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Prediction of Acetone Extractives, Klason Lignin and One percent Sodium Hydroxyde Solubility of *Eucalyptus* spp.

Fernando Bonfiglio,^a Serrana Pieri,^b Eloísa Santana,^c Javier Doldán^d

Regardless of the final product, the chemical characterization of wood is frequently one of the first steps to evaluate the future of a plantation or to adjust the process parameters. In the case of pulp production, there are some chemical analyses that are quite simple but also give significant information. Among these, the determination of acetone extractives, Klason lignin and one percent sodium hydroxide solubility are typical and usually demanded. Despite the simplicity, their determination is time consuming, and particularly if a simultaneous determination of them is required. The Near Infrared Spectroscopy (NIRS) is useful to save time and chemical products, and the practicality of the method has already been established. This work is the continuation of a previous NIRS calibration developed with Uruguayan *Eucalyptus* spp. for Wood Basic Density and Pulp Yield made by the Forest Department of the Technological Laboratory of Uruguay (LATU). In this study, samples of Uruguayan *Eucalyptus* spp. were collected and milled. From this milled wood the chemical analyses using Tappi standards were made. In parallel, the NIR spectrum was measured for each sample. Calibration models for the three chemical determinations were developed with satisfactory results.

Keywords: Near Infrared Spectroscopy, Acetone Extractives, Klason Lignin, One percent Sodium Hydroxyde Solubility.

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INTRODUCTION

The utilization of *Eucalyptus* spp. in Uruguayan pulp mills for their production is already well established, and therefore the characterization of the wood is one of the first steps to evaluate the process conditions or the suitability of the raw material. However, most of the conventional methods are time-demanding and usually have high costs. The Near Infrared Spectroscopy (NIRS) methodology has been developed to avoid these problems, rapidly, with a precision according to the needs and comparatively low cost. There are a significant number of properties that can be analyzed in a pulp, and we have selected three for this work.

The acetone extractives determination involves measuring substances as fatty acids, resin acids, sterols, waxes and non-volatile hydrocarbons. The selection of woods for cellulose pulp production is done considering those species having low acetone-extractable content. Also the quantity found in a sample depends on

seasoning or drying of wood (Tappi T 280, 1999). The presence of wood extractives can raise the chemical reagent consumption and produce foam during pulp wash (Núñez, 2008).

The one percent sodium hydroxide solubility of wood generally indicates the degree of a fungus decay or degradation by heat, light or oxidation: an increase in the solubility means a higher decay or degradation in wood. The principal components remaining in the hot alkali solution are hemicelluloses and degraded cellulose, and therefore the determination is also an indicator of the presence of lignin (Tappi T 222, 2006).

The third determination that was calibrated by the NIRS technique was the acid insoluble lignin or Klason lignin, which represents 80 % to 90 % of the total lignin (Hausalo and Söderhjelm, 2000; Sixta 2006).

In the NIR technique, the first step consists of a determination by the conventional method of a great number of representative samples. Next, it involves the measurement of the spectra of those samples and the development of a model that can quantify the variations in the properties. Finally, this model is used to predict the value of an unknown sample by measuring the near infrared spectra.

This work, a continuation of the previous calibration developed for wood basic density and pulp yield (Bonfiglio *et al.*, 2011), shows the calibration results for those three chemical properties previously discussed that are usually demanded.

EXPERIMENTAL

Materials

Samples of trees from commercial plantations and different locations of Uruguay with ages ranging from 8 to 10 years old were collected. The different *Eucalyptus* species were *E. dunnii*, *E. grandis*, *E. globulus* ssp. *globulus*, *E. globulus* ssp. *maidenii*, *E. biscostata* and hybrids.

Methods

Preparation of the samples:

For chemical analyses and NIR spectroscopy, sample disks were reduced in size, dried at 60 °C for 3 to 4 hours, grinded and screened in order to obtain a wood powder according to TAPPI 257.

