RAPID ASSESSMENT OF SOUTHERN PINE DECAYED BY G. TRABEUM BY NEAR INFRARED SPECTRA COLLECTED FROM THE RADIAL SURFACE

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Abstract. The use of near infrared (NIR) spectroscopy for predicting levels of degradation in southern pine (Pinus spp.) by Gloeophyllum trabeum for periods over 1-8 da was investigated. NIR spectra collected from the center of the radial face of each sample after laboratory soil block decay tests were used to develop calibrations. Calibrations were developed for mass loss, compression strength, and exposure period using data measured from prior methods and untreated and mathematically treated (multiplicative scatter correction and first and second derivative) NIR spectra from various ranges of wavelengths by partial least squares regression. Strong relationships were derived from the calibrations with the strongest $R^2$ values of 0.97 (exposure period), 0.94 (compression strength), and 0.91 (mass loss). Calibrations for exposure period showed the strongest statistics for predicting wood decay of the validation test set ($R^2 = 0.92$; $RPD_p$ [ratio of the standard deviation of the measured data to the standard error of prediction] = 3.95 [first derivative, 1100-2250 nm]), while predictions for mass loss of the decayed samples resulted in $R^2 = 0.86$ and an $RPD_p = 3.17$ (multiplicative scatter correction, 1100-2500 nm), and the strongest compression strength prediction resulted in $R^2 = 0.76$ and an $RPD_p = 2.50$ (second derivative, 1100-2500 nm). These results suggest that NIR spectroscopy can adequately predict wood decay from spectra collected from the radial face of southern pine.

Keywords: Near infrared spectroscopy, decay, southern pine, Gloeophyllum trabeum.

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INTRODUCTION

Decay can rapidly destroy the aesthetic appeal and structural stability of wood causing a need to replace wood products in structures. It is estimated that 10% of the timber cut each year in the US is used to replace deteriorated wood (Zabel and Morrell 1992b). Recent estimates suggest that deterioration of wood costs homeowners over $5 billion annually (Schultz and Nicholas 2008). Complete loss of wood can be prevented if decay is detected early. However, decay is rarely apparent until it is well advanced when the physical and mechanical properties of wood are seriously affected. Considerable reductions in strength are found in the early stages of decay by brown-rot because of the rapid degradation of the carbohydrates. In fact, compression strength losses of 45% with only 10% mass loss have been reported (Schmidt and Czeschlik 2006). Southern pine (Pinus spp.) is an extremely important commodity contributing to approximately 74% of sawn wood consumption in the US where it is most often used in construction for structural applications (Miller 1999; Howard and Westby 2009). Brown-rot fungi are more commonly associated with softwoods and therefore have dramatic effects on wooden structures when conditions for growth are suitable (Highley 1999).

Current methods used to measure decay in wood preservative research are often subjective and in some cases destructive. Furthermore, all of these methods are relatively ineffective at measuring early stages of decay (Zabel and Morrell 1992a; Nicholas and Crawford 2003). It would be desirable to have the ability to detect the early stages of wood decay because this may make it possible to significantly reduce the time required to accurately predict the performance of new wood preservative systems.

Near infrared (NIR) spectroscopy can simultaneously measure many wood properties affected by decay fungi rapidly and nondestructively with minimal or no sample preparation. Several studies (Raymond and Schimleck 2002; Kelley et al 2004; Jones et al 2006) have shown that NIR spectroscopy has the ability to measure the chemical properties of wood. Brown-rot fungi affect the carbohydrates (hemicelluloses and cellulose) early in the decay process and also modify lignin (Green and Highley 1997; Schmidt and Czeschlik 2006; Goodell et al 2008). Other studies (Schimleck et al 2002, 2003; Meder et al 2003; Kelley et al 2004; Jones et al 2005) have used NIR spectroscopy to measure the physical and mechanical properties of wood.

