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Rapid analysis of inner and outer bark composition of Southern Yellow Pine bark from industrial sources

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Abstract Differences in bark chemistry between inner and outer bark are well known and may affect the suitability of various bark supplies for a particular application. Accordingly, there is a need for quality control protocols to assess variability and predict product yields. Southern yellow pine bark samples from two industrial sources were separated into inner and outer bark tissues and used to prepare both predetermined and random bark compositions for analysis. Near infrared (NIR) spectroscopy, coupled with multivariate analysis, was successfully used to develop models to predict relative amounts of inner bark. Application of mathematical treatments to the NIR data improved the calibration performance leading to improved predictions for the test samples. Results presented here show promise for the further development of this technique as a means to provide rapid and accurate predictions of the quality of bark obtainable from industrial sources.

Schnellbestimmung der Zusammensetzung von Bast und Borke von kommerziell genutzter Southern Yellow Pine

Zusammenfassung Es ist bekannt, dass die chemische Zusammensetzung von Bast und Borke voneinander abweicht und sich dies auf die Eignung für bestimmte Verwendungen auswirken kann. Aus diesem Grunde ist eine Qualitätskontrolle zur Beurteilung der Schwankungen und zur Abschätzung der Ausbeuten notwendig. Aus zwei verschiedenen Holz verarbeitenden Betrieben wurden Rindenproben von Southern Yellow Pine entnommen und in Bast und Borke getrennt. Daraus wurden für weitere Untersuchungen Proben mit vorgegebenem und zufälligem Mischungsverhältnis hergestellt. Mittels NIR-Spektroskopie und multivariater Datenanalyse konnten Modelle zur Bestimmung des Anteils an Bast entwickelt werden. Durch weitere mathematische Modellierung der NIR-Daten konnte die Aussagegenau-

igkeit des Verfahrens weiter verbessert werden. Die vorliegenden Ergebnisse zeigen, dass diese Methode zur schnellen und genauen Vorhersage der Qualität von Rinde aus Holz verarbeitenden Betrieben grundsätzlich geeignet ist.

1 Introduction

Tree bark can be subdivided into the living inner bark (phloem) and non-living outer bark (rhytidome). The inner bark includes all tissues from the vascular cambium to the innermost periderm; the outer bark includes the tissues outside this periderm and serves the function of protecting the living inner bark. As a tree grows, new periderms are formed that seal off older phloem and thereby add tissue to the outer bark. Details on bark anatomy for several southern yellow pines (e.g., *Pinus taeda* L., *Pinus palustris* L., etc.) are well documented (Howard 1971). Together the inner and outer barks generally comprise 10%–20% of the tree stem with higher percentages for the branches in the crown (Fengel and Wegener 1983). Since the debarking of harvested timber typically takes place at centralized processing facilities, large amounts of bark are readily available for utilization as a fuel, raw material for mulch products, and as a resource for specialty chemicals. Southern yellow pine bark supplies generated by lumber, panel, and paper mills in the southeastern United States are of specific interest. The high degree of similarity among these pine species, and the fact that many facilities process almost exclusively one species, generally *P. taeda*, affords a bark resource that may have uses well beyond its fuel value.

Depending upon the level of detail needed, or suggested applications, researchers characterize the inner and outer barks separately. Several studies on the cell wall and extractives chemistry of the inner and outer barks have shown significant differences (Freire et al. 2002, Hafizoglu et al. 1997, Pearl and Buchanan 1976). For example, the amount of aqueous ethanol-soluble materials in benzene ethanol extracts were 4-fold greater for the inner bark; the amounts of specific components (e.g., fatty acids, fatty alcohols, sterols) also showed significant differences (Pearl

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and Buchanan 1976). Given that there are caveats for the absolute characterization of the cell wall components, data indicate that the outer bark is lower in polysaccharides and more lignified (Eberhardt and So 2005, Hafizoglu et al. 1997, Pearl and Buchanan 1976). It is readily apparent that the relative ratios of inner and outer bark would dictate specialty chemical yields and the performance of bark-based products (e.g., mulch, composites). A facile technique to determine the relative amounts of inner and outer bark in industrial supplies is therefore of interest.