Acetone extractives:

This determination was made in accordance with TAPPI 280. The acetone-soluble materials were removed using the Soxhlet extraction method. The acetone extractives content was then expressed as a percentage of the initial mass.

Acid-insoluble lignin:

The sample was treated with a 72% sulfuric acid solution and the acid-insoluble lignin or Klason lignin was then separated by filtering, dried and weighted, in reference to TAPPI 222. The acid-insoluble lignin content was expressed as a percentage of the initial mass.

One percent sodium hydroxide solubility:

The sample is extracted with hot 1% sodium hydroxide solution in line with TAPPI 212. Then the loss in weight is determined and the solubility is expressed as a percentage of the initial mass.

Preparation of the samples for NIR spectroscopy:

The sample was stored in a condition chamber (50 ± 2 % relative humidity, 23 ± 1 °C) at least for 24 hours before NIR measurement.

NIR spectroscopy:

The equipment used to obtain the NIR spectra was a Büchi NIRFlex N-500 with NIRFlex Solids measuring cell. The wood meal was placed in a High performance sample cup for NIRFlex Solids. Each measurement had thirty two scans, and the samples were measured by triplicate. The original spectral range was from 4000 to 10000 cm^{-1} (1000 to 2500 nm) with a resolution of 4 cm^{-1} .

Chemometric statistics:

Acetone extractives, acid-insoluble lignin and one percent sodium hydroxide solubility calibrations were developed using the software package NIRCal 5.2.3000 [10] (Büchi, Switzerland). The method of calibration was partial least squares (PLS) for the three properties. The spectra were divided in Calibration-set and Validation-set. Furthermore, a wavelength selection was carried out only in the acid-insoluble lignin calibration. Normalizations and derivatives pretreatments, as well as combinations of these, were also applied. To evaluate the calibrations the statistical Q-value was considered (calculated according to Equation 1 and Table 1). The calibrations sets are shown in table 2 for the acetone extractives, acid-insoluble lignin and one percent sodium hydroxide solubility. The values shown are the ones obtained by the conventional method (*original values*) in each case.

$$\text{Equation 1: } Q = \frac{1}{1 + \sum (\text{weights} \times \text{value})}$$

where the weights and values are indicated in the Table 1.

Table 1. NirCal 5.2 Q-Value Calculation

Weights	Formula for value	General Term
10	Number of C-Set spectra with residual too big	Rejection of known
1	Number of V-Set spectra with residual too big	Rejection of unknown
2	$\text{Abs (SEE-SEP)} / (\text{Abs (SEP)} + 1.0)$	Relative consistency
2	$\text{Abs (V-set BIAS)} / \text{Abs (Range)}$	Weighted BIAS
1	$1 - \text{V-set Regression}$	Validity
1	$\text{Abs (C-Set Regression} - \text{V-Set Regression)}$	Comparability
1	$\text{SEP} / \text{Abs (Range)}$	Precision
1	$\text{Abs (RSS)} / \text{Abs (Range)}$	Weighted Accuracy

*C-Set, Calibration Set; V-Set, Validation Set; SEE, Standard Error of Estimation of the C-Set; SEP, Standard Error of Prediction; RSS, V-Set Residual error Sum of Squares

Table 2. Calibration and validation set of the different properties (conventional method values)

	Acetone extractives		Acid-insoluble lignin		1 % NaOH solubility	
	C-set	V-set	C-set	V-set	C-set	V-set
N° of samples	86	26	28	10	58	20
Minimum	0.5 %	0.6 %	20.8 %	21.3 %	13.2 %	13.4 %
Maximum	4.2 %	4.1 %	30.7 %	30.6 %	24.6 %	23.7 %
Average	1.6 %	1.6 %	24.2 %	24.4 %	17.2 %	17.2 %
SD	0.8 %	0.9 %	2.6 %	2.7 %	2.1 %	2.2 %

*C-Set, Calibration Set; V-Set, Validation (Prediction) Set; SD, Standard Deviation

RESULTS AND DISCUSSION

The original near infrared spectra (as absorbance $\log 1/R$) of the samples are shown in the figure 1. Although in the NIR spectra the organic chemical bonds are related to the different absorption bands, there is no clear connection involving the spectra baseline shifts and the different properties. An exhaustive review made by Schwanninger *et al.* (2011) details and discusses the NIR bands for wood spectra.

