Assessment of laser induced breakdown spectroscopy (LIBS) for classification of preservative in CCA-treated lumber

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Abstract

In many parts of the world, efforts are being made to recycle chromated copper arsenate (CCA)-treated materials. While positive steps have been taken to identify CCA-treated lumber in the waste stream, little has been done to find a fast and accurate means to ascertain the level of preservative that exists in the lumber. The ability of the laser induced breakdown spectroscopy (LIBS) technique to determine the level of residual CCA preservative in reclaimed decking was assessed in this experimental pilot study. Control specimens at treatment levels of 0, 2.5, 3.7, 8.5, and 11.8 kg of CCA preservative per m^3 of material (kg/m^3) were analyzed to create a series of regression-fitted calibration lines. The most appropriate regression analysis with data reduction procedures were determined and subsequently used to comparatively predict the level of residual preservative relative to reclaimed decking lumber. Three different deck boards were investigated varying in age from 10, 18, and 25 years, and the remaining amount of preservative in the reclaimed specimens was verified using x-ray fluorescence. The current study revealed that LIBS possesses the potential to measure a threshold value of preservative, so that a reclaimed piece of lumber could be classified for an appropriate application that corresponds to its level of preservative retention. A more in-depth study is warranted to more fully evaluate the LIBS technique with greater certainty.

The disposal of treated lumber, in particular chromated copper arsenate (CCA) treated lumber, is an increasing concern for North America and many other nations. According to one estimate, 1.6×10^7 m^3 of CCA-treated lumber will enter the waste stream annually by 2020 (Cooper 1993). Furthermore, CCA-treated material finds its way in untreated wood material that is burned for energy recovery, and this ash is a cause for possible health concerns (Morrell 2004). To reduce the disposal burden, options for reusing CCA-treated lumber are being explored. Primary issues for the reuse of CCA-treated materials are the practice of collection and separation by contractors and demolition crews, but the likelihood of reuse is much greater if the practice is lucrative (Smith and Shiau 1998, Alderman 2001). Consequently, the reuse application must be value-added or the material will not be utilized. It has been discovered that CCA-treated wood maintains decay resistance and retains useful mechanical properties despite prior in-service use. Research by Bailey et al. (2004) revealed that reclaimed CCA-treated lumber loses some bending strength without significant changes to stiffness, so it could be reused in certain structural applications.

The first step in reusing CCA-treated lumber is on-site identification, and this step is where the majority of research has focused. To effectively use reclaimed CCA lumber, however, the amount of residual preservative must be estimated so that the resistance to decay is consistent to the new application. Furthermore, a technology capable of CCA quantification would ideally be transportable to the demolition/deconstruction site and be capable of quick analysis. One technology that could possibly meet these criteria is laser induced breakdown spectroscopy (LIBS).

LIBS has already been investigated as a sorting technique to distinguish between treated and untreated lumber (Moskal

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and Hahn 2002, Solo-Gabriele and Townsend 2002), but limited quantification studies on CCA-treated lumber and reclaimed lumber in particular, have been performed. LIBS has been used to quantify preservatives in freshly treated materials (Uhl et al. 2001), revealing the potential to quantify the remaining preservative in reclaimed materials.

The present investigation is a pilot study intended to assess the capability of LIBS to classify the amount of CCA preservative so that deconstruction material may be appropriately used in either aboveground or ground-contact applications. Aboveground and in-ground treatment with CCA specifies 0.25 pcf (4 kg/m^3) and 0.40 pcf (6.4 kg/m^3) gross treatment retention, respectively (AWPA 2001). The goal of this research was to evaluate the predictive capability of the LIBS technology to ascertain the residual level of preservative in reclaimed treated lumber. This study was designed to reveal if sufficient evidence exists to further explore LIBS as a classification technique for CCA-treated deconstruction materials.

Experimental study

LIBS equipment

All of the experiments for this study were performed in conjunction with Ocean Optics in Dunedin, Florida. The laser spectrometer device specifically used for experimentation was the LIBS 2000 apparatus (Ocean Optics 2006). The apparatus platform with computer (PC) control provided adjustable scanning and virtual data acquisition capacity with broad band e.g., full spectral analysis from 200 to 980 nm. This sampling device itself employs an energy intense 200 mJ Nd:YAG pulsed laser with a high resolution optical spectrometer (0.1 nm). The pulse duration for the laser was 10 ns with a PC-controlled sampling rate of 10 Hz. The Q-switch delay was set at −2.5 for all subsequent experimental measurements. In this study, measurements of a single reading for the particular laser excitation point (i.e., shot) were averaged over five laser pulses in air at ambient environmental conditions.

