Determination of Carvacrol Content in Alaska Yellow Cedar (*Callitropsis nootkatensis*) Extractives

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Extractives, such as carvacrol, play a major role in the durability of Alaska yellow cedar (*Callitropsis nootkatensis*) heartwood. However, it is a slow and complicated process to identify the levels of these compounds in individual timbers. This study investigated the feasibility of attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy and near-infrared (NIR) spectroscopy, coupled with hierarchical cluster analysis (HCA) and principal component analysis (PCA), for detecting carvacrol in wood. Alaska yellow cedar was extracted using sequential Soxhlet extraction with toluene-ethanol, followed by ethanol and hot water. The extracted samples were milled, and the powders were treated with different concentrations of carvacrol. The spectral analysis of the wood that contained carvacrol was conducted using ATR-FTIR and NIR spectroscopy, and the peaks indicative of carvacrol were identified. The chemometric analysis on the spectral data using PCA and HCA distinguished the wood with high (> 34%) and low (< 3.5%) carvacrol concentrations. The results suggest that infrared spectroscopy can be a non-destructive tool for the qualitative and quantitative evaluation of extractives, and possibly for the rapid assessment of Alaska yellow cedar durability.

Keywords: Alaska yellow cedar; Heartwood; Durability; Carvacrol; Infrared spectroscopy; ATR-FTIR; NIR

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INTRODUCTION

Alaska yellow cedar is native to western North America, where it is found along the coasts of southeast Alaska and British Columbia and at higher elevations as far south as northern California (Harris 1990; Sturrock *et al.* 2010). The strength and excellent durability of Alaska yellow cedar makes it suitable for many exterior applications (Grace and Yamamoto 1994; De Groot *et al.* 2000; Hennon *et al.* 2000), including decks, play structures, poles, furniture, and totem poles. It is also popular in Japan as a building material for temples and teahouses due to its termite resistance and its similarity to hinoki cypress (*Chamaecyparis obtusa* (Siebold & Zucc.) Endl.).

The durability of Alaska yellow cedar heartwood is related to its extractives content (Barton 1976; Taylor *et al.* 2006). The extractives are low molecular weight compounds that can be removed using organic solvents and water. They are present in low concentrations (1% to 5%) in temperate species and up to 30% for some tropical species (Scheffer and Cowling 1966; Haluk and Roussel 2000; Haupt *et al.* 2003; Hillis 2011). Alaska yellow cedar contains extractives from the tropolone group including nootkatin, as

well as carvacrol, which is a terpenoid (Kelsey *et al.* 2005; Manter *et al.* 2007; Karchesy *et al.* 2018). Typically, extractive contents higher than 1% to 2% have been associated with high durability in this species (Lipeh *et al.* 2018). Even dead standing Alaska yellow cedar trees appear to contain elevated levels of carvacrol decades after dying (Kelsey *et al.* 2005). In addition, carvacrol is known for its fungicidal and anti-termitic properties. This makes carvacrol a potential wood preservative for use in the forest products industry (Taylor *et al.* 2006; Xie *et al.* 2014; Zhang *et al.* 2016). Additionally, carvacrol has been found to be an effective control for household arthropod pests including ticks, mosquitoes, and fleas (Panella *et al.* 2005; Anderson and Coats 2012).

A qualitative assessment of the carvacrol concentration (durability) by infrared (IR) spectroscopy can potentially provide a rapid, non-destructive alternative for sorting Alaska yellow cedar lumber pieces. Infrared radiation activates molecular vibrations that are characteristic of a given chemical compound or a class of compounds (Stuart 2004). The two main vibrational spectroscopy techniques used in wood analysis are near infrared (NIR) and Fourier-transform infrared (FTIR) spectroscopy (Pandey 1999; Schimleck *et al.* 2000; Gierlinger *et al.* 2003; Poletto *et al.* 2012; Xu *et al.* 2013).

Many wood-related studies have used NIR spectroscopy because it requires minimal sample preparation and is less sensitive to wood moisture content variations than FTIR spectroscopy (Siesler *et al.* 2008). The NIR region ranges from 4000 cm^{-1} to 12500 cm^{-1} (2500 nm to 800 nm), with absorption bands resulting from overtones and combinations of C-O, O-H, C-H, and N-H bond vibrations (Siesler *et al.* 2008). Extractive analysis using NIR spectroscopy has been explored for mahogany, white oak, eucalyptus, larch, and poplar wood (Gierlinger and Wimmer 2004; Poke and Raymond 2006; Da Silva *et al.* 2013; He and Hu 2013). He and Hu (2013) showed the ability of NIR to predict hot-water-soluble extractive contents of different hardwood and softwood species and identify individual extractive compounds. The NIR method has also been used to determine basic density, mechanical strength, stiffness, and wood chemical components (Wright *et al.* 1990; Michell and Schimleck 1996; Schwanninger and Hinterstoisser 2001; Schimleck and Evans 2002; Schwanninger *et al.* 2004; Schauwecker *et al.* 2013).