Although NIR spectroscopy has successfully been used to measure many of the properties affected by decay fungi, little research has been directed toward the use of NIR spectroscopy to measure wood decay. Kelley et al (2002) obtained a correlation coefficient of 0.96 for the prediction of the mass loss of milled spruce samples decayed by brown-rot fungi using NIR spectroscopy. Other studies have used other decay measuring techniques such as pH, electrical resistance, cation composition, and chemical analysis in conjunction with NIR spectroscopy to develop calibrations for predicting wood decay (Jellison et al 2002; Ferraz et al 2004; Stirling et al 2007). Although these studies have shown that NIR could be used to measure wood decay, they used milled wood samples. Measuring solid wood samples can be beneficial by minimizing sample preparation, i.e. decreasing the amount of time it takes to acquire results, and avoids destroying the sample. In this regard, Fackler et al (2007a, 2007b) used Fourier transform NIR spectroscopy along with multivariate analysis to measure decay (mass loss and lignin change) in spruce and beech veneers.

Another obstacle to implementing NIR spectroscopy as an acceptable method for the measurement of wood decay that needs to be explored further is the effectiveness of this method for detecting early stages of decay. Jellison et al (2002) found that NIR calibrations developed for mass loss could detect brown-rot decay in red spruce when weight loss was as low as 3%. Another study (Schmutzer et al 2008) showed that NIR spectroscopy can be used for monitoring change in lignin content of milled spruce...
samples subjected to white-rot decay over a 10-da period. In a recent study (Green 2010) NIR spectroscopy was used to predict mass loss, compression strength, and the level of degradation by day (exposure period) of southern pine wafers decayed by *G. trabeum* from NIR spectra collected from the cross-sectional face. Strong calibrations were developed with coefficients of determination ($R^2$) of 0.98-0.94. When collecting spectra from the cross-sectional face, higher absorbance is generally noticed that is attributed to the energy flow along the wood fibers. In this regard, less energy is collected from a given NIR spectra (Schimleck et al 2003). To further develop the application of NIR spectroscopy for prediction of wood decay, this research was conducted to establish whether NIR spectra collected from the radial face could produce similar results to those collected from the cross-sectional face.

Specific objectives of this study were to:

1. Determine if NIR spectroscopy could be used as a method for measuring progressive decay in solid wood samples by using NIR spectra collected from the radial face to develop calibrations; and
2. Examine the efficacy of wood decay calibrations to predict wood decay when subjected to a data set independent of the calibration.

**MATERIALS AND METHODS**

**Samples**

Two hundred seventy-two southern pine wafers (18 × 18 × 5 mm in the L × R × T direction) were cut from two clear wood sticks. Samples from each stick were kept separate to create two separate tests. Each sample was marked sequentially as cut. Unexposed wafers (odd-numbered wafers) were obtained from each side of the designated exposed wafers so that differences in compression strength could be used to determine the strength loss of the exposed samples. This test consisted of 16 groups consisting of 17 samples (8-9 exposed samples) per group (8 groups from each stick).

**Soil Block Decay Test**

The samples were inoculated with the brown-rot fungus *G. trabeum* in accelerated soil block decay tests following the procedure outlined in E22-09 (AWPA 2009), except that no preservatives were added. Two of the 16 groups (one group from each stick consisting of a total of 16-18 wafers) were assigned to each of the 8 exposure periods consisting of 1-8 consecutive days. Once the wafers reached their predetermined exposure period, they were removed from the incubator (set at 28°C) and the mycelium was wiped off with cotton balls. The wafers were then placed in a controlled environment room (20°C and 40% RH) to bring them to an estimated moisture content (EMC) of approximately 8%. The wafers were then weighed and the difference in the initial and postexposure weights was used to calculate the percentage mass loss.

**Compression Strength**

The E22-09 (AWPA 2009) procedure was followed when performing compression strength testing on the exposed and unexposed wafers. Before being subjected to compression testing, all of the wafers were saturated with deionized water using a vacuum/soak method. Before implementing compression testing, the length, width, and thickness of each wafer were measured with an automated micrometer that automatically recorded the data. These measurements were then loaded into a program used for compression testing that provides the necessary data needed to calculate the compression strength of the samples.

After saturation and volume measurement, each wafer was subjected to compression tests using the testing apparatus at the Mississippi State Forest Products Laboratory. The wafers were held in place by a spring-loaded clamp directly under the crosshead. Wafers were positioned so that the load was applied in the radial direction.

Software designed for this machine regulated the speed, load, and amount of compression at a
controlled rate. This software retains the deformation and applied load and converts the data into a stress/strain relationship. The load cell used for compression was rated at 45 kg. A linear transducer monitored the crosshead until the wafer reached 5% compression at a rate of 0.5 mm/min and retracted, completing a full cycle.