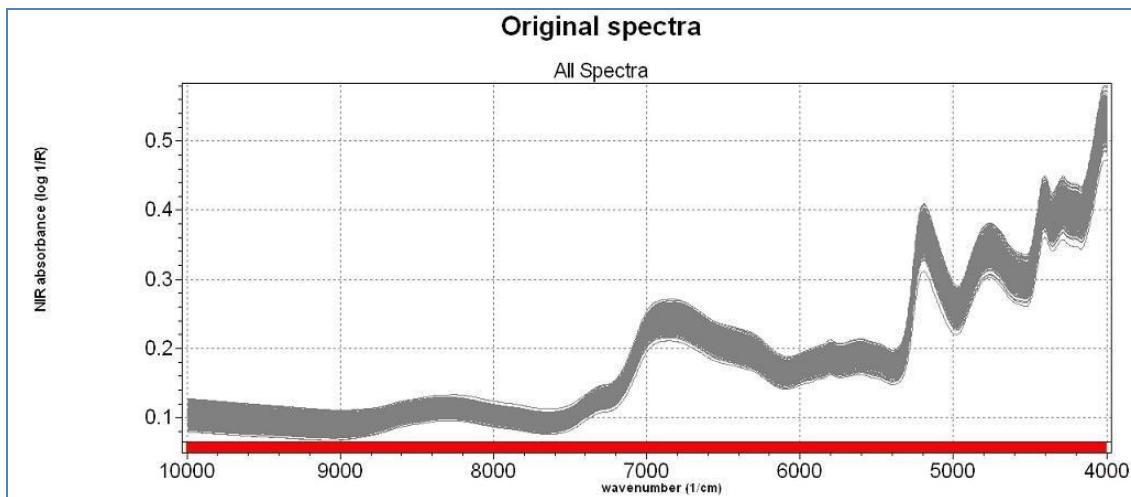


Figure 1. Original NIR spectra

Acid Insoluble Lignin (Klason Lignin)

As shown in the Table 3, the final calibration pretreatment obtained for the Klason Lignin is a Standard Normal Variate (SNV) and then a First Derivative (db1) which smoothes and eliminates the random variations in the spectrums of the samples. Figure 1 shows the good correlation between the results obtained by the conventional method determination and predicted values, as represented by the 'perfect calibration' line. However, it also shows that most of the samples are concentrated in the lower part of the calibration range resulting in a not homogenous distribution along the calibration range. Therefore, warning ranges –i.e. alert limits where the values are not completely robust- should be considered when using this calibration for future predictions. In this case, the estimated warning ranges were between 20.8 % - 21.8 % and 27.8 % - 30.7 %. Thereby, when the reported value of an unknown sample lies in the warning range, a good practice would be to analyze the sample by performing a conventional method determination. By doing this, the sample could be added to the calibration curve, improving it. When the predicted value of an unknown sample is outside the calibration limits (Table 3) it should be dismissed and a conventional method determination performed.

Table 3. NIRS calibration statistics for acid-insoluble lignin, 1% sodium hydroxide solubility an acetone extractives

Property	Q-value	V-set regression coefficient	SEP	Pretreatments	Factors
Acid-insoluble lignin	0.82	0.99	0.42	SNV, db1	4
1% sodium hydroxide solubility	0.72	0.93	0.80	MSC-full	8
Acetone extractives	0.82	0.98	0.20	db1, ncl	7

*MSC-full: Multiplicative Scatter Correction; SNV: Standard Normal Variate; db1: First Derivative BCAP; ncl: Normalization by closure; V-set: Validation Set; SEP: Standard Error of Prediction