There has been extensive use of FTIR in wood analysis, as variations in FTIR spectra (4000 cm^{-1} to 400 cm^{-1}) can be directly related to functional groups (Lin-Vien *et al.* 1991). Several applications of FTIR analysis have been developed in combination with multivariate data analysis. These applications allow for the qualitative and quantitative determination of wood properties, including lignin content and chemical changes during and after treatments (Ajuong and Breese 1998; Rodrigues *et al.* 2001; Pandey and Pitman 2003; Rana *et al.* 2010; Fabiyi *et al.* 2011; Shangguan *et al.* 2014). However, extractives studies using attenuated total reflectance (ATR) FTIR are still lacking, especially those relating extractives to durability using spectral data. Extractives studies on eucalyptus, rosewood, and Scots pine indicate the potential of FTIR for the detection of extractives that impart durability (Holmgren *et al.* 1999; Nuopponen *et al.* 2003; Popescu *et al.* 2007; Wang *et al.* 2015b).

This study investigated the feasibility of using ATR-FTIR spectroscopy, NIR spectroscopy, and chemometric analysis to detect varying concentrations of carvacrol in Alaska yellow cedar. The capability of this method was examined to determine whether the method had the sensitivity to reliably identify timbers that would be classified as durable.

EXPERIMENTAL

Materials

A total of 15 Alaska yellow cedar (*Callitropsis nootkatensis*) boards (130 mm × 80 mm × 200 mm) were provided by a sawmill in British Columbia, Canada. No obvious color differences were observed between heartwood and sapwood. One board was selected randomly and cut into smaller strips along the radial face (15 mm × 90 mm × 140 mm, r × t × l). The strips were further divided into five subsamples (15 mm × 15 mm × 140 mm) that were conditioned for one month at 20 °C ± 2 °C and 65% ± 5% relative humidity (RH). The samples were then oven-dried at 50 °C ± 2 °C for 48 h, and their densities were determined using the ASTM standard D4442-16 (2017). Low temperatures were used to minimize the possibility of extractives degradation (Scheffer 1973).

Methods

Extractive-free wood blocks

Thirty cubes (15 mm × 15 mm × 15 mm) were cut from the 140-mm-long strips and used to prepare the extractive-free wood using the Soxhlet extraction method of Kirker *et al.* (2013), based on a modification of the ASTM standard D1105-96 (2017). Prior to extraction, the blocks were conditioned for one week, equilibrated at 20 °C to 23 °C, conditioned at 30% RH, and weighed (Ohaus Adventurer Lab Balance; Ohaus Corp., Pine Brook, NJ, USA).

Six blocks from each radial location were retained as the unextracted control samples. The remaining 18 blocks were extracted in 320 mL of 95% ethanol-toluene (2:1 v/v) in a Soxhlet extractor for 6 h at 60 °C to remove the low molecular weight compounds typically found in the cell lumen and on cell surfaces. These compounds are predominantly non-polar, aliphatic compounds (*e.g.*, fatty acids and their monohydric esters, gummy substances, and minor amounts of aromatic compounds) (Ajuong and Breese 1998; ASTM D1105-13 2017). The samples were then rinsed with 95% ethanol, oven-dried at 50 °C ± 2 °C overnight, and weighed. The blocks were extracted again with 320 mL of 95% ethanol for 6 h at 60 °C to remove compounds within the cell walls, which consisted of cyclic aromatic compounds of increasing polarity (such as tannins). The samples were then drained, washed with 95% ethanol, oven-dried (50 °C ± 2 °C) overnight, and weighed. Finally, the blocks were boiled in a hot water bath for 8 h at 100 °C to remove the tannins, gums, sugars, starches, and coloring matter (ASTM D1105-13 2017). The blocks were then washed with distilled water and air-dried overnight.

The extracted blocks were then oven-dried at 50 °C ± 2 °C for 72 h and weighed to determine the total mass loss due to the extractive removal process. Six blocks representing each radial face were ground using a Wiley mill (Model 4; Arthur H. Thomas Co., Swedesboro, NJ, USA) to pass through a 60-mesh screen and then sealed inside air-tight bags that were stored in the dark at 5 °C for further use.

Carvacrol preparation

Carvacrol at a 99% concentration (Sigma-Aldrich, St. Louis, MO, USA) was diluted in ethanol (≥ 99.5%, Sigma-Aldrich, St. Louis, MO, USA) to produce concentrations of 0%, 1%, 3%, 5%, 10%, 25%, 50%, and 100% (wt/wt). All the samples were placed in 4-mL glass vials that were stored in the dark at 5 °C. Two drops of a given concentration of carvacrol were applied to the extracted wood powders. These powders

were dried for 1 h at room temperature prior to each analysis. The actual carvacrol content in each wood after treatment was calculated and recorded (Table 1) using Eq. 1,

$$\%\ Carvacrol\ in\ wood = \frac{(c \times (b - a))}{b} \quad (1)$$

where a is the weight of the extracted wood (g), b is the weight of the carvacrol with the wood (g), and c is the carvacrol concentration (%). The treated wood samples contained 0.7%, 2.0%, 3.5%, 6.8%, 10.8%, 34.7%, and 78.2% (wt/wt) carvacrol.

Table 1. FTIR Bands Related to the Wood Extractives Found in the Alaska Yellow Cedar Heartwood

Peak (cm^{-1})	Reference Peak (cm^{-1})	Description	Associated Wood Compounds	References
1735	1730	C=O stretching vibrations produced by ester carbonyl	Fat, wax, or esterified resin acids	Zhou *et al.* (2015)
1620 to 1589	1600	C=C stretching or aromatic ring deformation	Aromatic compounds, phenolic group	Pandey and Pitman (2003); Zhou *et al.* (2015)
1620	1633	Olefinic double bond	-	Zhou *et al.* (2015)
1503 to 1522	1510	Deformation vibration within benzene rings	Aromatic compounds	Zhou *et al.* (2015)
1251	1271	Carbon single-bonded oxygen	-	Zhou *et al.* (2015)
811	811	Out-of-plane CH wagging vibrations	Carvacrol	Schulz *et al.* (2005)

Collection of spectra

The spectra of the powdered samples of the extracted and non-extracted Alaska yellow cedar (0.01 g ± 0.001 g) were measured three times. Three different extracted samples for each concentration were analyzed using ATR-FTIR and NIR spectroscopy.