Treated sample materials

The control specimens were southern pine (*Pinus* spp.) sample material treated to several CCA retentions as supplied by the USDA Forest Products Laboratory in Madison, Wisconsin. Control specimens of the recently CCA-treated pine material were 19 by 19 by 38 mm. The levels of preservative treatment for the control specimens were as follows: 0, 2.5, 3.7, 8.5, and 11.8 kg of CCA per m^3 of material (kg/m^3). Retention values were verified according to AWPA standard A9-01, x-ray fluorescence (AWPA 2001), with cooperation by two independent laboratories.

The reclaimed lumber used in the study was also all southern pine (SP) decking boards removed from in-service decks. The boards dimensioned 25 by 140 mm (nominal 5/4 by 6 in. decking) were not processed to the same corresponding width and length as the control specimens. Rather the recovered materials were retained at longer length (2 to 3 ft) and width to better allow planer processing to remove increments of surface material to examine CCA distribution within the weather exposed CCA boards. After the recovered boards were planed, samples for LIBS analysis were cut from the boards from each depth of planing. Processing equipment at the Ocean Optics Laboratory required that the samples be cut to sizes that were smaller in comparison to the control specimens. Three different deck samples of variable age were identified to include a range of exterior exposure ages with similar weather exposure conditions. One sample was taken from a 10-year-old residential deck structure located near State College, Pennsylvania, and two samples were taken from decks in the Pittsburgh, Pennsylvania area, which were 18 and 25 years old. The 10-year-old deck was confirmed by the installer to be treated at 4.0 kg/m^3. The original preservative treatment in the older deck specimens from Pittsburgh could not be confirmed due to lack of treatment markings, but it was assumed to be 4.0 kg/m^3, the standard treatment for SP product decking in aboveground contact applications (AWPA 1994). The residual preservative retention of the specimens was later verified applying the same analytical laboratory evaluations as per the control specimens, AWPA standard method A9-01.

Study data collection

LIBS technology is based on atomic emission spectroscopy applying an intense pulse of laser energy to excite the surface of the sample to create a plasma state that represents the material matrix. Since all of the elements emit electromagnetic radiation of a characteristic wavelength when excited, the elemental composition of the cooling plasma can be uniquely identified. Theoretically, the magnitude of the radiation at this wavelength can serve to identify the concentration of the identified element, so LIBS has the potential to not only identify the presence of preservative metals (copper, chromium, and arsenic in this case), but quantify them in the treated material.

LIBS spectral reading measurements take a few to several seconds to complete, which varies with number of pulse excitation samplings. This time requirement is minimized based on the sampling rate permitted by modern LIBS equipment technology. Accordingly this does not possess a significant hindrance toward rapid determinations of CCA content acceptable for use at demolition and deconstruction sites or material recycling centers.

The primary limitation to LIBS is that the elemental analysis is limited to the small region of excitation, typically 1 mm in diameter. This limitation may be overcome by taking readings at a variety of places on the surface of a sample. Since the turnaround for real time spectral analysis is very short, increasing the total readings does not impose a burden to perform repeated test sampling.

The variability in preservative concentration on the surface of the sample was measured by passing the laser across the width and length of the samples. **Figure 1** shows the paths of laser shots taken on a sample, where approximately 20 readings were taken across the width and 40 readings along the length of control samples. In this study, the measurements taken across the width of the sample were used, as they possess greater wood heterogeneity and thus represent the "worst case scenario" to judge the applicability of the LIBS instrument (Gething et al. 2006). Because the area of analysis for the reclaimed samples was smaller than the control samples, the number of measurements across the specimen width was restricted to approximately 15 measurement points. To investigate the effect of weathering, measurements were taken at various depths from the weathered top surface of the reclaimed boards. For the 10-year-old sample,

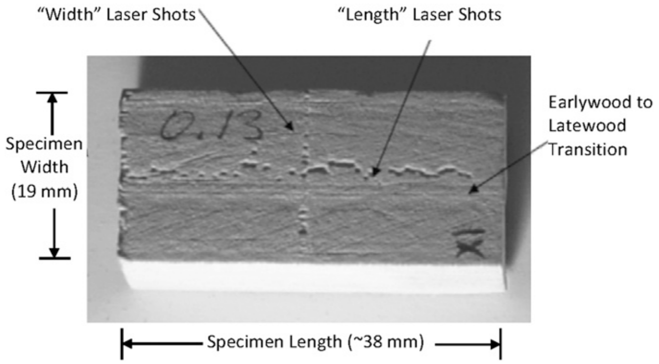

Figure 1. — Visual of the experimental approach to measure concentration variation, showing the tangential face of the processed sampling specimen treated at 2.1 kg/m^3.

one measurement was taken at 3.1 mm from the surface. For the 18-year-old sample, measurements were taken at 2.5, 6.7, and 8.1 mm from the surface, and 1.3, 2.6, and 5.6 mm for the 25-year-old sample. The results from these depth measurements will not be presented, since the LIBS measurement readings taken at the surface for each reclaimed specimen are the focus of this study.