Compression strength was derived from the stress/strain relationship beyond the proportional limit when the wafers were compressed by 5% of their thickness. All of the sample (exposed and unexposed) compression strength values were downloaded from the computer software, and the mean of the exposed and unexposed samples within each exposure period of each stick was compared to determine the effects of decay. SAS software was used to ensure that sample compression strength correlated between the two sticks and to determine at what exposure period a significant difference could be found between exposed and unexposed samples using the same procedures as described for mass loss analysis.

Mass Loss Analysis

The mass of each wafer was then entered into SAS version 9.2 (SAS Institute Inc, Cary, NC) where the samples were tested for correlation between both sticks (using the general linear model [GLM] and Tukey procedures) to ensure that each sample within each stick degraded similarly, and each group was tested for a significant difference using the same procedure as stated previously to discover when (by exposure period) mass loss could effectively detect decay.

Near Infrared Spectroscopy

Samples were placed in a controlled environment chamber set at 20°C and 40% RH to attain an EMC of approximately 8% before NIR analysis. NIR spectra were collected from the center of the radial face of each wafer. Diffuse reflectance NIR spectra were collected from each wafer by an Optiprobe analyzer fiberoptic probe attached to a FOSS NIRSystems Model 5000 scanning spectrophotometer (Silver Spring, MD). Spectra were collected at 2-nm intervals over the wavelength range of 1100-2500 nm. A ceramic standard was used as the reference. A single spectrum was obtained by averaging the 32 scans collected from each measurement. NIR spectra from the decayed samples and other data from decay measuring methods (mass loss analysis, compression strength, and exposure period) were used to develop calibrations.

Wood Decay Calibrations

The wood decay calibrations were created by The Unscrambler version 8.0 software (Camo AS, Norway). Calibrations were created using both the raw and mathematically treated NIR spectra (68 spectra) and using the results from mass loss analysis and compression strength along with partial least squares regression. Calibration was also developed for the time that samples were exposed to the fungus (exposure days) to determine if NIR could accurately measure the levels of decay and designate the amount of decay measured to a particular exposure period throughout the 8-da exposure. The full wavelength range of the spectrometer (1100-2500 nm) was initially used to develop calibrations. After noticing a considerable amount of noise in the 2300-2500 nm range, pruning the spectra was explored as a way of improving the strength of the calibration statistics. Noise can be seen in Fig 1 after approximately 2300 nm and is similar to that reported in Jones et al (2007). Further reductions (50 nm steps from 2500-2200 nm) were implemented because of increases in calibration statistics (possibly because of reductions in both noise and variables presenting variation) until the wavelength range of 1100-2200 nm was reached, where statistical strength stabilized.

First and second derivative data (produced by the Savitzky-Golay approach with left and right gaps of 8 nm) and multiplicative scatter correction (MSC) are spectral noise reduction methods used to acquire improved calibrations.
Four crossvalidation segments and a maximum of 10 factors were used to produce the calibrations. The number of factors used was determined by The Unscrambler software. The $R^2$, standard error of calibration, SECV (standard error of crossvalidation), and RPDc (ratio of the standard deviation of the measured data to SECV) (Williams and Sobering 1993) was used to evaluate the calibration performance.

Prediction of Wood Decay

Calibrations developed by NIR, mass loss, and compression strength were examined for their ability to predict wood decay of 68 samples not included in the calibration set (validation set). The exposure period calibrations were used to determine how well NIR spectroscopy could predict the exposure period by the degree of degradation in the validation set. Statistics for analyzing the efficacy of the calibration to accurately predict an independent data set included $R^2_p$ (value calculated to show the ability of the calibration to account for the variation in the prediction set), standard error of prediction (SEP) (the measure of the calibrations ability to predict wood decay of a separate data set not included in the calibration), and the RPDp, which evaluates the predictive ability of the calibrations and is the ratio of the standard deviation of the measured data to the SEP. The RPD was used as the identifier of the strongest calibrations and predictions in this study, because it allows evaluation of calibrations created from data with differing units, mathematical treatments, and wavelength ranges.

