

QUANTIFICATION OF METALS IN PRESERVATIVELY-TREATED LUMBER USING LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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SUMMARY

The laser induced breakdown spectroscopy (LIBS) technique was evaluated for its capability of quantifying CCA in preservative-treated wood. The results of the study reveal that the LIBS technique can be used to predict the amount of preservative based on chromium peak analysis, but further refinement of the process is necessary before the technique is practiced. The largest variation measured by the LIBS system is the result of heterogeneity in the wood matrix, specifically between transitions corresponding with earlywood and latewood growth.

INTRODUCTION

An estimated 1.6×10^7 m³ of lumber treated with copper-chromium-arsenate (CCA) will be disposed of annually in the United States by the year 2020 (Cooper, 1993). The disposal of this lumber is a growing issue for the waste management industry in North America and across the globe. Although these materials are removed from their initial application, disposed CCA-treated lumber has potential use after service. In many cases, CCA-treated wood is removed for aesthetic reasons caused by in-service exposure with age related weathering. However, in most cases the wood retains most if not all of its decay resistance properties and is structurally viable. Bailey *et al.* discovered that the stiffness of recycled CCA-treated lumber was equal to that of virgin material with some loss in bending strength, such that the recycled lumber could be suitable in certain applications (Bailey *et al.* 2004). CCA-recycling is unlikely unless the practice is lucrative (Smith and Shiau, 1998). Therefore, the likelihood of CCA-recycling hinges upon the use of reclaimed lumber.

Past research efforts at the University of Florida have focused on the separation of CCA-treated lumber from untreated lumber to utilize the untreated lumber, for landscaping and energy recovery, applying both x-ray fluorescence and laser induced breakdown

spectroscopy (LIBS) analytical methods (Moskal and Hahn, 2002, Solo-Gabriele and Townsend, 2002). X-ray units are typically very expensive and require a relatively long sampling time, whereas LIBS systems are less expensive and have a sample time of a few seconds. Thus the LIBS system is an attractive option for the analysis of reclaimed, treated lumber.

LIBS techniques employ a high-intensity laser pulse to produce microplasma at the surface of the sample, which may be analyzed to identify the atomic emission lines that correspond to the elemental content (copper, chromium, arsenic) of the sample. The magnitude of these emission lines allows for the quantification of the elements, revealing that LIBS may be used to predict the amount of CCA in preservatively-treated lumber.

The present study focuses on extending the capability of the LIBS technology beyond sorting to quantifying the amount of CCA preservative in the lumber so that it may be appropriately recycled. The goal of this research is to evaluate the predictive capability of the LIBS technology to ascertain the residual amount of preservative in treated control samples. This research is a first step toward the analysis of recycled CCA-treated lumber, for example in nail-laminated post frames.

METHODOLOGY

All experimentation for this study was performed the Ocean Optics research lab in Dunedin, FL. The apparatus used was a LIBS 2000 unit, which employs a 200mJ Nd:YAG laser in conjunction with a high resolution spectrometer. The laser operated at a 10 ns pulse width with a 10 Hz repetition rate, and the Q-switch delay was set at -2.5 and held constant throughout the experiment. All readings were taken after 5 laser pulses and experiments were performed in air at ambient environmental conditions.

The wood specimens used in this study were Southern yellow pine (*Pinus spp*) treated to specific CCA retention at the Forest Products Laboratory in Madison, WI. Dimensions of the specimens were 19x19 mm (1" by 1" dimensional lumber), and cut to lengths of approximately 38 mm. The pine specimens were treated to the following retention levels: 4.6, 8.8, 14.2, and 23.7 kilograms of CCA preservative per cubic meter of material (kg/m^3).

To investigate the concentration gradient on the surface of the sample, the laser measurements were traversed across the width and length of the samples as shown in Figure 1. Approximately 20 shots across the width and 40 shots along the length were taken for each sample at the specified treatment level, with the response variable being the intensity (in arbitrary units) of a characteristic wavelength (425.4 nm) for chromium. Chromium has been used in the past because copper is used in other preservatives such as alkaline copper quat (ACQ) and arsenic is more difficult to detect than chromium (Moskal and Hahn, 2002).