In this study, the response variable is the intensity (in arbitrary units) of the characteristic peak for chromium (Cr) that appears in the spectrometric array of elemental peaks. Several peaks for Cr exist, but the peak at 425.4 nm was chosen because it possessed the largest magnitude. The Cr peak was chosen because copper exists in other preservatives such as alkaline copper quat (ACQ), and arsenic is more difficult to detect than Cr (Moskal and Hahn 2002). Moreover, Cr is less leachable, which provides a better representation of the original level of preservation in the weathered specimens.

Quantification using LIBS

A calibration curve consisting of element signal (intensity) vs. mass or concentration of detected element is typically used for LIBS quantitative analysis (Cremers and Radziemski 2006). The ideal shape of a calibration curve is a straight line function that passes through the origin, with a slope that corresponds to a doubling of the signal intensity as concentration doubles. A calibration curve is constructed for a discrete element, providing a basis to determine the amount in an unknown by taking averaged readings to back-calculate the preservative chemical concentration.

Real calibration curves tend to deviate from the ideal situation and require a less straightforward approach. Occasionally, only a portion of the response data exhibits linearity that is useful and most appropriate for the quantitative estimations. Cremers and Radziemski (2006) aptly refer to this as the *linear dynamic range*. Nonlinear behavior is also witnessed at high and low concentrations, which is caused by a loss in sensitivity in the LIBS unit. To circumvent nonlinearity, one common approach taken is to plot the elemental signal ratioed by another element of a known, constant concentration, or "internal standard," in the matrix. Any artifact in the data created by the measurement apparatus is propagated through the entire specimen analysis, so that the ratio of an element of constant concentration to an unspecified element will eradicate the propagated error. In this study, analysis was performed on the control specimens of known preservative treatment level to create the calibration line, applying carbon as the internal standard.

Data analysis

Several sources of experimental errors may be associated with the LIBS apparatus that can cause artifacts in the data, including fluctuations in the laser spark from pulse to pulse and departure of the sample from the focal point of the laser. The error can be minimized by increasing signal integration time as the number of shots increases (Uhl et al. 2001). Another source of error occurs in the spectrophotometer analysis, where background light may be analyzed in addition to the plasma created by the laser pulse, resulting in a vertical shift in intensity. The LIBS unit available for study purposes did not include a filter to eliminate background light.

While these errors may influence the precision and accuracy of the results, the homogeneity of samples can have a more significant effect. Large discrepancies in local concentration of preservatives may exist because of the heterogeneous nature of the wood matrix, type of preservative, and treatment. Furthermore, the heterogeneity issue is exacerbated when reclaimed wood materials are evaluated, considering research has shown that preservatives may redistribute themselves during years of exposure and weathering (Choi et al. 2004). The heterogeneity issue may be diminished by increasing the number of laser shots at a given location, which will increase the amount of ablated material and give a less localized observation. Five laser shots per location were used in the study for this reason.

Despite the preemptive efforts made to minimize variability and imprecision, considerable amounts of both were observed. In order to improve the quantitative accuracy, some data refinement was performed. The first refinement included deleting data that may be termed as "outlying." Outliers are created because small fluctuations of the laser pulse can lead to variations in the resulting plasma. Since the spectrometer analyses this plasma, artifacts can be created which may influence the data significantly. Body and Chadwick (2001) eliminated this variability by deleting the upper and lower 10 percent of the data and using the remaining 80 percent of the data for the analysis of LIBS intensity readings. Secondly, background light can be eliminated by taking the ratio of the intensity of the adjacent baseline of the spectrometric spectrum to the characteristic peak intensity. From this point, this correction will be referred to as the peak-to-base ratio (Moskal and Hahn 2002).

The third adjustment is made to the data because of the heterogeneous nature of the wood matrix. An important distinction must be made when considering matrix variability to clarify the goal of this study. Because the goal was to investigate the concentration of CCA preservative in an entire sample and not a localized point, the LIBS measurements must be normalized to eliminate the variability between point locations in a specimen of wood.

Changes in density occur in wood because of seasonal growth rates, creating regions of low density (earlywood or spring wood) and high density (latewood or summer wood). These density variations may cause a subsequent change in the local concentration of preservative. Regions of high density have higher amounts of wood material, creating more opportunity for preservative fixation and thus a higher concentration. This concentration change could be significant enough to create a variation in the measured spectrum intensity such that high-density regions could affect the overall preservative concentration measurement in a specimen. For example, if two specimens are treated with the same amount of preservative, but sample "A" was measured in the latewood (high density) and "B" measured in the earlywood (low density), the results could reflect that sample "A" was treated to a higher level of preservation. For this reason, some remedial action must be taken to normalize the data so that density variations will not adversely bias the results.