Near infrared spectroscopy (NIR) coupled with multivariate analysis is gaining wide use for the prediction of the chemistry and properties of wood (Kelley et al. 2004a) and agricultural residues (Kelley et al. 2004b). In the case of bark, recent reports have demonstrated the applicability of this technique to determine the amount of hot water extractives (e.g., tannins) in samples of black wattle (*Acacia mearnsii* De Wild) and radiata pine (*Pinus radiata* D. Don) barks (Schimleck and Yazaki 2003a, Schimleck and Yazaki 2003b). For samples of southern yellow pine bark obtained from different sources (e.g., paper mill, plywood plant), we observed that different ratios of inner and outer bark were reflected by differences in sugar and lignin contents (Eberhardt and So 2005). A preliminary assessment with bark from one source suggested that NIR spectroscopy, coupled with multivariate analysis, may be useful for bark characterization. Here we report a more rigorous assessment of this methodology to predict the relative ratios of inner to outer bark for industrial bark samples from different sources.

2 Materials and methods

2.1 Preparation of bark samples

Southern yellow pine bark samples (essentially all *P. taeda*) were obtained from a local plywood plant (PP) and a local pulp mill (PM). The bark from the plywood plant contained many small pieces of friable outer bark whereas the bark from the paper mill was mostly a stringy inner bark with attached outer bark. Samples of air-dried bark were ground as received in a Wiley mill equipped with a No. 10 mesh screen. Samples of inner and outer bark were prepared by peeling bark fragments apart, drying, and grinding as above. Aliquots of the milled bark samples were dried in an oven ($103 \pm 2^\circ\text{C}$) to determine the average moisture content ($10.5 \pm 1.1\%$). The milled inner and outer barks were made to five predetermined compositions (0, 25, 50, 75, and 100 wt % inner bark) in triplicate for a calibration set, with another fifteen prediction samples made to random compositions. This was carried out for both bark sources (PP and PM), with a third sample set created by combining them both (ALL). Summary statistics for these sets are shown in Table 1.

2.2 Spectroscopy and model development

NIR spectra of milled bark samples (1 g each) were obtained with an ASD Field Spec Pro (Analytical Spectral Devices, Boul-

Table 1 Summary statistics of inner bark content for sample sets
Tabelle 1 Übersicht über den Anteil an Bast der verschiedenen Stichproben

| Sample Set | Calib/Pred | Inner Bark Content | | | |
|------------|------------|--------------------|-------|------|----------|
| | | Min | Max | Mean | St. Dev. |
| PP | Calib | 0.0 | 100.0 | 50.0 | 36.6 |
| | Pred | 11.0 | 92.0 | 52.4 | 25.4 |
| PM | Calib | 0.0 | 100.0 | 50.0 | 36.6 |
| | Pred | 9.0 | 96.0 | 52.6 | 28.6 |
| ALL | Calib | 0.0 | 100.0 | 50.0 | 36.0 |
| | Pred | 9.0 | 96.0 | 52.5 | 26.6 |

der, CO) spectrometer. The spectra were collected at 1 nm intervals over a wavelength range of 350–2500 nm. Samples were transferred to a bottle cap, leveled, and rotated at 45 rpm to minimize specular interference and surface heterogeneity. Spectra were collected with a fiber optic probe oriented perpendicular to the sample surface while illuminated with a DC lamp oriented at 30 degrees above the surface (So et al. 2004a).

Multivariate analysis of the data was performed using the Unscrambler (version 8.0) software, CAMO, Corvallis, OR. The NIR spectra were first averaged to one spectrum per sample. Principal component analysis (PCA) was used to observe any clustering and/or separation in each of the sample sets, while partial least squares (PLS) regression was used to predict the amount of inner bark in the samples. Models were generated using full cross validation (Martens and Naes 1989) with the number of factors limited to only two due to the low number of samples. The effect of standard mathematical treatments on the calibrations was also studied. First and second derivatives of the spectra were obtained using the Savitsky-Golay technique with left and right gaps of 10 nm. Multiplicative scatter correction (MSC) was also applied to the untreated spectra. The performance of the models was assessed using several common statistical measures. The correlation coefficient, R^2 , is a measure of the strength of the fit to the data, and the root mean square error of calibration or prediction (RMSEC or RMSEP) is a measure of the calibration or prediction error in the fit, and is often expressed as a percentage of the mean value of interest (% RMSEC or % RMSEP of mean).

3 Results and discussion

Since there are anatomical and chemical differences between the inner and outer barks of trees, either the inner or outer bark may be more suitable for a target application. We have observed that southern yellow pine bark, from different sources, differ in their amounts of outer bark relative to inner bark. This undoubtedly results from the age/size of the roundwood processed, the debarking system, and handling operations for the bark residues. Accordingly, should a target application for bark residues perform better with either inner or outer bark, quality control measures would be needed to select bark supplies for processing and predicting product yields.