RESULTS

Decay Evaluation

Table 1 shows the percentage mass and compression strength losses from the effects of decay throughout the 8-da exposure. Slight increases in compression strength, resulting in negative percentage decreases from the unexposed samples, are apparent for 1- to 3-da exposure. A separate study has shown that this is because of a slight increase in compression strength as a result of autoclaving the wafers exposed to the fungus. A statistically significant difference in both mean mass loss and mean compression strength loss for both sets of data are apparent after a 5-da exposure ($p < 0.0001$).

<table>
<thead>
<tr>
<th>Days</th>
<th>Mass loss (%)</th>
<th>Statistical significance</th>
<th>Strength loss (%)</th>
<th>Statistical significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>NS</td>
<td>0.00</td>
<td>NS</td>
</tr>
<tr>
<td>1</td>
<td>0.62</td>
<td>NS</td>
<td>−3.20</td>
<td>NS</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>NS</td>
<td>−2.65</td>
<td>NS</td>
</tr>
<tr>
<td>3</td>
<td>0.52</td>
<td>NS</td>
<td>−0.26</td>
<td>NS</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>NS</td>
<td>4.13</td>
<td>NS</td>
</tr>
<tr>
<td>5</td>
<td>1.22</td>
<td>S</td>
<td>6.65</td>
<td>S</td>
</tr>
<tr>
<td>6</td>
<td>1.90</td>
<td>S</td>
<td>14.46</td>
<td>S</td>
</tr>
<tr>
<td>7</td>
<td>3.22</td>
<td>S</td>
<td>30.65</td>
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<td>8</td>
<td>5.80</td>
<td>S</td>
<td>41.71</td>
<td>S</td>
</tr>
</tbody>
</table>

NS, percent loss is not significantly different from 0.0% loss; S, percent loss is significantly different from 0.0% loss at $\alpha = 0.05$.

Wood Decay Calibrations

The two strongest calibrations for mass loss, compression strength, and exposure period of decayed Pinus spp. can be seen in Table 2. The calibrations were created using mathematically treated (second derivative, MSC) NIR spectra.
and various wavelength ranges. The exposure period calibration developed with second derivative spectra and wavelengths from 1100-2250 nm had the strongest statistics with an $R^2 = 0.97$, and an $RPD_c = 5.00$, using 3 factors. The strongest mass loss calibration was produced from raw spectra over 1100-2200 nm ($R^2 = 0.91$, $RPD_c = 3.13$, 4 factors), while the strongest compression strength calibration was produced with first derivative data and wavelengths ranging from 1100-2400 nm ($R^2 = 0.94$, $RPD_c = 2.27$, 6 factors).

**Wood Decay Predictions**

Table 3 shows a summary of the prediction statistics (two strongest predictions) acquired from testing each calibration’s (mass loss, compression strength, and exposure periods) ability to predict properties of the validation set. Predictions were very good with the first derivative (1100-2250 nm) exposure period calibration being the strongest ($R^2_p = 0.92$, $RPD_p = 3.95$, 4 factors) followed by the mass loss calibration produced from MSC-treated spectra over the range 1100-2500 nm ($R^2_p = 0.86$, $RPD_p = 3.17$, 3 factors). The compression strength calibration based on second derivative spectra (1100-2500 nm) also showed strong predictive ability with $R^2_p = 0.76$, $RPD_p = 2.50$, using 7 factors.

**DISCUSSION**

In this study, calibrations for mass loss, compression strength, and exposure period were developed using NIR spectra obtained from the radial face of southern pine samples decayed by *G. trabeum* (1-8 da). The calibrations provide a rapid nondestructive technique for quantitatively measuring decay in its earliest stages. Calibrations were tested against an independent validation set to determine their predictive capability. Calibrations for the number of days of exposure to the fungus (exposure period) showed the strongest statistics, indicating that