In theory, the change in localized density will be proportional to the amount of measured carbon, which is the principal element of any lignocelluosic material. If the amount of carbon can be measured and ratioed to the amount of preservative, then the variability can be normalized and will no longer distort the results in favor of the high-density regions. Carbon was identified with a characteristic peak at 247.85 nm and then quantified by means similar to the characteristic Cr peak. Uhl et al. (2001) previously employed this method of using carbon as an internal standard for quantification of boron in treated wood materials.

In summary, the response variable for this study is presented in arbitrary units (a.u.). An example of the data refinement protocol is as follows:

Step 1: Eliminate the upper and lower 10 percent of the data collected
Step 2: Peak-to-base ratio

$$I_{Cr(425),p/b} = \frac{I_{Cr,425.4\,nm}}{I_{Avg.\ adjacent\ baseline}} \qquad [\mathbf{1}]\leftarrow$$

where:

$I =$ the spectrometer output (intensity or counts)

Step 3: Density correction for $I_{Cr(425),p/b}$

$$a.u. = \frac{I_{Cr(425),p/b}}{I_{C(247),p/b}} \qquad [\mathbf{2}]\leftarrow$$

The final consideration for the data involves the statistical treatment of the uncertainty of the quantification predictions. A definite amount of uncertainty, associated with the relative lack of fit to the data, exists in the calibration equation, but it does not translate directly to the uncertainty associated with the predictions derived from the particular equation. The prediction uncertainty, expressed through a prediction interval (P.I.), is calculated in Eq. [**3**] (Bethea et al. 1995).

$$P.I. = \bar{x} + \frac{\hat{\beta}_1(\bar{y}_0 - \bar{y})}{\lambda} \pm \frac{t}{\lambda}\hat{\sigma}'\left[c(\bar{y}_0 - \bar{y})^2 + \lambda\left(\frac{n+m}{nm}\right)\right]^{1/2} \qquad [\mathbf{3}]\leftarrow$$

where:

$$c = \frac{1}{\sum_i (x_i - \bar{x})^2} \qquad [\mathbf{3b}]$$

$$\lambda = \hat{\beta}_1^2 - ct^2\hat{\sigma}^2 \qquad [\mathbf{3c}]$$

$$(\hat{\sigma}')^2 = \frac{(n-2)\hat{\sigma}^2 + \sum_{i=1}^{m}(y_{0i} - \bar{y}_0)^2}{n+m-3d} \qquad [\mathbf{4}]\leftarrow$$

The size of the interval is dependent on level of significance, or alpha value (α). In this study, an alpha value of 0.05 was used as the level of significance. As such, it may be interpreted that the *P.I.* has a 95 percent chance of containing the true quantity of preservative in the unknown sample. **Table 1** provides a complete listing of all of the expressional terms with associated nomenclature for the above formulae (Eqs. [**1**] to [**3**]).

Results and discussion

Construction of calibration curve

The ideal calibration curve defined by Cremers and Radziemski (2006) was used as a baseline for the calibration analysis. In **Figure 2**, the result of each data refinement step on the ideal calibration line is shown. The raw data in **Figure 2a** does not follow the expected trend of increasing response with increasing concentration, as the 4 kg/m^3 sample generally has a higher intensity than the higher concentration specimens. The measurements are so high that a negative coefficient of determination (R^2) is achieved. This discrepancy is reduced by the removal of the top and bottom 10 percent in **Figure 2b** and furthermore by removal of background light in **Figure 2c**, but neither of these corrections made a significant enough improvement to create a calibration line of any integrity. The density normalization step shown in **Figure 2d** makes the greatest improvement on the correlation between the data and calibration line, yielding an R^2 value of 0.64. While a coefficient of determination of this value is not extremely useful for calibration purposes, it does reveal the effectiveness of the data refinement to achieve the expected increasing trend in response with

Table 1. — Nomenclature of the various expressional terms within Eqs. [1] to [3].

Symbol	Description
α	Level of significance of a statistical test
$\hat{\beta}_0$	Intercept of regression line
$\hat{\beta}_1$	Slope of regression line
λ	Prediction interval parameter defined by Eq. [**3c**]
$\hat{\sigma}^2$	Mean square error (MSE) of regression line
$(\hat{\sigma}')^2$	MSE for multiple predictions on one regression, defined by Eq. [**3d**]
a.u.	Arbitrary unit, resulting measured response after data augmentation
C	Prediction interval parameter defined by Eq. [**3b**]
I	Intensity of spectrometer peak (counts), raw data for LIBS measurements
P.I.	Prediction interval for residual preservative
M	Number of new observations
N	Number of data points used to make regression line
$s^2_{\hat{\beta}_1}$	Estimated variance of the slope of the regression line
T	t-statistic evaluated at $t_{n+m-3,\alpha/2}$
$\bar{x}$	Mean predicted preservative concentration
X_i	Individual preservative concentration point used to create regression line
$\bar{X}$	Mean preservative concentration of points used to create regression line
$\bar{y}$	Mean a.u. from points used to create the regression line
$\bar{y}_0$	Mean a.u. from new observations