3.1 Spectroscopy and model development

Our initial assessments suggested that without the application of mathematical treatments to the data, multiple factors would be needed to obtain strong correlations. Since mathematical treatments are often used to improve calibration performance (Martens and Naes 1989, Honigs 1992, So et al. 2004b), first and second derivatives and multiplicative scatter correction (MSC) were applied to our NIR data prior to analysis. Typical examples of the treated (and untreated) spectra between 1100–2500 nm are shown in Fig. 1. It was immediately evident that the second derivative spectrum exhibited high levels of noise above 2000 nm, suggesting that it might be beneficial, in this situation, to use narrower wavelength ranges.

Principal component analyses (PCA) were carried out incorporating all the samples. These were compared using different wavelength ranges (1100–2000 nm and 1100–2500 nm) as well as different mathematical treatments. The clearest results were observed with the PCA scores plot for the first derivative data, using the smaller wavelength range (Fig. 2), showing separation between the PM (filled shapes) and PP (unfilled shapes) bark samples. The inner bark values show a gradation in inner bark composition for the calibration samples, along principal component 1, with the prediction samples of random composition interspersed between the calibration samples. Given these results, partial least squares (PLS) modeling was then performed on the NIR spectra to predict inner bark content.

For each of the three samples sets (PP, PM and ALL), the predetermined compositions were used for calibration and the random compositions as the prediction sets. A comparison of calibrations was first undertaken between the wavelength ranges of 1100–2000 nm and 1100–2500 nm showing the second derivative transformation fared much poorer in the larger range, clearly due to the excessive noise in the spectra. The untreated and MSC results were also poorer, with only the first derivative leading

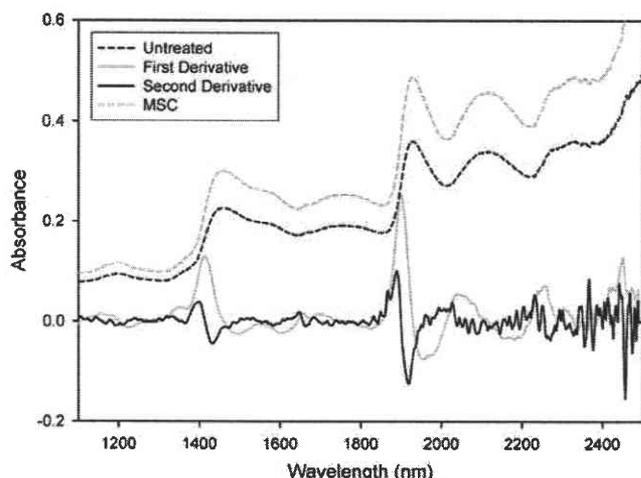


Fig. 1 Treated and untreated NIR spectra of bark between 1100–2500 nm (scaled to fit)

Abb. 1 Mathematisch umgeformte und originale NIR-Spektren von Rinde im Bereich von 1100 und 2500 nm

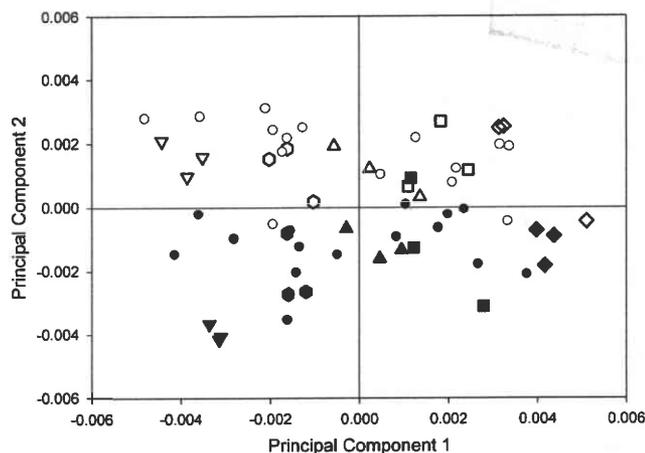


Fig. 2 PCA scores plot of PP (unfilled) and PM (filled) bark samples based on first derivative data between 1100–2000 nm. Inner bark levels of: 0 (diamond), 25 (square), 50 (upward triangle), 75 (hexagon) 100% (downward triangle) and random prediction (small circle) samples are denoted
Abb. 2 Hauptkomponentenanalyse von Rindenproben aus einem Sperrholzwerk (PP, nicht ausgefüllte Symbole) und aus einem Zellstoffwerk (PM, ausgefüllte Symbole) im Bereich von 1100 und 2000 nm. Anteil an Bast: 0% (Raute), 25% (Quadrat), 50% (nach oben gerichtetes Dreieck), 75% (Sechseck), 100% (nach unten gerichtetes Dreieck) und zufälliges Mischungsverhältnis (Kreis)

to a slight improvement in the correlations. For subsequent assessments, only the results obtained using the 1100–2000 nm were considered.

