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Section 1 **Biology**

Natural durability, ethanol-toluene extractives and phenol content prediction of eight wood species from Madagascar using NIRS multispecific models

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ABSTRACT

Madagascar has nearly 4000 species of trees and shrubs, but wood properties of only 200 species have been studied. Some properties, such as the natural durability or chemical composition are of importance for adequate and optimal use of these timber species. Since durability tests take long time and chemical analyzes can be very expensive, alternative methods such as near infrared spectroscopy (NIRS) and calibration, could be used to characterize these properties. Thus, the objective of this study is to analyze the NIRS potential to predict natural durability and chemical composition for eight (8) species from rainforest of eastern Madagascar.

Natural durability tests in the laboratory were conducted on both leached and un-leached wood samples. Two types of fungi (Coniophora puteana and Coriolus versicolor) were used. The chemical composition analyzed were ethanol-toluene extractives and phenol content. The NIR spectra were acquired with a microNIR spectrometer (spectral range: 950-1650 nm, spectral resolution: 6.2 nm) on the solid unleached wood samples. Models were established with PLS regression, with wavelength selection, using the best pre-processing method and tested with repeated cross-validation method. Results showed that for each property, samples can be considered to have enough variability to allow the establishment of a good prediction model. Established models are evaluated satisfactory to good, with R2CV always higher than 0.69. Concerning the model for phenol content, R2CV is 0.89. For mass loss, R2CV ranges from 0.71 to 0.79. These models can be used to predict wood properties and can be improved by including new samples. In the future, it would be interesting to analyze these reference samples but using a more efficient spectrometer with a wider spectral range to establish NIRS models.

Keywords: Natural durability, extractives, phenol, multispecific model, prediction, Near Infrared Spectroscopy

1. INTRODUCTION

Madagascar has nearly 4000 species of trees and shrubs (MEF 2009), but only the wood properties of at least one tenth of these species have been characterized (Rakotovao *et al.* 2012, Ramananantoandro *et al.* 2015). This rich biodiversity is an asset and should be valorized. But due to lack of information about wood properties, this rich biodiversity is used and valorized to an inappropriate use and has been under evaluated. So the properties of these wood species should be characterized for their adequate use.

Thus, in the framework of the SPIRMADBOIS project (Ramananantoandro *et al.* 2016), a study of the natural durability, in connection with chemical composition, was carried out concerning some species from the eastern Madagascar rainforest. Various tests of natural durability and determination of the chemical composition of wood were then made from samples belonging to eight (8) species of the Mandraka forest. Since durability tests take long time and chemical analyzes can be very expensive, then attempts have been made to establish multispecifc NIRS prediction models for these properties. According to their performance, models could be used later to predict the natural durability and chemical composition of other samples. There are already previous studies on the NIRS prediction of wood natural durability and chemical properties, which have been successful for such predictions (Esteves and Pereira 2008, Meder *et al.* 1999, Gierlinger *et al.* 2003, Barré *et al.* 2017). But most of these studies have used high-performance spectrometers (high spectral resolution and wide spectral range). It would be interesting to test the ability of a portable and less expensive device to predict these properties. Moreover, few studies on natural durability and chemical composition have been yet performed on Malagasy species. No study on mulispecific NIRS model calibration concerning the natural durability and chemical composition of Malagasy species has been developed. And finally, the use of a portable microNIR spectrometer that is adapted on the malagasy context is interesting.

Thus, the objective of this study is to establish and analyze multispecific NIRS prediction models for natural durability and chemical composition based on 8 species from of the rainforest of eastern Madagascar, using portable NIRS device.

2. EXPERIMENTAL METHODS

This study is focused on 7 indigenous species (*Tambourissa trichophylla* (“ambora”), *Agauria* sp. (“angavo”), *Trilepisium madagascariense* (“dipaty”), *Neotina isoneura* (“felamborona”), *Garcinia* sp. (“kija”), *Weinmannia rutenbergii* (“lalona”) *and Nuxia capitata* (“valanirana”)) and an introduced species (*Cedrela odorata (“cedrela”)*). 11 to 15 samples per species were considered, with a total of 110 samples. Those samples were taken from trees growing in Mandraka forest and 4 to 5 trees per species were cut. Wood samples were taken at breast height at regular intervals from the pith to the bark to consider radial variability.

Spectra were measured on these wood samples with a VIAVI MicroNIR 1700 spectrometer device (spectral range: 950-1650 nm, spectral resolution: 6.2 nm). The spectra were acquired on the transversal plane of the solid un-leached wood and stabilized at 20°C, 65% Relative Humidity.