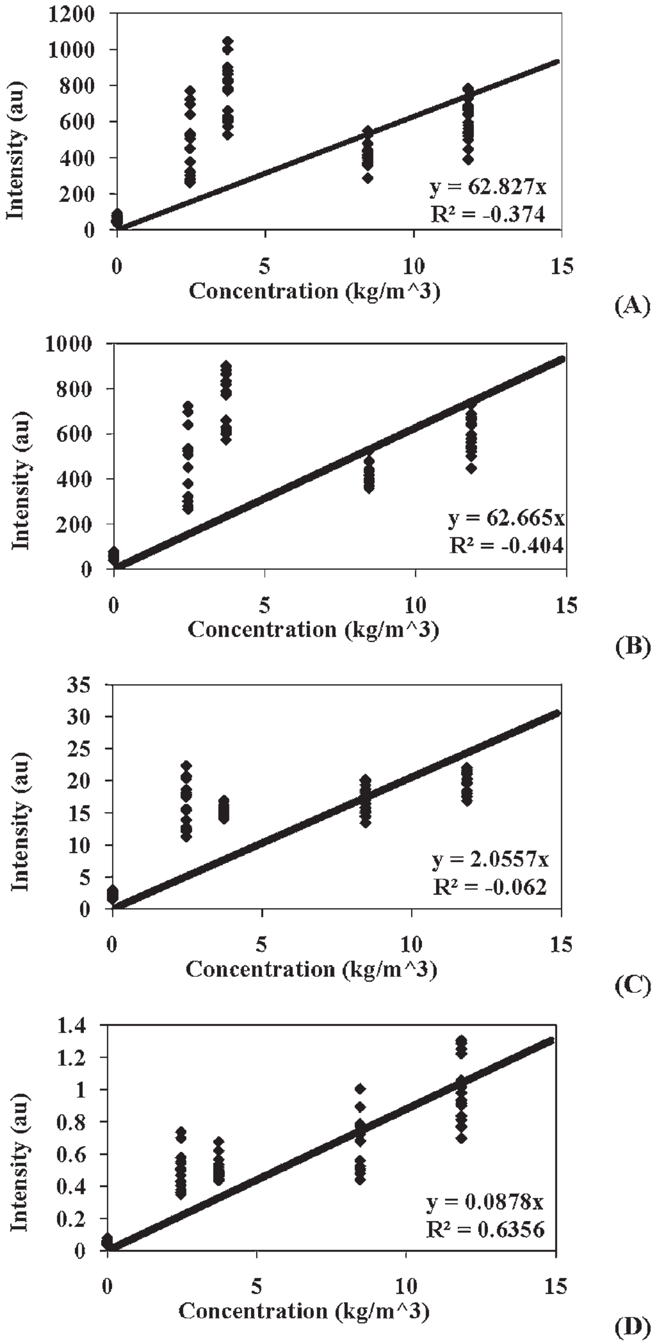

Figure 2. — Summary of the consequence of each step in the LIBS data refinement process on the ideal calibration line: (a) raw data; (b) with upper and lower 10% removed; (c) background light removed (peak to base ratio); and (d) density normalization (carbon ratio).

treatment level in the control data. The first part of **Table 2** shows the control data means and standard deviations (SD) after data refinement. No trend exists in the variability of the measurements at each treatment level.

Unfortunately, the heterogeneous nature of wood prevents any opportunity for an element to have a constant concentration throughout the entire matrix, so the use of an "internal standard" suggested by Cremers and Radziemski (2006) to eliminate non-linearity is not possible. The most straightforward method is to use a linear calibration line with a non-zero intercept. The linear dynamic range can also be studied by eliminating the highest (11.8 kg/m^3) and lowest (0 kg/m^3) treatment levels. Finally, a non-linear analysis may be achieved by performing a transformation of the predictor data (concentration of preservative). In this case, the data appears to have a logarithmic shape, so a square root transformation is most appropriate (Neter et al. 1996). To perform the transformation, the square root of the concentration values is taken and then plotted against the response.

Table 2. — Statistical LIBS data for control and reclaimed CCA specimens.

Control data			
Treatment level	No. of measurements	Mean	SD[a]
(kg/m^3)		----- (a.u. (counts))[b] -----	
0	14 (16)	0.045 (42)	0.012 (11)
2.5	16 (18)	0.49 (480)	0.11 (160)
3.7	16 (20)	0.51 (740)	0.07 (150)
8.5	17 (19)	0.66 (419)	0.16 (63)
11.8	16 (20)	1.0 (600)	0.2 (120)
Reclaimed data			
Years of service	No. of measurements	Mean	SD
		----- (a.u. (counts)) -----	
10	17 (19)	0.48 (80)	0.06 (15)
18	14 (16)	0.30 (50)	0.07 (20)
25	16 (18)	0.64 (80)	0.18 (20)

[a] SD = standard deviations.