In this study, the number of factors was limited to only two, with the Unscrambler software determining whether one or two factors were selected. Excellent correlations were obtained between the measured and NIR-predicted inner bark levels for the calibration samples. An example is shown in Fig. 3 for the ALL

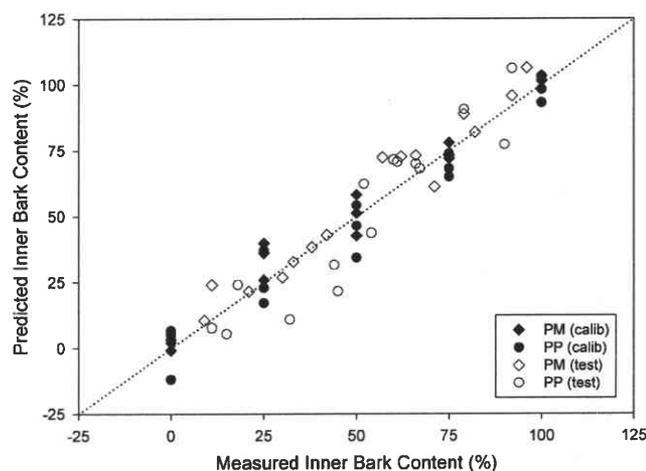


Fig. 3 Relationship between predicted and measured inner bark content using the ALL calibration and prediction samples based on first derivative data between 1100–2000 nm

Abb. 3 Zusammenhang zwischen geschätztem und gemessenem Anteil an Bast unter Verwendung aller Proben und der Werte im Bereich von 1100 und 2000 nm

calibration and prediction sets using the first derivative transformation. The prediction samples, with their random compositions, can be seen to provide a strong fit with the calibration data. Tables 2 and 3 list the calibration and prediction statistics for all the sample/treatment combinations. These show that direct comparisons between samples and/or treatments cannot always be made due to the varying number of factors required. Thus, the statistics for models based on one factor are also listed in the brackets. In some cases, mathematical treatments using only one factor outperformed the other treatments with two factors, this was the case for the ALL sample set with the first derivative. It was very evident that a large improvement was observed with the untreated data for the PP and PM sample sets when using two factors; this effect was much smaller for the treated data.

Table 2 Calibration statistics for inner bark content (numbers in brackets correspond to the values based on one factor)

Tabelle 2 Kalibrierungsergebnisse für den Anteil an Bast (Die Zahlen in Klammern geben die Werte bei nur einem Faktor an)

| Sample Set | No. of Samples | Mathematical Treatment | Factors | R ² | RMSEC ^a | % RMSEC of mean |
|------------|----------------|------------------------|---------|----------------|--------------------|-----------------|
| PP | 15 | None | 2(1) | 0.96(0.58) | 6.71(22.78) | 13.4(45.6) |
| | | 1 st Deriv. | 2(1) | 0.97(0.94) | 6.13(8.63) | 12.3(17.3) |
| | | 2 nd Deriv. | 1(1) | 0.92 | 9.82 | 19.6 |
| | | MSC | 1(1) | 0.96 | 6.85 | 13.7 |
| PM | 15 | None | 2(1) | 0.88(0.29) | 12.05(29.78) | 24.1(59.6) |
| | | 1 st Deriv. | 1(1) | 0.98 | 4.39 | 8.8 |
| | | 2 nd Deriv. | 2(1) | 0.96(0.95) | 6.83(7.93) | 13.7(15.9) |
| | | MSC | 1(1) | 0.92 | 9.81 | 19.6 |
| ALL | 30 | None | 2(1) | 0.79(0.77) | 16.39(16.81) | 32.8(33.6) |
| | | 1 st Deriv. | 1(1) | 0.96 | 6.89 | 13.8 |
| | | 2 nd Deriv. | 2(1) | 0.95(0.92) | 8.28(9.75) | 16.6(19.5) |
| | | MSC | 2(1) | 0.91(0.89) | 10.47(11.97) | 20.9(23.9) |