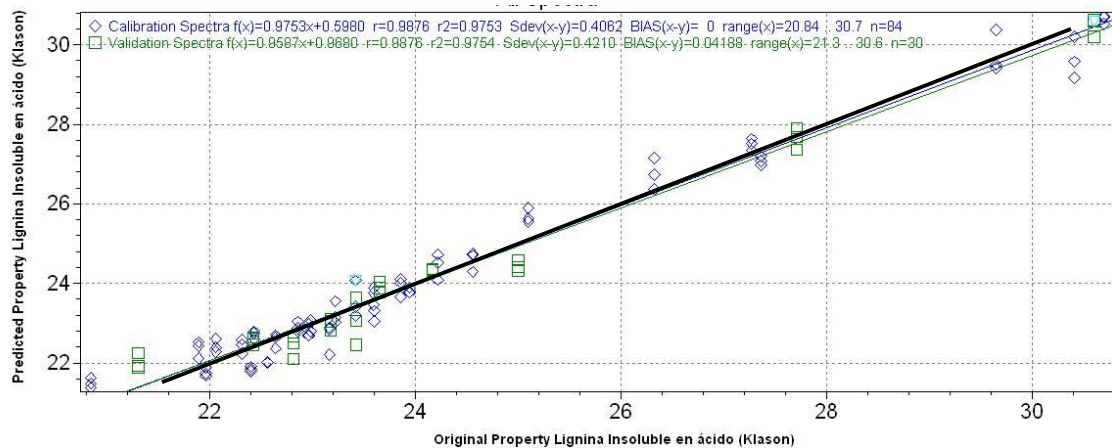


Figure 2. NIR Spectroscopy predicted acid-insoluble lignin versus conventional method determined acid-insoluble lignin. The black line represents the perfect calibration axis: same predicted value as the original.

Nevertheless, it is interesting to note the similarity in the error reported by the laboratory (0.3 %) and the error of prediction of the NIR method (0.4 %). This aspect could be also interpreted as an indicator of the accuracy of the method.

One percent Sodium Hydroxyde solubility

In the case of this property, the pretreatment that gave a better spectrum and PCA combination was a Multiplicative Scatter Full (MSC-full) as Table 3 shows. Figure 3 shows the correlation between predicted and original values, where it can be seen the not homogeneous distribution of the samples, similarly to the previous discussed parameter. Likewise, the estimated warning ranges were 13.2 % to 13.4 % and 21.4 % to 24.6 %. A calculation of the bias in the upper warning range gave an average of 0.8 % more in the value predicted than in the original value. In the same manner as with lignin calibration, this deviation will be corrected with the addition of samples, *i.e.* making the conventional method determination when the predicted value is in the warning range or outside the calibration limits. Furthermore, the Q-value of 0.72 (Table 3) implies a useable calibration that still needs improvement.