[b] Values in parentheses represent the raw data before refinement was performed.

The results of applying each of the non-ideal techniques are presented in **Figure 3**. All of the plots show an improvement over the ideal calibration line, with **Figure 3d** (transformed data) showing the greatest improvement. The transformed calibration line exhibits the highest coefficient of determination (0.81), which likely approaches the maximum attainable value considering the scatter in the data. Furthermore, the transformed calibration line most closely resembles the ideal line because of the small intercept value (0.047).

Other analysis techniques may be investigated to increase the analytical resolution by deviating from an ideal (linear) calibration line applying alternative logarithmic and exponential regression fits to the experimental data ($R^2 = 0.65$ and 0.95, respectively). While these approaches provide a good theoretical investigation, they require an arbitrary value for the control specimens since a zero value cannot be included in the models. Additionally, the very high value for the coefficient in the exponential case is an excellent example of misinterpretation of R^2.

Reclaimed lumber analysis

The second part of **Table 2** shows the statistical data for the reclaimed lumber LIBS analysis for the readings taken on the outer surface of the specimens. The means for each specimen vary between 0.26 and 0.64 a.u., and the variance was of the same order of magnitude as the control specimens. The control mean at 3.7 kg/m^3, the expected similar level as the target treatment level for the reclaimed lumber, was 0.51 a.u. The predictions of the residual preservative in the reclaimed deck boards, along with the x-ray analysis (AWPA A9), are

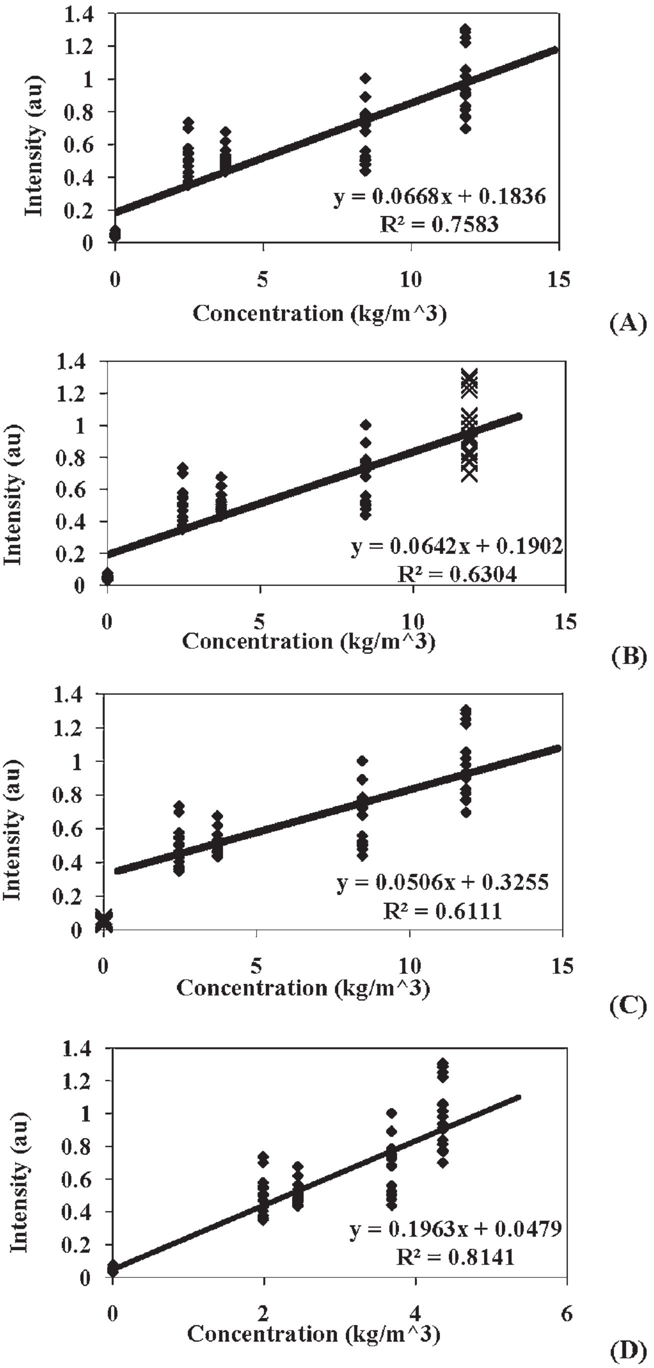

Figure 3. — Possibilities for non-ideal calibration lines: (a) non-zero intercept; (b) no 11.8 kg/m^3 data included in the regression; (c) no 0 kg/m^3 data included in the regression; and (d) concentration data transformed by $\sqrt{x}$.

