE, AND K. CAMMANN. 1998. Detection of inorganic wood preservatives on timber by near infrared spectroscopy. J. Near Infrared Spectrosc. 6:A171–173.

FOURTY, T., F. BARET, S. JACQUEMOUD, G. SCHMUCK, AND J. VERDEBOUT. 1996. Leaf optical properties with explicit description of its biochemical composition: direct and inverse problems. Remot. Sens. Environ. 56:104–117.

HIUKKA, R. 1998. A multivariate approach to the analysis of pine needle samples using NIR. Chemom. Intell. Lab. Sys. 44:395–401.

HOFFMEYER, P., AND J. G. PEDERSEN. 1995. Evaluation of density and strength of Norway spruce wood by near infrared reflectance spectroscopy. Holz Roh-Werkst. 53:165–170.

MARTENS, H., AND T. NAES. 1991. Multivariate calibration. John Wiley, New York, NY. 419 pp.

MASSART, D. L., B. G. M. VANDEGINSTE, L. M. C. BUYDENS, S. DE JONG, P. J. LEWI, AND J. SMEYERS-VERBEKE. 1998. Handbook of chemometrics and qualimetrics: Part B. Elsevier, New York, NY, Pp. 158–160.

MICHELL, A. J. 1995. Pulpwood quality estimation by near-infrared spectroscopic measurements on eucalypt woods. Appita J. 48(6):425–428.

RIALS, T. G., S. S. KELLEY, AND C. SO. 2002. Use of advanced spectroscopic techniques for predicting the mechanical properties of wood composites. Wood Fiber Sci. 34(3):398–407.

SCHIMLECK, L. R., A. J. MICHELL, AND P. VINDEN. 1996. Eucalypt wood classification by NIR spectroscopy and principal component analysis. Appita J. 49(5):319–324.

———, R. EVANS, AND J. ILIC. 2001. Estimation of *Eucalyptus delagatensis* wood properties near infrared spectroscopy. Can. J. Forest Res. 49(5):319–324.

SCHRODER, W., G. MATZ, AND J. KUBLER. 1998. Fast detection of preservatives on waste wood with GC/MS, GC-ECD and ion mobility spectrometry. Field Anal. Chem. Tech. 2(5):287–297.

THUMM, A., AND R. MEDER. 2001. Stiffness prediction of radiata pine clearwood test pieces using near infrared spectroscopy. J. Near Infrared Spectrosc. 9:117–122.

WALLBACKS, L., U. EDLUND, B. NORDEN, AND I. BERGLUND. 1991a. Multivariate characterization of pulp using 13C NMR, FTIR and NIR. Tappi J. 74(10):201–206.

———, ———, ———, T. IVERSEN, AND U. B. MOHLIN. 1991b. Multivariate characterization of pulp. Part 2. Interpretation and prediction of beating processes. Nordic Pulp Paper Res. 6(3):104–109.

WRIGHT, J., M. BIRKETT, AND M. GAMBINO. 1990. Prediction of pulp yield and cellulose content from wood using near infrared reflectance spectroscopy. Tappi J. 73:164–166.

(ISSN 0735-6161)
CODEN WOOFAJ

WOOD AND FIBER SCIENCE

JOURNAL OF THE SOCIETY OF WOOD SCIENCE AND TECHNOLOGY

VOLUME 36 JULY 2004 NUMBER 3

CONTENTS

Editorial

SMITH, PAUL M., AUDREY ZINK-SHARP, DOUGLAS D. STOKKE, MICHAEL P. WOLCOTT, AND STEPHEN M. SHALER. Setting the research agenda for wood—If not now, when? 289

Articles

CUI, WEINING, D. PASCAL KAMDEM, AND TIM RYPSTRA. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and color changes of artificial weathered wood 291

SRETENOVIC, ALEKSANDRA, ULRICH MÜLLER, WOLFGANG GINDL, AND ALFRED TEISCHINGER. New shear assay for the simultaneous determination of shear strength and shear modulus in solid wood: Finite element modeling and experimental results 302

LU, WEI, AND JINGLU TAN. Grain pattern characterization and classification of walnut by image processing 311

BOWE, SCOTT A., AND MATTHEW S. BUMGARDNER. Species selection in secondary wood products: Perspectives from different consumers 319

SO, CHI-LEUNG, STAN T. LEBOW, LESLIE H. GROOM, AND TIMOTHY G. RIALS. The application of near infrared (NIR) spectroscopy to inorganic preservative-treated wood 329

XIE, YONGQUN, MARTIN FENG, AND JAMES DENG. Quantification of UF and PF resins in MDF fiber with an X-ray fluorescence spectrometer 337

MANSFIELD, SHAWN D., R. PAUL KIBBLEWHITE, AND MARK J. C. RIDDELL. Characterization of the reinforcement potential of different softwood kraft fibers in softwood/hardwood pulp mixtures 344

BUSTOS, CECILIA, ROGER E. HERNÁNDEZ, ROBERT BEAUREGARD, AND MOHAMMAD MOHAMMAD. Influence of machining parameters on the structural performance of finger-joined black spruce 359

WANG, XIPING, ROBERT J. ROSS, BRIAN K. BRASHAW, JOHN PUNCHES, JOHN R. ERICKSON, JOHN W. FORSMAN, AND ROY F. PELLERIN. Diameter effect on stress-wave evaluation of modulus of elasticity of logs 368

JORDAN, BRIAN A., ELMER L. SCHMIDT, PATRICK H. HUELMAN, SAGAR V. KRUPA, AND BERNHARD MAYER. Deuterium as a novel tracer for determining moisture sources in building systems 378

GIERLINGER, NOTBURGA, AND RUPERT WIMMER. Radial distribution of heartwood extractives and lignin in mature European larch 387

BEJO, LASZLO, AND ELEMER M. LANG. Simulation based modeling of the elastic properties of structural composite lumber 395

ERDIL, YUSUF Z., EVA HAVIAROVA, AND CARL A. ECKELMAN. Product engineering and performance testing in relation to strength design of furniture 411

YEO, HWANMYEONG, AND WILLIAM B. SMITH. Control of interior darkening in hard maple 417

JIMÉNEZ, LUIS, ALEJANDRO RODRÍGUEZ, ILDEFONSO PÉREZ, ANTONIA MARÍA CALERO, AND JOSÉ LUIS FERRER. Ethylene glycol/soda organososv pulping of olive tree trimmings 423

NICHOLLS, DAVID L., GEOFFREY H. DONOVAN, AND JOSEPH ROOS. Consumer preferences for kitchen cabinets made from red alder: A comparison to other hardwoods 432

MANESS, THOMAS C., ROBERT A. KOZAK, AND CHRISTINA STAUDHAMMER. Reliability testing of statistical process control procedures for manufacturing with multiple sources of variation 443

SIMPSON, WILLIAM T. Two-dimensional heat flow analysis applied to heat sterilization of ponderosa pine and Douglas-fir square timbers 459