<table>
<thead>
<tr>
<th>Wavelength range (nm)</th>
<th>Laboratory measurement</th>
<th>Mathematical treatment</th>
<th>$R^2$</th>
<th>SEC</th>
<th>SECV</th>
<th>Factors</th>
<th>$RPD_c$</th>
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</thead>
<tbody>
<tr>
<td>1100-2200</td>
<td>Mass loss</td>
<td>Raw</td>
<td>0.91</td>
<td>0.60%</td>
<td>0.64%</td>
<td>4</td>
<td>3.13</td>
</tr>
<tr>
<td>1100-2300</td>
<td></td>
<td></td>
<td>0.91</td>
<td>0.60%</td>
<td>0.66%</td>
<td>4</td>
<td>3.03</td>
</tr>
<tr>
<td>1100-2400</td>
<td>Compression strength</td>
<td>1st derivative</td>
<td>0.94</td>
<td>0.10 MPa</td>
<td>0.17 MPa</td>
<td>6</td>
<td>2.27</td>
</tr>
<tr>
<td>1100-2350</td>
<td></td>
<td>1st derivative</td>
<td>0.92</td>
<td>0.11 MPa</td>
<td>0.17 MPa</td>
<td>6</td>
<td>2.24</td>
</tr>
<tr>
<td>1100-2250</td>
<td>Exposure (da)</td>
<td>2nd derivative</td>
<td>0.97</td>
<td>0.40 da</td>
<td>0.49 da</td>
<td>3</td>
<td>5.00</td>
</tr>
<tr>
<td>1100-2250</td>
<td></td>
<td>1st derivative</td>
<td>0.97</td>
<td>0.42 da</td>
<td>0.49 da</td>
<td>4</td>
<td>5.00</td>
</tr>
</tbody>
</table>

SEC, standard error of calibration; SECV, standard error of crossvalidation; $RPD_c$, ratio of the standard deviation of the measured data to SECV.

<table>
<thead>
<tr>
<th>Wavelength range (nm)</th>
<th>Laboratory measurement</th>
<th>Math treatment</th>
<th>$R^2$</th>
<th>SEP</th>
<th>Factors</th>
<th>$RPD_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100-2500</td>
<td>Mass loss</td>
<td>MSC</td>
<td>0.86</td>
<td>0.63%</td>
<td>3</td>
<td>3.17</td>
</tr>
<tr>
<td>1100-2500</td>
<td></td>
<td>1st derivative</td>
<td>0.85</td>
<td>0.66%</td>
<td>3</td>
<td>3.03</td>
</tr>
<tr>
<td>1100-2500</td>
<td>Compression strength</td>
<td>2nd derivative</td>
<td>0.76</td>
<td>0.15 MPa</td>
<td>0.15 MPa</td>
<td>7</td>
</tr>
<tr>
<td>1100-2250</td>
<td></td>
<td>1st derivative</td>
<td>0.76</td>
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<td>4</td>
</tr>
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<td>1100-2250</td>
<td>Exposure</td>
<td>1st derivative</td>
<td>0.92</td>
<td>0.62 da</td>
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<tr>
<td>1100-2250</td>
<td></td>
<td>MSC</td>
<td>0.92</td>
<td>0.63 da</td>
<td>0.63 da</td>
<td>3</td>
</tr>
</tbody>
</table>

SEP, standard error of prediction; $RPD_p$, predictive ability of the calibrations and is the ratio of the standard deviation of the measured data to the SEP; MSC, multiplicative scatter correction.
NIR spectroscopy could accurately measure the amount of degradation in the earlier stages of decay. Changes in the wood were detected as early as 5 da; this is likely attributable to the early chemical changes to the wood either by the addition of mycelium in the wood or the breakdown of wood chemical constituents. Small chemical variation within the makeup of wood using NIR was seen by Kelley et al. (2004) and Jones et al. (2006) when considering chemical analysis. By examining the spectra of the samples before and after exposure to the decay fungi, differences were noticed within the wavelengths of 2100-2200 nm. This is similar to what Stirling et al. (2007) found in ground samples from lodgepole pine samples and is likely because of the decrease of cellulose in the samples. The known bands nearest the changes are 2100 nm which is related to cellulose and 2132 nm which is known to be lignin (Shenk et al. 1992; Osborne et al. 1993; Michell and Schimleck 1996; Schimleck et al. 2005).

Calibrations for mass loss and compression strength presented strong statistics. The mass loss calibration was the stronger of the two, but compression strength calibrations produced reasonable RPD_p values suggesting that either of the two calibrations could be used for precise decay prediction. Results from mass loss predictions of decayed wood were similar to those found by Jellison et al. (2002) and Kelley et al. (2002) who found good correlations with mass loss calibrations used to measure decay in milled samples subjected to brown-rot fungi.