ATR-FTIR spectroscopy

All of the ATR-FTIR spectra were acquired on a Nicolet iS50 FTIR spectrometer equipped with Smart iTR ATR (Thermo Fisher Scientific, Waltham, MA, USA). Approximately 0.1 g of a given Alaska yellow cedar powder sample was placed on top of the optical medium, pressed against a single-reflection diamond crystal with a torque knob, and a spectrum was immediately acquired. Prior to the analysis, the wood powders were oven-dried at 50 °C for 2 h to reduce the interference of wood moisture on the spectral readings. The spectra were collected against air as a background every 15 min over a wavenumber range of 4000 cm^{-1} to 650 cm^{-1}, with a resolution of 4 cm^{-1} to exclude the signals that were not relevant within the sample. Sixty-four scans were co-added and averaged for each spectrum to obtain a good signal-to-noise ratio.

The internal reflectance element was a small, diamond prism that allowed for a sampling diameter of approximately 2.0 mm. The OMNIC™ 9.2 software (Thermo Fisher Scientific, Waltham, MA, USA) was used for the instrument management, spectra acquisition, spectra preprocessing, and file transformation from the OMNIC spectra to the spreadsheet (comma separated value(s) (CSV)).

A total of 6942 data points were recorded from 650 cm^{-1} to 4000 cm^{-1}. The ATR-FTIR spectra were available for 24 Alaska yellow cedar samples treated with carvacrol concentrations from 0% (solvent only) to 100% (wt/wt). The ATR-FTIR spectra were collected in triplicate by taking a newly treated sample for each carvacrol concentration. The average of the three spectra was used for further analysis. The raw spectra were pretreated for baseline correction and smoothing to help reduce the nonlinearity and multicollinearity among variables.

NIR analysis

The NIR spectra of the ground Alaska yellow cedar samples were obtained using a FOSS NIRSystems 6500 spectrometer (Foss NIRSystems Inc., Silver Spring, MD, USA) that was fitted with a feed and forage analyzer spinning module (Foss NIRSystems Inc., Silver Spring, MD, USA). The samples were placed inside a 13-mm diameter insert within a ring cup that was 36 mm in diameter and 9 mm thick. Vision 4.1 software (Metrohm, Herisau, Switzerland) was used for the instrument operation and acquisition of the spectra. Approximately 0.1 g of the extracted Alaska yellow cedar powder that was treated with carvacrol was placed inside the ring cup, and a spectrum was immediately acquired. On average, each spectrum was scanned 32 times. A total of 700 data points were recorded from 1100 nm to 2500 nm (9090 cm^{-1} to 4000 cm^{-1}). The NIR spectra were available for 24 Alaska yellow cedar samples treated with carvacrol concentrations from 0% to 100% (wt/wt). The NIR spectra were collected in triplicate by taking a new treated sample for each carvacrol concentration. The average of the three spectra was used for further analysis.

Statistical analysis

All analyses were performed on R Studio software (Version 1.0.136; RStudio, Boston, MA, USA) using the Chemospec R package (DePauw University, Greencastle, IN, USA) on the spectral dataset. The hierarchical cluster analysis (HCA) was completed using Euclidean distance to identify groupings based on the similarity of the IR spectra (Siesler *et al.* 2008). These spectra were grouped into a "cluster" or a "hierarchical group." The cluster analysis was used for grouping of concentrated groups, with no information on the group membership (*i.e.*, finding groups containing similar objects). The principal component analysis (PCA) was performed for differentiating between the samples with varying carvacrol concentrations. The PCA was completed using classical or robust methods (Varmuza and Filzmoser 2009; Wehrens 2011). The classical methods used all the data provided to compute the scores and loadings. The robust methods used the core of the data, so some samples may have been down-weighted. The robust technique is useful when there are outliers because it is less sensitive compared with classic PCA (Gharibnezhad *et al.* 2011). Both methods search for the components that explain as much variance in the data as possible.

RESULTS AND DISCUSSION

Spectral Assignment for Carvacrol

ATR-FTIR

Changes in the ATR-FTIR spectra were detected at different carvacrol concentrations (Fig. 1). A broad band with increasing absorbance at higher carvacrol contents was observed from the stretching vibrations of O-H at 3417 cm^{-1}. In addition, an

aliphatic C-H stretching absorption around 2950 cm^{-1} was detected at 5% carvacrol (D), and the signal increased with the increasing carvacrol concentrations (Fig. 1a).