shown in **Table 3**. The prediction values are determined by correlating the mean measured intensity with the calibration equation, yielding a straightforward linear relationship. A particular point of interest is the prediction error, which is now on the same order of magnitude as the prediction value, where the measured variability of the intensity readings was generally much smaller than the intensity. The observed increase in variability is not surprising, considering the prediction error results from a combination of the variability in the calibration line and the variability in the intensity measurements. Furthermore, the prediction error increases with a decrease in the coefficient of determination of the calibration line, which is why the no-zero data calibration line exhibits the largest prediction error of the three.

Figure 4 shows the mean values for the predictions with the prediction intervals. **Figure 4** and **Table 3** can be used to determine the most appropriate calibration line to use when making predictions. If the prediction interval resides entirely in one treatment level, then it can be used for accurate classification of a specimen. For the 18-year-old specimen, all three calibration lines reasonably predict that residual retention is below the level of aboveground contact (4.0 kg/m^3 or 0.25 pcf) treatment, while the non-zero intercept line can predict the actual amount of residual preservative. For the 10-year-old specimen, none tended to predict the amount of residual preservative. The only line to accurately classify the specimen retention is the transformed calibration line. Finally, for the 25-year-old specimen, all three lines can predict the amount of preservative and all misclassify the specimen, with the transformed line closest to correctly classifying the specimen. It should be noted that the 25-year-old specimen reveals a limitation in the classification analysis considering that the average x-ray retention is relatively close to the treatment level and thus difficult to classify. In the case of specimens close to the classification boundaries, a prediction of quantification, rather than classification, would be more functional for the reuse of the lumber.

From the results, it can be concluded that the most appropriate calibration line is the transformed line. In two out of three specimens, the transformed calibration line correctly classifies the residual level of preservative. A small increase in precision of the LIBS instrument or number of measurements could decrease the prediction error such that the transformed line would accurately classify all three specimens (10, 18, and 25 years). While the non-zero intercept calibration line does predict the residual amount of preservative, precision is largely inadequate (two of three the observed specimens) to correctly classify those specimens. In practical terms, however, this means in the worst scenario case, the treated material might be reused in a less than appropriate new use application.

The comparison of the LIBS readings to the x-ray results requires some clarification in order to completely understand the implications of this study analysis. The x-ray measurement is more a bulk (gross section) analysis, where LIBS is strictly a surface analysis. If the specimens were uniform in treatment, or homogeneous, in amount of preservative at the surface, no problem would arise. Wood is often not treated uniformly, where the outer portion of the specimen may contain a disproportionate amount of the preservative treatment; also this zone will be most highly leached in service. Therefore, the bulk x-ray analysis may be considered a type of average measurement of the concentration throughout the cross section. Some variance in retention occurs, which is reflected by the two independent laboratory x-ray values to assign a measurement of the CCA preservative within the wood specimens (aged and control). Despite the fact that samples were taken from the same sampled specimens, the heterogeneity was great enough to create a discrepancy in readings.

On the other hand, the LIBS technique only measures the surface, an area of the specimen that contains the greatest amount of preservative. What this study has attempted to do is measure these surface concentrations of preservative

Table 3. — Prediction of residual CCA preservative in reclaimed decking based.

Calibration type	Mean intensity	Predicted mean preservative	Error	95% prediction interval	x-ray avg. retention
	(a.u.)	(kg/m^3)			
10-year-old specimen					
Non-zero intercept	0.48	4.69	1.21	(3.48, 5.90)	1.0 [1.4, 0.6][a]
No zero data		3.24	1.69	(1.54, 4.93)	
Transformed		3.23	0.53	(2.70, 3.76)	
18-year-old specimen					
Non-zero intercept	0.30	1.79	1.40	(0.39, 3.19)	1.6 [1.2, 1.9]
No zero data		−0.68	2.24	(−2.92, 1.56)	
Transformed		1.03	0.35	(0.68, 1.38)	
25-year-old specimen					
Non-zero intercept	0.64	7.07	1.38	(5.69, 8.45)	6.0 [4.7, 7.4]
No zero data		6.43	1.81	(4.62, 8.24)	
Transformed		5.92	0.83	(5.09, 6.75)	

[a] Values in parentheses represent the actual x-ray readings taken by the independent laboratories.