Regarding measurements of reference values:

- Normalized natural durability tests were carried out at CIRAD (Montpellier) laboratory using 2 types of fungus : *Coniophora puteana* (CP) and *Coriolus versicolor* (CV). Tests were carried out on leached (according to EN 84, 1997) and un-leached wood samples according to the standard XP Cen TS 15083-1 (2006).
- Chemical composition measurement was carried out at “Ecole Supérieure du Bois (ESB)” in Nantes. The two chemical compositions analyzed were the ethanol-toluene extractives and the phenol content because natural durability is largely due to these wood properties (Taylor *et al.* 2002). Extractives were determined according to standard TAPPI method T 204 om-88 adapted using organic solvents (ethanol and toluene). And for the determination of the phenol content, Folin-Ciocalteu method (Singleton and Rossi 1965) was used.

NIRS calibration models were established using PLS method (Wold 1966, Geladi and Kowalski 1986), with wavelength selection. Spectral outliers were also detected and removed. Nine (9) types of spectral pre-processing methods were tested (Standard Normal Variate, detrending, first derivative, second derivative and their combination) and the best pretreatment has been considered in each case. The models were subsequently tested in repeated cross-validation (with 50 repetitions) with 4 randomly established cross-validation groups. The parameters used for model validation were R^2, RMSE and RPD. All analyzes were performed on R version 3.0.2 software (R Development Core Team 2016).

2. RESULTS AND DISCUSSIONS

For each property (ethanol-toluene extractive content; phenol content; CP mass loss and CV mass loss on leached and un-leached wood samples), the reference values used differ significantly from one species to another. Samples can be considered to have enough variability to allow the establishment of a good prediction model. For extractives, the reference values range from 0.72 to 12.00% and from 2.59 to 89.66 µg/g for the phenol content. Respectively for the leached and un-leached wood samples, the values of the mass loss by CP attack vary from 1.2 to 55.0% and from 2.5 to 51.5% for, mass loss by CV attack from 3.5 to 48.6% and from 6.5 to 54.4% (table 1). Based on the species median mass loss and type of fungus attack, the class of durability of these species vary from not durable (class 5) to very durable (class 1) (table 2).

Table 1: Natural durability and chemical composition: mean and standard deviation

	Ethanol-toluene extractives [%]	**Phenol [µg/g]**	**Natural durability - mass loss [%]**			
			Inoculation with *Coniophora puteana*		**Inoculation with *Coriolus versicolor***	
			un-leached wood samples	**Leached wood samples**	**un-leached wood samples**	**Leached wood samples**
Total number of samples	35	50	108	106	106	110
Agauria sp.	8.74 (3.47)	56.99 (28.94)	3.13 (1.92)	7.42 (4.73)	17.7 (10.93)	21.18 (8.93)
Cedrela odorata	4.78 (1.27)	20.36 (9.34)	28.23 (16.11)	23.94 (11.8)	27.05 (10.5)	32.08 (12.39)
Garcinia sp.	1.96 (1.26)	4.21 (0.43)	25.02 (6.52)	29.04 (7.7)	28.66 (2.29)	32.73 (6.28)
Neotina isoneura	5.76 (0.91)	8.80 (3.40)	24.54 (5.92)	28.74 (6.61)	35.43 (5.79)	38.92 (5.45)
Nuxia capitata	7.51 (2.06)	11.22 (1.76)	5.75 (3.32)	11.88 (8.17)	8.40 (2.45)	12.33 (3.34)
Streblus dimepate	3.16 (0.29)	4.36 (0.92)	36.09 (10.15)	39.08 (5.44)	37.53 (5.31)	41.08 (6.26)
Tambourissa tricophylla	3.01 (2.59)	4.21 (2.48)	9.97 (6.76)	34.5 (13.8)	21.53 (2.98)	27.15 (4.51)
Weinmannia rutenbergii	5.80 (1.20)	8.90 (3.78)	26.29 (7.65)	23.61 (5.49)	29.9 (7.02)	25.5 (5.57)
Pinus sylvestris (control virulence)	-	-	37.16 (11.60)	33.74 (2.95)	-	-
Fagus sp. (control virulence)	-	-	41.85 (3.94)	35.12 (1.59)	34.78 (2.92)	34.12 (6.37)

The quality of the NIRS prediction models for all analyzed properties is summarized in Table 3. The quality of the models can be considered satisfactory to good with R^2_{CV} always higher than 0.69. The best model concerns the phenol content with a R^2_{CV} of 0.89 and a RPD_{CV} of 3.15. For natural durability, models are satisfactory whether for mass loss for leached and un-leached wood samples with R^2_{CV} ranging from 0.71 to 0.77.

NIRS model for phenol content is better than ethanol-toluene extractives model. Wood extractives include heterogeneous groups of chemical compounds, and they can also be grouped by the type of solvent used during their extraction. Some may be better predicted than others, for example

Esteves and Periera (2008) obtained R^2_{CV} of 0.64 for ethanol extractives and 0.84 for total extractives based on 24 samples.