In Fig. 1b, the region from 1800 cm^{-1} to 600 cm^{-1} provided the greatest evidence of unique characteristics, as shown by the fingerprint region. The fingerprint region typically shows evidence of complex deformations of molecules. The region may arise from specific characteristics of molecular symmetry or combination bands that arise from multiple bands that simultaneously deform (Siesler *et al.* 2008). Carvacrol consists of the phenolic functional group -OH and aromatic rings. The presence of double bonds and/or aromatic rings was signified by the weak absorption of C=C near 1650 cm^{-1}, while the presence of an aromatic ring was indicated by the medium to strong absorptions at 1600 cm^{-1} to 1450 cm^{-1}. The aromatic ring region showed a higher absorbance as the carvacrol concentration increased, while the weak C=C absorption (1650 cm^{-1}) was almost undetectable in the spectra (Fig. 1b).

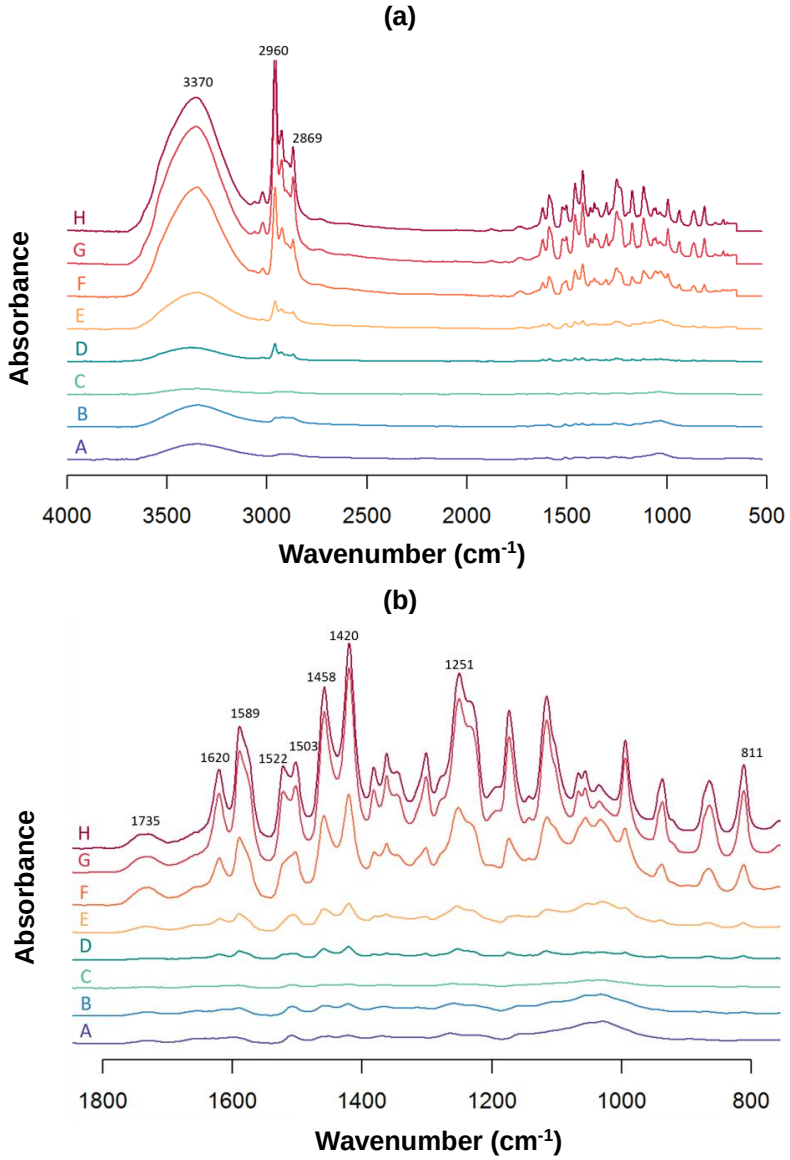

Fig. 1. Representative FTIR spectra of the extracted Alaska yellow cedar treated with the eight carvacrol concentrations at a) 4000 cm^{-1} to 650 cm^{-1} and b) 1800 cm^{-1} to 650 cm^{-1} (A = 0.0%, B = 0.7%, C = 2.0%, D = 3.5%, E = 6.8%, F = 10.8%, G = 34.7%, and H = 78.2%)

The peak at 1503 cm^{-1} was indicative of the deformation vibration within the benzene rings in carvacrol (Lin-Vien *et al.* 1991; Stuart 2004). The benzene rings were cleaved at higher carvacrol concentrations (34.7% and 78.2%). Additionally, Shahlinny and Morrell (2017) observed that the extracted and non-extracted Alaska yellow cedar samples indicated a reduction in the peak height on the extracted samples, which suggested the loss of some phenolic compounds after the extraction. The band at 811 cm^{-1}, which corresponded to the out-of-plane CH wagging vibrations, indicates carvacrol (Schulz *et al.* 2005). The peak for this band increased as the carvacrol concentrations increased. In addition, this band is used to differentiate different types of aromatic ring substitutions (Lin-Vien *et al.* 1991). The 811 cm^{-1} peak was detected on samples with a minimum of 3.5% carvacrol, although it is difficult to observe in the resulting spectra due to the scale used for the absorbance (Fig. 1). The low concentration of carvacrol detected indicated the sensitivity of the ATR-FTIR spectrometer.