^a RMSEC is the root mean square error of prediction

Table 3 Prediction statistics for inner bark content (numbers in brackets correspond to the values based on one factor)

Tabelle 3 Vorhersagegenauigkeit für den Anteil an Bast (Die Zahlen in Klammern geben die Werte bei nur einem Faktor an)

| Sample Set | No. of Samples | Mathematical Treatment | Factors | R ² | RMSEP ^a | % RMSEP of mean |
|------------|----------------|------------------------|---------|----------------|--------------------|-----------------|
| PP | 15 | None | 2(1) | 0.87(0.44) | 11.02(22.76) | 21.0(43.4) |
| | | 1 st Deriv. | 2(1) | 0.91(0.83) | 9.80(13.72) | 18.7(26.2) |
| | | 2 nd Deriv. | 1(1) | 0.82 | 15.53 | 29.6 |
| | | MSC | 1(1) | 0.87 | 11.63 | 22.2 |
| PM | 15 | None | 2(1) | 0.81(0.04) | 15.21(31.58) | 28.9(60.0) |
| | | 1 st Deriv. | 1(1) | 0.95 | 6.26 | 11.9 |
| | | 2 nd Deriv. | 2(1) | 0.95(0.94) | 6.89(7.97) | 13.1(15.2) |
| | | MSC | 1(1) | 0.86 | 10.81 | 20.6 |
| ALL | 30 | None | 2(1) | 0.60(0.64) | 20.03(18.33) | 38.1(34.9) |
| | | 1 st Deriv. | 1(1) | 0.89 | 10.23 | 19.5 |
| | | 2 nd Deriv. | 2(1) | 0.90(0.86) | 11.21(12.45) | 21.4(23.7) |
| | | MSC | 2(1) | 0.80(0.79) | 12.83(13.33) | 24.4(25.4) |

^a RMSEP is the root mean square error of prediction

Comparing calibrations, using only one factor, it is clear to see that the application of mathematical treatments to the calibration data greatly improved the R² and RMSEC values (Table 2). The first derivative models generally performed the best followed by the second derivative, multiplicative scatter correction (MSC) and lastly, the untreated models. Donkin and Pearce (1995) similarly found that a first derivative transformation of the data outperformed all other standard transformation techniques for tannin analysis. Although the wavelength range was reduced to 1100–2000 nm, the second derivative correlations may still have been affected by noise. The spectrum in Fig. 1 appears relatively noisy compared to those of Schimleck and Yazaki (2003a), (2003b) even accounting for gap sizes. They developed calibrations with very good R² values for NaOH extractives, Stiasny value, hot water extractives, and polyflavonoid content using second derivative transformations. It was also shown that the sample sets all behaved fairly similarly with the PM sample set performing slightly better than the ALL or PP samples.

The calibrations were tested by predicting inner bark values for new samples; these prediction sets are listed in Table 1. As one may expect, the correlations for the predictions were, in most cases, clearly poorer than their calibration counterparts (Table 3). One exception was the PM sample set which was shown to have excellent correlations in prediction, only slightly poorer than in calibration, providing an indication of the strength of these models. The other sample sets also provided acceptable predictions except for those with no treatment in which the % RMSEP of mean was noticeably high. The performance of these calibrations and predictions indicate that this technique can be used to reliably estimate inner and outer bark compositions for the southern yellow pines. Applications of this technique to bark supplies from other softwood or mixed hardwood furnishes may also be feasible. However, significant differences in the NIR spectra for the inner barks from each species in the mixture, as well as those for the outer bark, would adversely affect the calibrations. Refinement of the models to account for seasonal variations would only be needed to address changes, if any, in the inner bark; the outer bark is essentially non-living, and therefore, significant changes during the year would be unlikely. Seasonal variation in extractives compositions could be addressed by adjusting projected product yields by analytical data corresponding to the time of year that the bark is processed.

4 Conclusions

NIR spectroscopy coupled with multivariate analysis can be used to develop models to predict relative amounts of inner and outer bark in industrial bark samples, thus allowing the bark to be sorted for particular applications. The results show that calibrations performed well when applied to the prediction sets. It was evident that the application of mathematical treatments to the NIR data improved both the calibration and prediction performance, often requiring fewer factors. In practical terms, measurement of

the relative ratio of inner to outer bark by this technique, coupled with analytical data for both of these components, shows promise as a quality control tool for predicting compositions of bark obtainable from industrial sources.

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