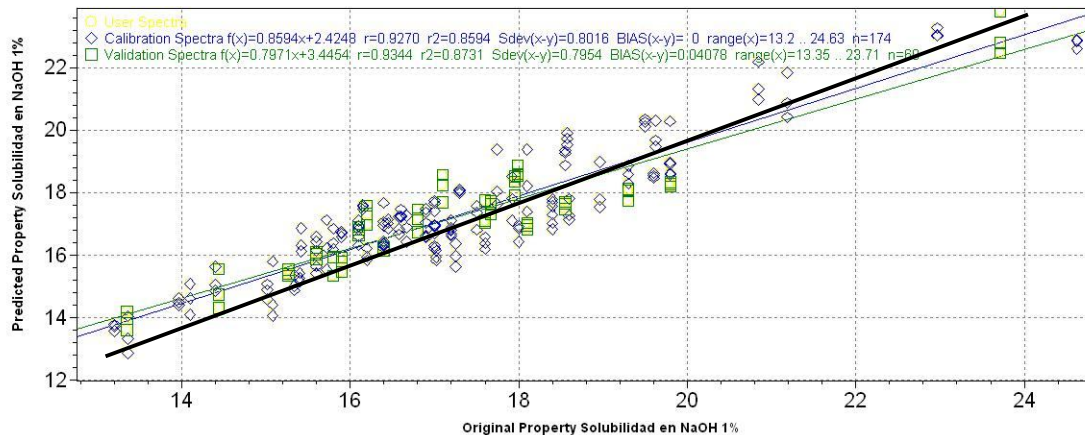


Figure 3. NIR Spectroscopy predicted 1% NaOH solubility versus conventional method determined 1% NaOH solubility. The black line represents the perfect calibration axis: same predicted value as the original.

Moreover, it is interesting to analyze the spectra of the unprocessed wood in comparison with the wood remaining after the test, as shown in the figure 4. In the figure, both spectra are pretreated with the mathematical MSC-full. Some aspects that are interesting to notice are the difference in the intensity of the spectra in the range from 6000 to 7000 cm^{-1} , the small valley at 5900 cm^{-1} that is present in the original wood but not in the digested sample, and the difference in intensity of the valley at 5100 cm^{-1} .

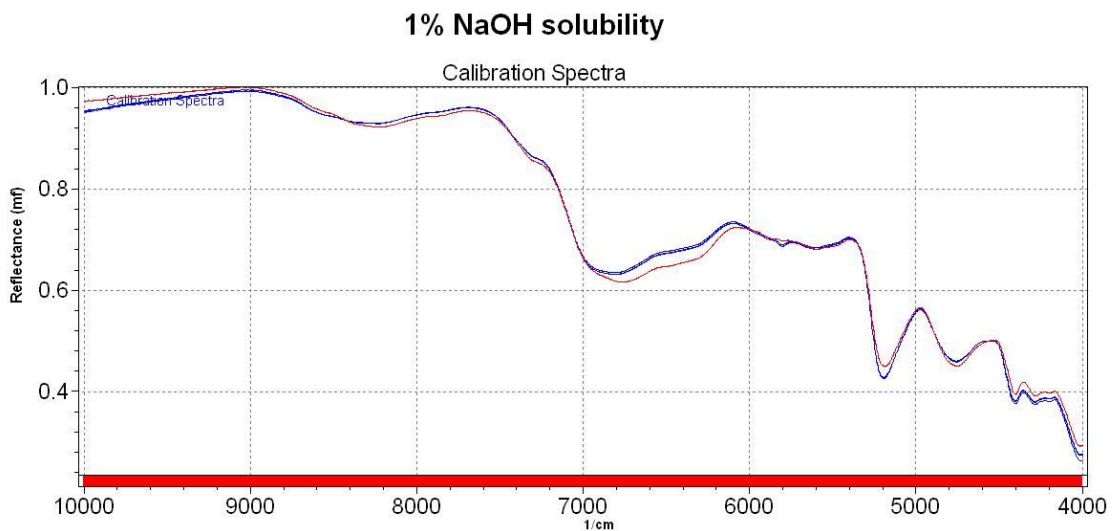


Figure 4. Pretreated spectra of the sample before and after the test. The blue line represents the sample before and the red line after.

Acetone extractives

Figure 5 shows the calibration correlation between the original and predicted values for the determination of acetone extractives. Although the apparent small range calibrated, it must be noted that the conventional method has also low error. Therefore, in concordance with previous studies, there are at least two methods to determine the suitability of the calibration. In the method discussed by Murray (cited by Cozzolino), the ratio SEP/SD is evaluated; in the case of this work, it was 0.24 which

indicates a good calibration. Additionally, the suitability can be evaluated by the fact that the range is recommended to be 20 times the SEP. In this case, the SEP is 0.2 % while the total range is 3.7 %, a close ratio (18.5 times) that could be improved by the addition of more samples or by diminishing the error.