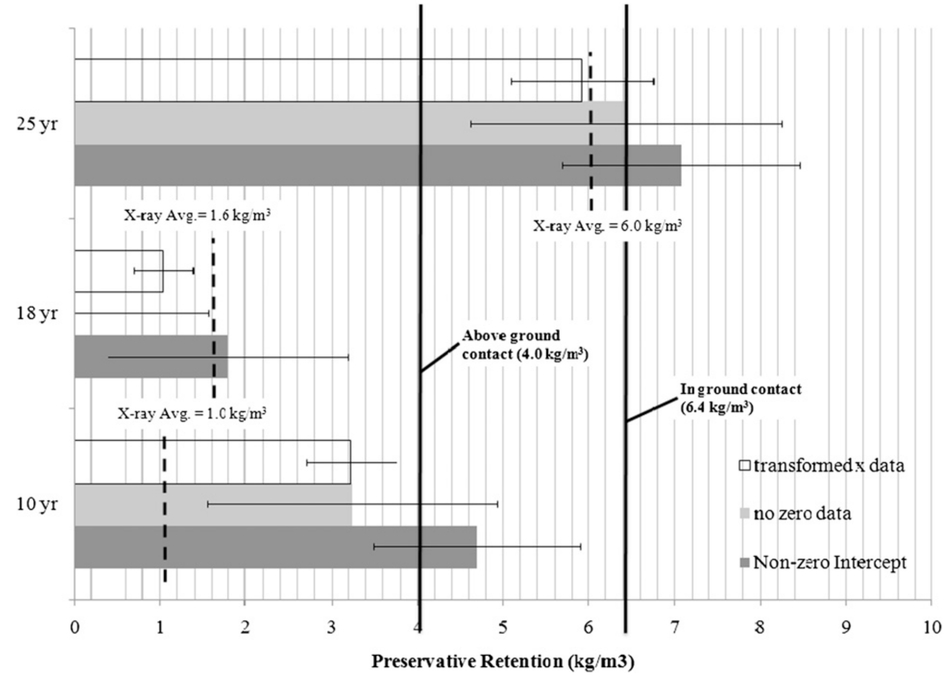

Figure 4. — Predictions of residual preservative in reclaimed decking based on the three different calibration lines.

and see if they may be correlated to the overall bulk concentrations. The problem is that if the concentration gradients are not the same for every specimen, error may be introduced into the analysis. In this study, the best determined calibration line correctly classified two out of three specimens. This small sample size makes it difficult to make any conclusive determinations, but it does provide enough insight to warrant a more in-depth study. A study with a larger number of samples, and samples of a larger variety of treatment levels, would better assess ability of the LIBS analysis to classify reclaimed treated wood.

The variability in the LIBS data must be reduced in order for the technique to accurately predict the amount of residual preservative with a high degree of certainty. The challenge exists in determining if the variability exists in the LIBS measurements or in the variability in the wood matrix. An attempt to reduce the wood variability was made by taking the ratio of the carbon peak and the Cr peak (Step 3 density correction). The reason this step may not have accurately depicted the actual amount of preservative present pertains to the original flow properties of the wood. The ratio assumes that all of the wood material would be exposed to treatment, meaning that all of the wood tissue would be treated. On the other hand, the possibility exists that treatment would not be uniform, considering defects and agglomerations that would restrict flow in certain areas or the specimen was not properly treated. Either of these events would affect the amount of local preservative in the wood and create an artifact in the data. Consequently, a secondary study must be performed in order to quantify the amount of preservative and compare the results to the LIBS data.

To differentiate the variability in the LIBS measurements with the variability in the wood matrix, a secondary method must be used. Uhl et al. successfully employed inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to assess the accuracy of the LIBS quantification measurements, thus making it an ideal method for secondary measurements (Uhl et al. 2001). Another useful approach would involve an x-ray analysis that more closely resembles a LIBS analysis. Instead of taking a boring through the cross section and grinding the specimen for evaluation, grindings from particular depths could be taken and analyzed, and then compared to LIBS measurements taken on the surface of specimens at corresponding depths. Such an analysis would not only give a direct comparison between the techniques, but would also permit an examination of the redistribution of preservative that may occur during service. According to Choi et al. chemical redistribution can occur in the checks of weathered decking material, and this redistribution results in higher concentrations of preservatives around the peripheral zones of surface checks (Choi et al. 2004). Furthermore, it may be of interest to investigate copper peaks to measure redistribution of preservative, as it will yield a second data point and could be compared to the Cr concentrations.

Conclusions

From the analyzed results of this preliminary investigation to examine the applicability of LIBS technology, several summary conclusions have been formulated:

1. The results of this study revealed that the current LIBS technique cannot quantify residual CCA-preservative in reclaimed decking with acceptable certainty.
2. The current LIBS technique exhibits the potential to be used as a method for identifying threshold values of residual preservative in reclaimed CCA-treated decking.
3. There are several opportunities for a follow-up study that would greatly improve upon the assessment capacities of the applied LIBS technique, including a study that includes more samples and samples of varying treatment level, and the use of a secondary analysis that more closely resembles the LIBS analysis.

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