Extractive-related peaks in the wood have been observed at 1730 cm^{-1}, 1633 cm^{-1}, 1600 cm^{-1}, 1510 cm^{-1}, and 1271 cm^{-1} in previous studies (Nuopponen *et al.* 2003; Pandey and Pitman 2003; Colom and Carrillo 2005; Schauwecker *et al.* 2013; Mattos *et al.* 2014; Zhou *et al.* 2015). All of these peaks, albeit with slight shifts in the peak position, were observed in this study (Table 1). Additional similar findings were observed by Lipeh and Morrell (2017) using transmission FTIR spectra. Broad peaks at 1735 cm^{-1} corresponded to C=O bonds that are typical of non-conjugated ketones and conjugated carboxylic acids in hemicellulose and lignin. This peak did not appear to change with the addition of carvacrol and may be indicative of other extractive groups in Alaska yellow cedar that were not removed during the extraction process (Moore and Owen 2001). Based on the resulting spectra (Fig. 1), only the regions between 4000 cm^{-1} to 2500 cm^{-1} and 1800 cm^{-1} to 650 cm^{-1} were retained for further analysis.

NIR spectra

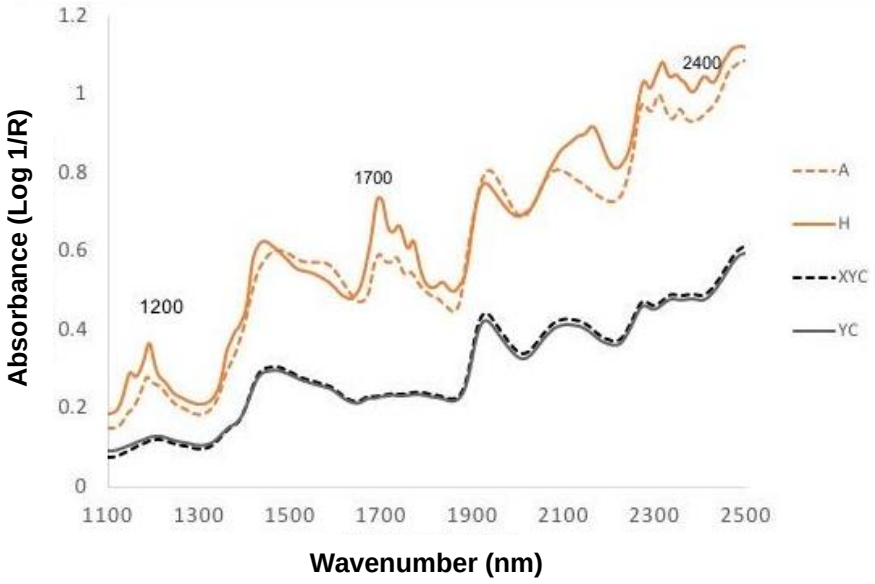

Fig. 2. Representative NIR spectra (1100 nm to 2500 nm) for *C. nootkatenis* treated with carvacrol at eight concentrations (A = 0.0% and H = 78.2%)

The NIR spectra of the extracted and non-extracted Alaska yellow cedar were compared to the extracted Alaska yellow cedar treated with 0% carvacrol (A) or 78.2% carvacrol (H) (Fig. 2). There were no differences detected between the extracted and non-extracted samples. The samples with 78.2% carvacrol (H) had different peaks at 1200 nm, 1700 nm, and 2400 nm, compared with the samples with 0% carvacrol. The band at 1700 nm denoted the C-H stretch's first overtone (-CH_2). This is one of the major bands for wood (Xu *et al.* 2013). Absorption at 1200 nm is the second overtone of the C-H stretching vibration (Siesler *et al.* 2008).

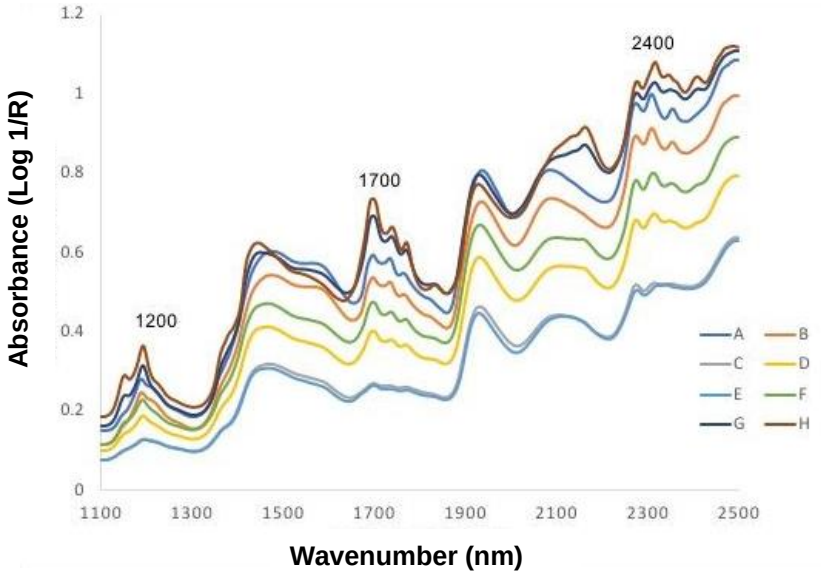

Fig. 3. Representative NIR spectra (1100 nm to 2500 nm) for Alaska yellow cedar treated with carvacrol at eight concentrations (A = 0%, B = 1%, C = 3%, D = 5%, E = 10%, F = 15%, G = 50%, and H = 100%)

The NIR spectra for the Alaska yellow cedar treated with different carvacrol concentrations were observed at 1100 nm to 2500 nm (9090 cm^{-1} to 4000 cm^{-1}) (Fig. 2). The peaks that were indicative of carvacrol (1700 nm, 1200 nm, and 2400 nm) increased as the carvacrol concentrations increased. The peak around 2400 nm appeared at a carvacrol concentration of 3.5% (D), and a stronger peak was observed with the increasing carvacrol concentrations. However, sample B appeared to have a slightly higher absorbance than expected. The spectrum of sample B was between the samples treated with carvacrol concentrations of 6.8% (E) and 10.8% (F) (Fig. 3). It was possible that some of the samples were not as thoroughly mixed during the treatment process with carvacrol, which resulted in more variable concentrations that influenced the resulting spectrum. Additionally, the conversion of spectral data to derivatives might highlight the differences between the spectra and be more suitable for analysis. The chemometric analysis of the carvacrol concentrations was only applied to the ATR-FTIR spectra because it contained more information compared with the NIR spectra.