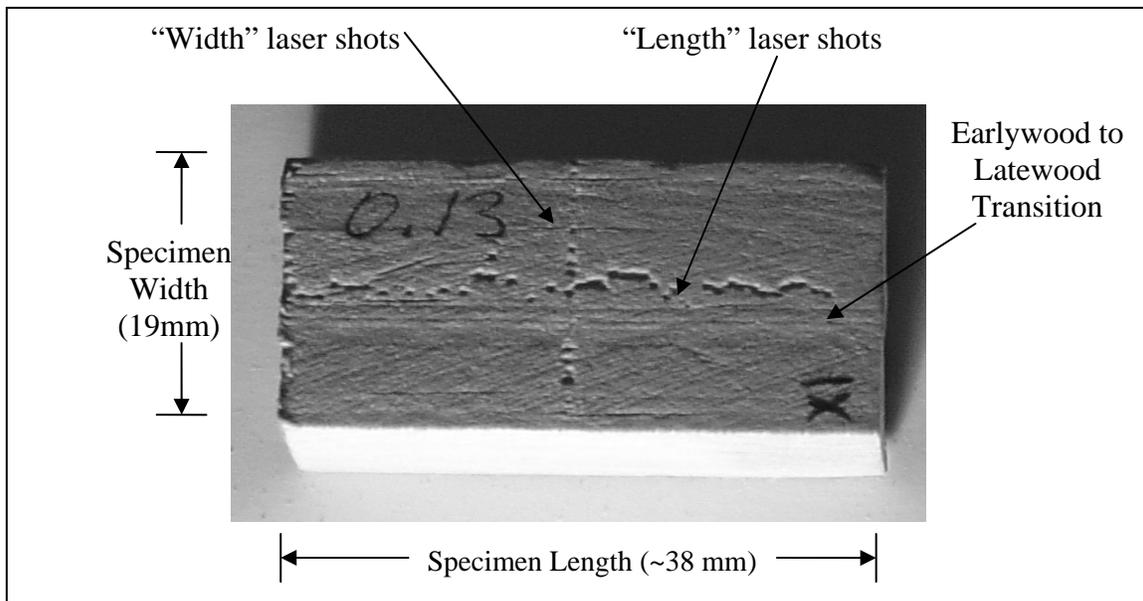


Figure 1: Visual of the experimental approach to measure concentration variation, showing the tangential face of the specimen treated at 4.6 kg/m^3 .

Prior research has revealed that intensity readings taken with a LIBS apparatus require manipulation in order to represent accurate and precise measurements. A brief explanation of these manipulations will follow along with rationale.

The first and most straightforward change in data is made by discarding data that may be termed “outlying”, or erroneous data that result from the sensitive nature of the plasma generated by the laser. Body and Chadwick successfully employed an 80% interval, where the top and bottom 10% of the data was removed from consideration (Body and Chadwick, 2001). This particular method of data manipulation was employed for removal of outlying intensity readings.

A second augmentation made to the data pertains to the background “noise”, or light intensity that is measured by the spectrometer that is not produced by the plasma. Background noise could be created by inconsistent focus of the laser on the specimen surface. This artifact can be removed by taking a ratio of the baseline of the spectrum next to the peak and the intensity of the peak itself, which is why this ratio has been called the peak-to-base ratio (Moskal and Hahn, 2002).

The final adjustment made to the data pertains to the variability of the wood matrix. Density changes occur in wood according to earlywood and latewood growth, subsequently creating possible differences of relative preservative concentration with respect to the wood matrix. This density change is large enough to create a significant variation in measured spectrum intensity. To correct for the matrix heterogeneity, the intensity of the Cr peak can be normalized by a carbon peak at 247.85 nm. This normalization approach has been suggested an effective approach to better determine the quantity of boron chemical preservative (Uhl *et al.* 2001) within treated wood.

In this study, intensity is measured in arbitrary units (a.u.). Intensity can be defined according to the following relations:

- Step 1: Peak-to-base ratio:

$$I_{Cr(425),p/b} = \frac{I_{Cr,425.4nm}}{I_{Avg. adjacent baseline}}$$

where I is the spectrometer output (frequency or counts)

- Step 2: Carbon Normalization of $I_{Cr(425),p/b}$

$$a.u. = \frac{I_{Cr(425),p/b}}{I_{C(247),p/b}}$$

RESULTS AND DISCUSSION

The resultant Cr intensity measurements may be used to produce a regression of concentration of preservative versus arbitrary intensity (Figure 2). Measurements taken across the width of the samples were used in this example rather than the length, in order to present the largest variation observed. This phenomenon will be explained in more detail below.

Theoretically, the regression line in Figure 2 could be used to predict the concentration of an unknown sample, but the coefficient of determination (R^2) is a modest value, meaning that concentration can only explain the change in intensity (and thus predict intensity) two-thirds of the time. Clearly, the predictive capability of the regression must be improved to predict preservative concentration with more confidence, but the potential of the LIBS unit to predict concentration is noteworthy.