Although strong results were presented from calibrations and predictions for mass loss and compression strength, they were weaker than those found in Green (2010), where similar tests were conducted but the NIR spectra were collected from the cross-sectional face as opposed to the radial face used in this study. This contradicts the Schimleck et al. (2003) report that spectra collected from the radial face for measuring microfibril angle, air-dry density, and stiffness were superior compared with those obtained from the cross-sectional face. In the cross-sectional samples, it is likely that more information about the changes in the cell wall structure were detected because of the relationship of the energy from the spectrometer to the cell wall. Scanning the radial face would minimize the loss of NIR energy into the cell lumen but limits the penetration into the cell wall. Scanning the cross-sectional face would allow the spectrometer to measure changes across the cell wall, but much of the energy would not be returned from the lumen, showing more absorbance across the whole spectrum than what is occurring because of the wood. The reductions in the ability to predict properties obtained from the radial face of wood decay can be acceptable because measurement of the cross-sectional face is not always accessible because of the typical orientation of wood in structures.

Calibrations were developed from the full NIR wavelength achievable with the instrument used in this study (1100-2500 nm) and shorter wavelength ranges to reduce spectral noise along with untreated and mathematically treated spectra. Results varied across both mathematical treatment and wavelength range similarly to the results found in earlier studies (Jones et al. 2005; Green 2010). Although the strongest calibrations were developed with spectra pruned to 1100-2400 nm or less, the strongest predictions for mass loss and compression strength were derived from calibrations created with spectra from 1100-2500 nm and with fewer factors in most cases. The true test of a calibration is its predictive ability when subjected to an unknown data set. Therefore, pruning the spectra was not necessary for mass loss and compression strength. However, the strongest exposure period prediction was produced with spectra from the wavelength range 1100-2250 nm (RPD_p = 3.95) but was followed closely by 1100-2500 nm (RPD_p = 3.89). These mixed results indicate that the extra work of pruning spectra for perceived noise may not be necessary.

The nondestructive aspect of this study allows the samples to be used further in studies where samples need to be in an intact state. Having intact samples may become more important for
the emerging bioenergy industry, that is, looking for conversion methods of woody biomass using decay fungi (Kumar et al. 2009). There is also the possibility for an increase in the throughput of samples by measuring them with NIR. Because there is definite gain in speed from the compression strength method, there will not be a direct gain for the measurement of mass loss. However, when looking at measuring multiple properties together such as mass loss and compression strength, both properties can be measured by scanning the sample with the spectrometer once and reducing handling and data entry errors.

The work presented here provides a basis for measuring the mass loss and compression strength from the radial surface of laboratory decay samples under controlled conditions. There are two gains from this work that are important in the laboratory setting: an increased throughput of samples by reducing the time required to measure compression strength and mass loss (samples do not have to be saturated to get compression strength) and by measuring both properties at the same time. While this work does not apply to in-service wood, it does open the possibility for determining the ability to consider that in the future.

There are two opportunities for further research now that it has been shown that NIR spectroscopy can be utilized to measure wood decay in solid southern pine wafers. One is examining the application of the technique in situ on preservative-free samples. While there are limitations to NIR related to moisture and sample uniformity that cannot be controlled in the field, mathematical treatments or reducing the wavelengths examined may aid in this. While it is likely that the predictive ability of models may be limited, NIR would allow for monitoring and possible threshold guidelines to determine when wood has decayed beyond its useful lifespan. The current research presented is limited to preservative-free wood, therefore the second item to be examined is the interaction of preservative treatments with the spectra. By examining the changes in spectra caused by the chemical treatments, it may be possible to create calibrations that are specific to a particular preservative or the creation of broad-based calibration that encompasses several different chemical treatments. Once again these models may be limited in their ability to give precise measures of decay but may allow for threshold measurements or even differentiation decay rates.

CONCLUSIONS

This study indicates that wood decay of solid southern pine samples subjected to G. trabeum can be accurately measured using mass loss, compression strength, and exposure period calibrations based on NIR spectra collected from the radial face. Exposure period calibrations showed the strongest predictive ability, although both mass loss and compression strength calibrations also had strong RPDp values. No single mathematical treatment or wavelength range proved to be best for developing calibrations for all models.

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