Chemometrics Analysis

Hierarchical cluster analysis

The ATR-FTIR data for all of the carvacrol treated samples were examined to determine whether specific differences could be identified for each treatment. The resulting HCA dendrogram produced two major clusters (Fig. 4). One cluster contained samples

with less than 10.8% carvacrol, while the other cluster contained samples with higher concentrations. However, the sample containing 6.8% (E) carvacrol did not follow the trend. The left cluster was further separated into one group with carvacrol concentrations from 0% to 2.0% (A, B, and C), and another group with concentrations between 3.5% (D) and 6.8% (E).

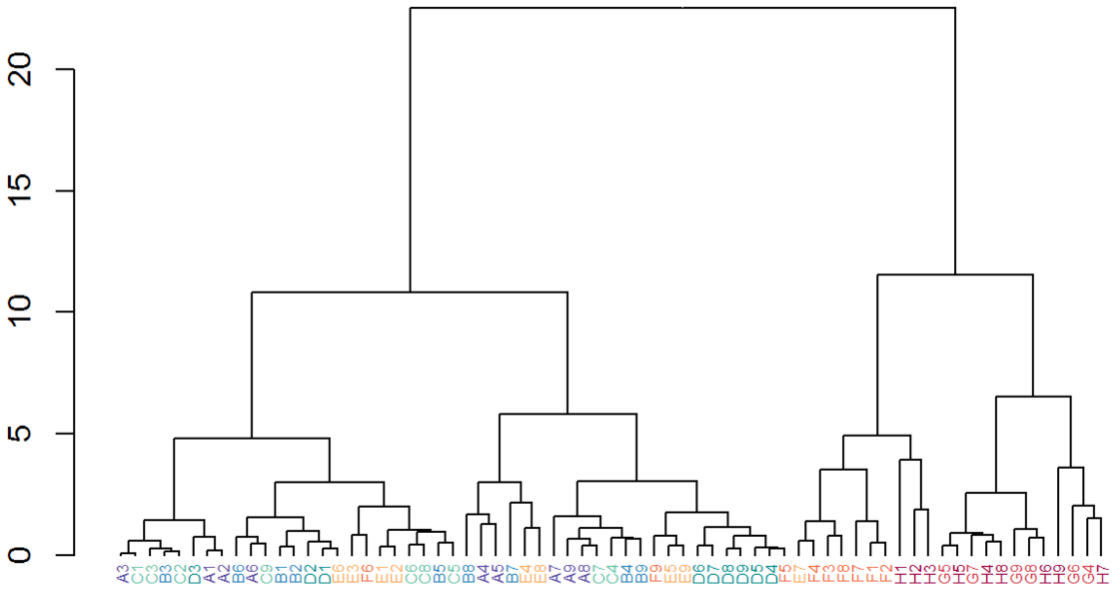

Fig. 4. Dendrogram of hierarchical clustering (with Euclidean distance) of the extracted Alaska yellow cedar treated with the eight carvacrol concentrations. (A = 0.0%, B = 0.7%, C = 2.0%, D = 3.5%, E = 6.8%, F = 10.8%, G = 34.7%, and H = 78.2%)

Principal component analysis

The PCA was performed on the 4000 cm^{-1} to 2500 cm^{-1} and 1800 cm^{-1} to 650 cm^{-1} regions on 24 samples with three replicates at each carvacrol concentration. The classic and robust PCA showed similar values for the first two principal components (PCs) but with different directions (Fig. 5). Both the analyses showed that the first two PCs explained more than 99% of the variation in the data. No outliers were detected, as observed from the orthogonal distance analysis on the spectral data sets. As a result, both the classic and robust PCA were used for analysis where appropriate.

The samples with 34.7% (G) or 78.2% (H) carvacrol were grouped together on the far right of the PC1 scores and had negative PC2 scores (Fig. 5a). The samples with 6.8% (E) or 10.8% (F) carvacrol were grouped close together along PC1 and PC2. The samples treated at concentrations of 3.5% carvacrol or lower had similar scores (Fig. 5a). However, the robust PCA showed that the 3.5% (D) carvacrol samples were located close to the '0' value along PC2 scores (Fig. 5b). In addition, the robust PC showed separation between the 34.7% (G) and 78.2% (H) carvacrol treatments and samples receiving lower carvacrol concentrations.