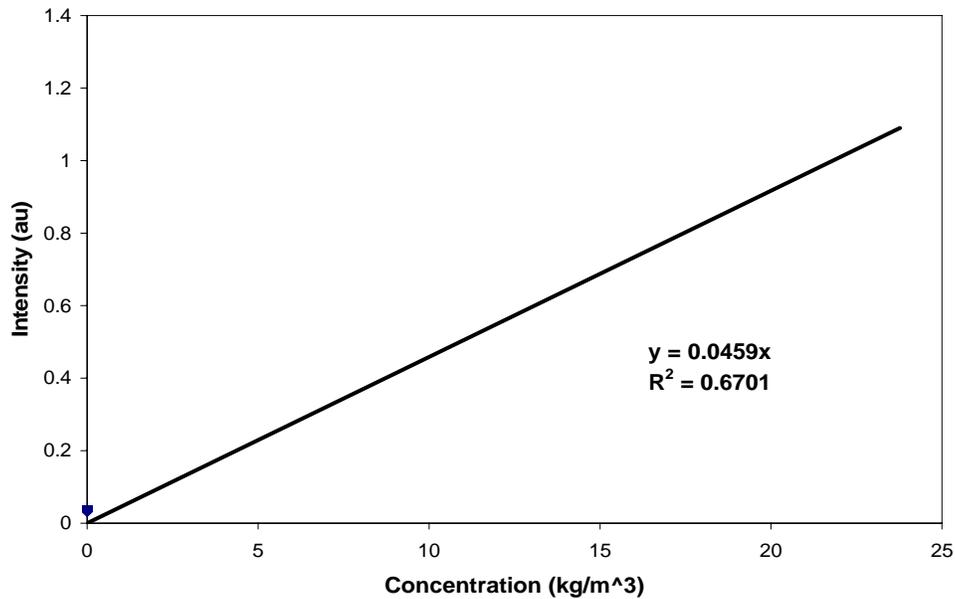


Figure 2: Regression plot revealing the dependence of preservative treatment on the intensity of Cr peak at 425.4 nm.

As noted earlier, the larger variation in intensity was witnessed for the observations made across the width of the samples. Figure 3 depicts the values of the traversed intensities measured for a Cr wavelength at 425.4 nm. The reason for the larger variation across the width relates to the density changes experienced due to growth rings. Along the length, fewer transitions from early to late-wood will occur (See Figure 1), resulting in less variation.

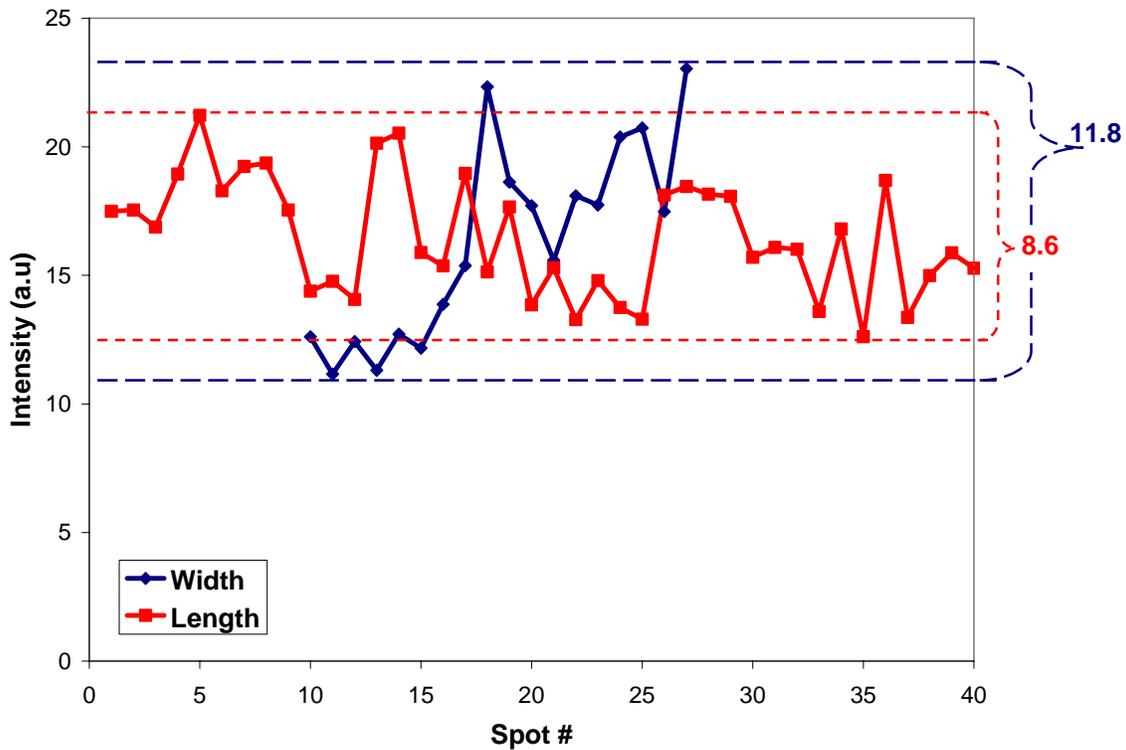


Figure 3: Depiction of LIBS spot traverses across the width and along the length of the specimen treated at 4.6 kg/m^3 .

CONCLUSIONS

The LIBS apparatus demonstrates a potential capability for predicting the quantity of Cr (425.4 nm wavelength) in a wood specimen, but more refinement must be achieved before it can produce reliable calculations. The largest variation in analysis process originates from the heterogeneous nature of the wood material, which presents a significant challenge for the improvement of the analysis technique.

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