Table 2 : Median mass loss and class of durability

	Natural durability - mass loss [%]			
	Inoculation with *Coniophora puteana*		Inoculation with *Coriolus versicolor*	
	Un-leached wood samples	Leached wood samples	Un-leached wood samples	Leached wood samples
Total number of samples	**108**	**106**	**106**	**110**
Agauria sp.	2.69 (class 1)	6.74 (class 2)	19.78 (class 3)	23.38 (class 4)
Cedrela odorata	30.97 (class 5)	27.13 (class 4)	29.32 (class 4)	33.92 (class 5)
Garcinia sp.	25.47 (class 4)	29.82 (class 4)	27.92 (class 4)	33.57 (class 5)
Neotina isoneura	25.85 (class 4)	28.46 (class 4)	35.40 (class 5)	39.21 (class 5)
Nuxia capitata	4.81 (class 1)	8.06 (class 2)	7.63 (class 2)	12.23 (class 3)
Streblus dimepate	37.19 (class 5)	38.88 (class 5)	37.39 (class 5)	41.75 (class 5)
Tambourissa tricophylla	7.03 (class 2)	36.72 (class 5)	21.23 (class 4)	27.10 (class 4)
Weinmannia rutenbergii	27.09 (class 4)	24.71 (class 4)	29.99 (class 4)	27.77 (class 4)
Pinus sylvestris (control samples)	33.95 (class 5)	33.85 (class 5)	-	-
Fagus sp. *(control samples)*	40.65 (class 5)	35.450 (class 5)	35.99 (class 5)	33.90 (class 5)

Class 1: very durable; class 2: durable; class 3: moderately durable; class 4: slightly durable; class 5: not durable

The number of latent variable of the models are quite high, but the wavelength numbers selected are weak, hence more robust models. The results obtained in this study are in agreement with those found in the literature. Gierlinger *et al.* (2003) obtained on larch species a R^2_{CV} of 0.97 for CP mass loss and a R^2_{CV} of 0.91 using the 1003-1961 nm spectral range for mass loss after *Pria placenta* attack. Sykacek *et al.* (2006) obtained a R^2_{CV} = 0.93 on mass loss after *Gloeophyllum trabeum* attack on several species and with 1003-2439 nm spectral range. Gerlinger (2003) also obtained on larch wood a R^2_{CV} of 0.97 for total phenol using the 1003-1961 nm spectral range.

Table 3: Results of PLS models with wavelength selection and applying the best pre-processing methods

	Ethanol-toluene extractives	Phenol	Natural durability - mass loss			
			Inoculation with *Coniophora puteana*		Inoculation with *Coriolus versicolor*	
			Un-leached wood samples	Leached wood samples	Un-leached wood samples	Leached wood samples
N samples	34	46	108	106	106	110
N outliers	01	04	01	04	03	00
N LV	02	06	09	08	11	09
R^2_C	0.72	0.94	0.77	0.85	0.84	0.77
R^2_{CV}	0.64	0.89	0.71	0.79	0.77	0.71
RMSECV	1.54	5.39	7.64	5.91	5.49	6.12
RPD_{CV}	1.71	3.15	1.85	2.20	2.08	1.88
N var	04	10	16	24	16	14

N samples: Number of samples; N LV: Number of latent variable; R^2_C: coefficient of determination of calibration; R^2_{CV}: coefficient of determination of cross validation; RMSECV: root mean square error of cross validation; RPD_{CV}: Ratio Performance Deviation in cross validation; RMSECV: root mean square error of cross validation; N outliers: Number of outliers; N var: Number of wavelength selected

Nevertheless, quality of models obtained in this study can be explained by the spectral range used being rather restricted (950-1650 nm). The selection of wavelengths has improved the model, with 4 to 24 wavelengths selected out of 113. Wenming and Huiren (2013) found that 1600-2380 nm spectral range is well suited for extractives than the NIR spectral range bellow. Concerning the mass loss, most of the spectral range used in studies with good NIRS models is greater than 1650 nm.
Although our models are slightly less efficient compared to those that the authors have previously found, it can be said that the portable microNIR spectrometer is suitable for developing country contexts since the high performing laboratory spectrometer is very expensive, and that it is suitable for predicting natural durability and chemical composition. Even so, these models could be improved for a better prediction of the properties, mainly by including new samples in the set of calibration to have more variability.

3. CONCLUSIONS

This study allowed to evaluate the quality of the NIRS multispecific models concerning natural durability and some chemical compositions using the microNIR spectrometer. The models obtained are satisfactory to good, but could be improved for a better prediction of the properties, mainly by including new samples to have more variability. The models were established with wavelength selected so that these established models can be very specific to the species in the calibration set and may not be well suited for predicting properties on other species. Thus, studies on the transfer of calibration between species should be carried out. Moreover, this study is the first analyzing NIRS model calibration concerning the natural durability and chemical composition of Malagasy species.
The results of these durability tests were obtained in the laboratory by standardized methods while the agents of degradation of wood in a natural environment in Madagascar can be varied and different. Thus, it would be interesting to analyze the relationship between the results of natural durability tests in the laboratory and those obtained in the field (on-going), and also to analyze the quality of the NIRS prediction models concerning the loss of mass obtained in the field. It may also be interesting to analyze these reference samples but using a more efficient spectrometer with a wider spectral range to establish NIRS models.

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