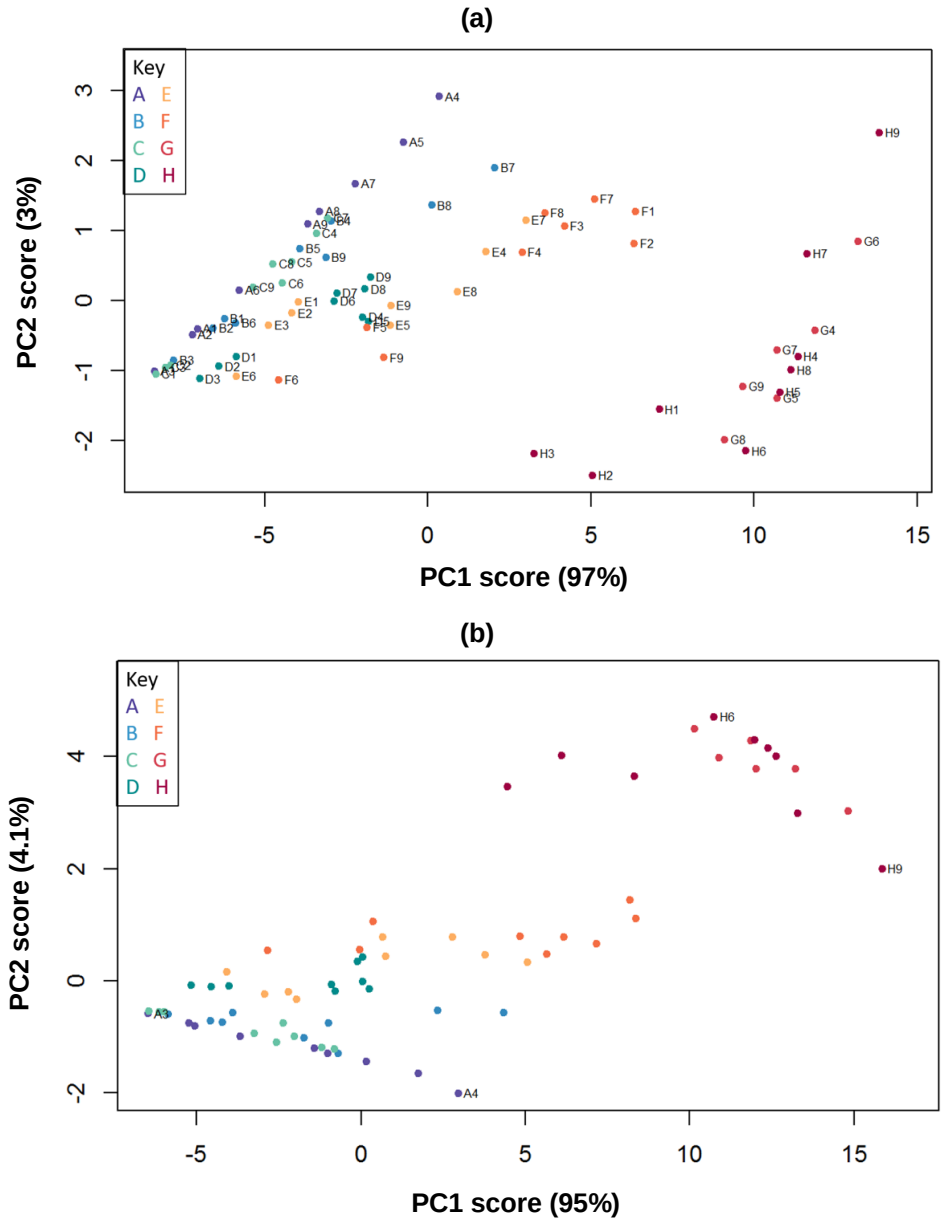

Fig. 5. Score plot showing the first two PC scores for a) classical PCA and b) robust PCA on Alaska yellow cedar treated with different concentrations of carvacrol (A = 0.0%, B = 0.7%, C = 2.0%, D = 3.5%, E = 6.8%, F = 10.8%, G = 34.7%, and H = 78.2%)

The loading plots for PC1 and PC2 indicated that the peak at 2950 cm^{-1} strongly influenced the PC1 scores, which allowed for separation between the high (50% to 100%) and low carvacrol concentrations (Fig. 6). The differences in the PC2 scores were attributed to the strong negative values at 2950 cm^{-1} and the positive values at 1115 cm^{-1}.

The samples showed strong peaks with increasing carvacrol concentrations, which suggested a relationship between the peak height and the carvacrol concentration as an indirect measure of durability. The ATR-FTIR analysis showed sensitivity for detecting carvacrol at concentrations above 3.5%. These concentration differences may be difficult to observe based on visual inspection of the spectra alone but can be discerned with chemometrics analysis using PCA or HCA.

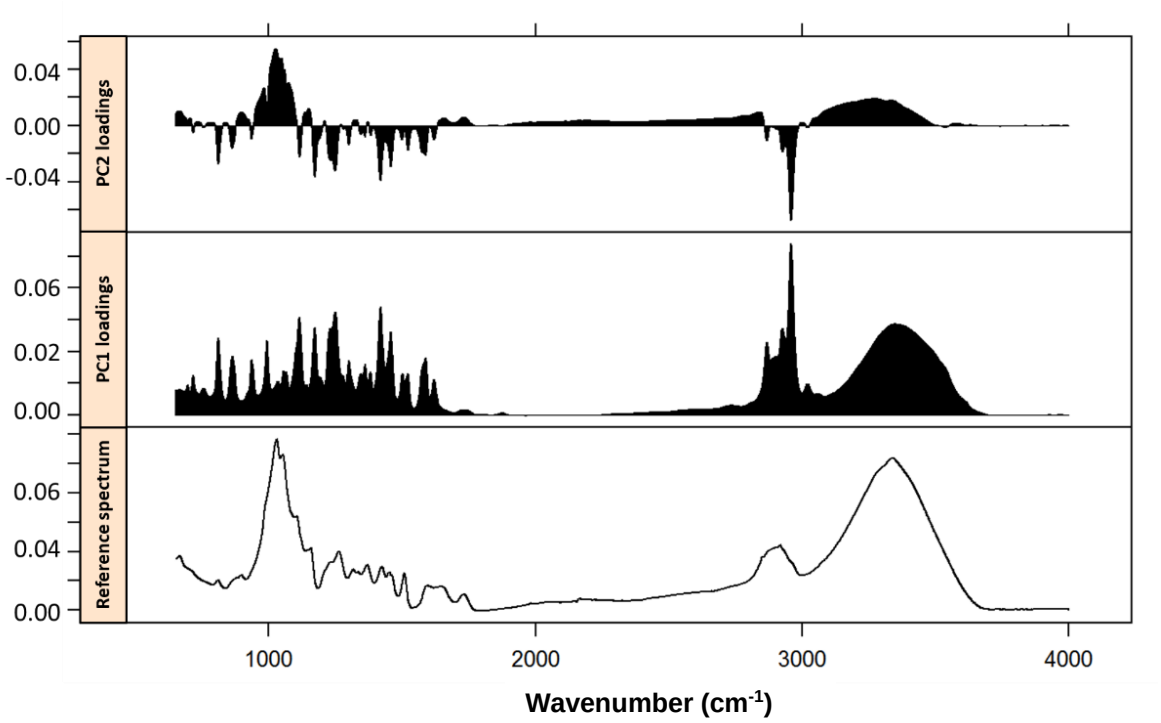

Fig. 6. The loading plots for PC1 and PC2 for the ATR-FTIR spectra of Alaska yellow cedar treated with varying concentrations of carvacrol

The extractives content of Alaska yellow cedar is reported to be between 3% and 5% (wt/wt) (Kirker *et al.* 2013). Thus, the ability of IR spectroscopy to detect a single extractive at 3.5%, as shown in the current study, provides the potential for quantitative and qualitative assessment of extractives and, indirectly, wood durability. Better prediction may be possible using wood species with higher extractives content (Sjöström 1993; Amusant *et al.* 2007), although more extensive testing is required to establish a relationship between extractives and durability.

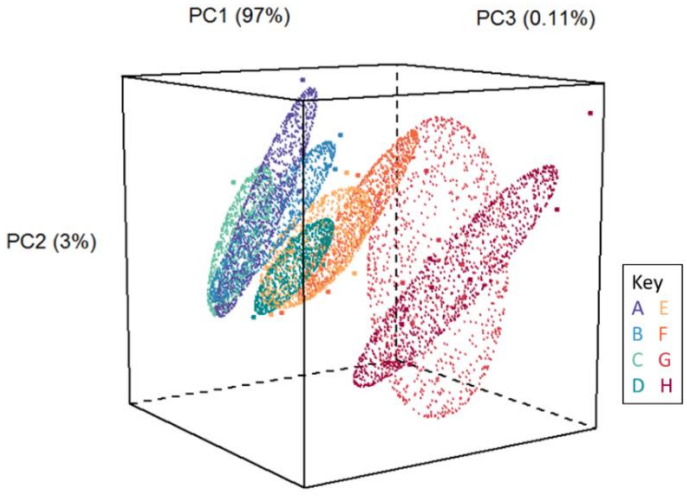

Fig. 7. Score plot using the classic method showing three-dimensional representations of the first three principal components (PCs) of the ATR-FTIR spectra of Alaska yellow cedar treated with different concentrations of carvacrol (A = 0%, B = 1%, C = 3%, D = 5%, E = 10%, F = 15%, G = 50%, and H = 100%)

The heterogenous nature of wood made the spectral analysis complex and challenging. Continued advancements in chemometrics analysis and the development of more sensitive spectrometers might improve the process, but the technique could still provide only a relative guide to durability. Furthermore, spectral pretreatments and examinations of more wavelength ranges prior to chemometrics analysis could help improve predictions. Various forms of data pre-processing (*e.g.*, no pre-processing, offset correction, multiple scatter correlation, and first and second derivatives) have been explored (Candolfi *et al.* 1999; Byrne *et al.* 2016). However, additional studies using specific extractives could help optimize the quantification and prediction of these compounds as an indirect measure of durability. Data pre-processing, specifically the use of first and second derivatives, should be explored in the future and might improve the classification. Several studies have utilized derivatives in spectral analysis and showed better prediction models relating to other wood quality parameters (Schwanninger *et al.* 2004; Wang *et al.* 2015a). Further studies on the relationship between the extractives content, resistance to fungal or insect attacks, and spectral information will be required to determine the feasibility of using IR spectroscopy for rapid, non-destructive determination of wood durability.

CONCLUSIONS

1. ATR-FTIR spectra detected changes in the carvacrol levels in Alaska yellow cedar at low concentrations, which suggested the potential for the qualitative and quantitative analysis of extractives in wood.
2. The NIR spectra detected differences in the carvacrol levels but were less sensitive to these differences. The chemometric analysis of the FTIR spectra was capable of more clearly delineating the carvacrol levels in the Alaska yellow cedar samples.

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