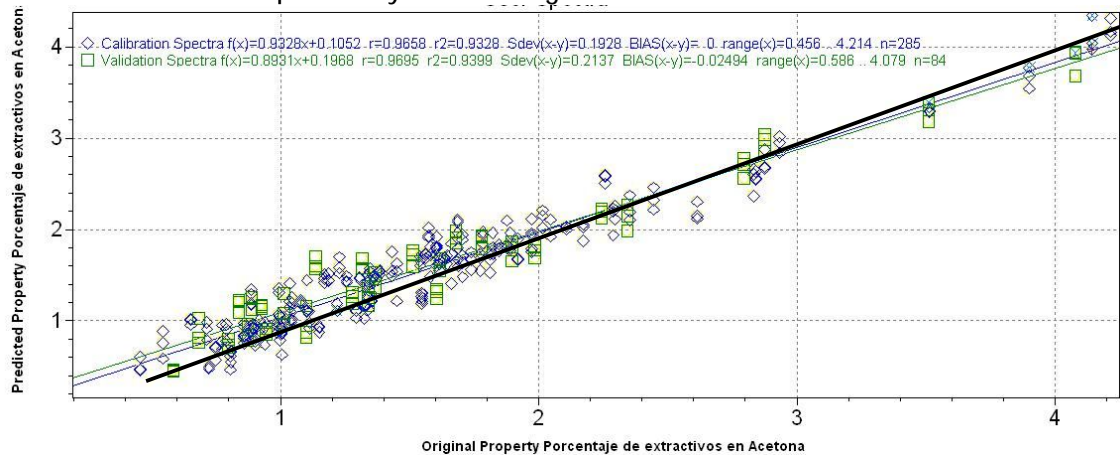


Figure 5- NIR Spectroscopy predicted acetone extractives versus conventional method determined acetone extractives. The black line represents the perfect calibration axis: same predicted value as the original.

The pretreated spectra of the Eucalyptus wood and the sample without the extractives is shown in figure 6. In this case the difference is not clear, even in the zoom of the figure 7 where the most remarkable difference found was in the 4800 cm^{-1} to 5000 cm^{-1} zone.

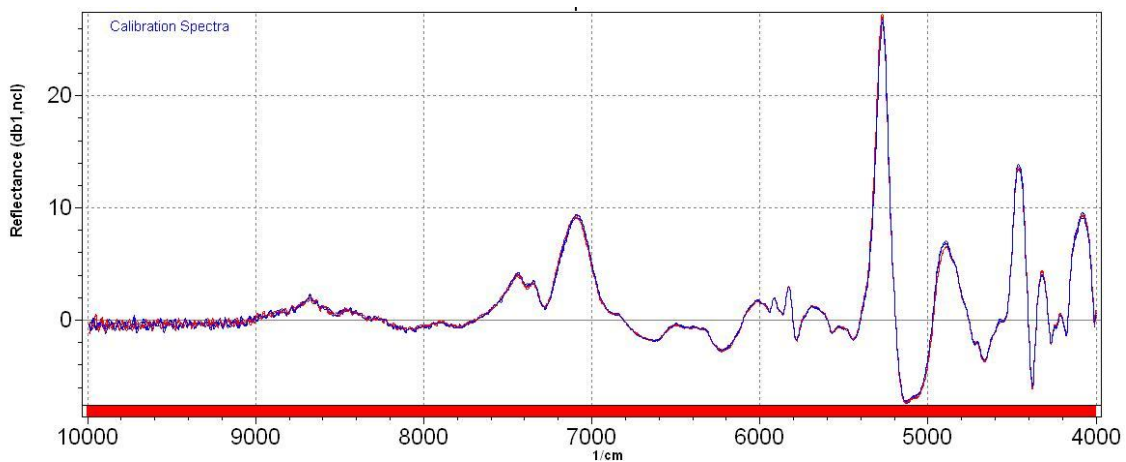


Figure 6. Pretreated spectra of the sample before and after the test. The blue line represents the sample before and the red line after.

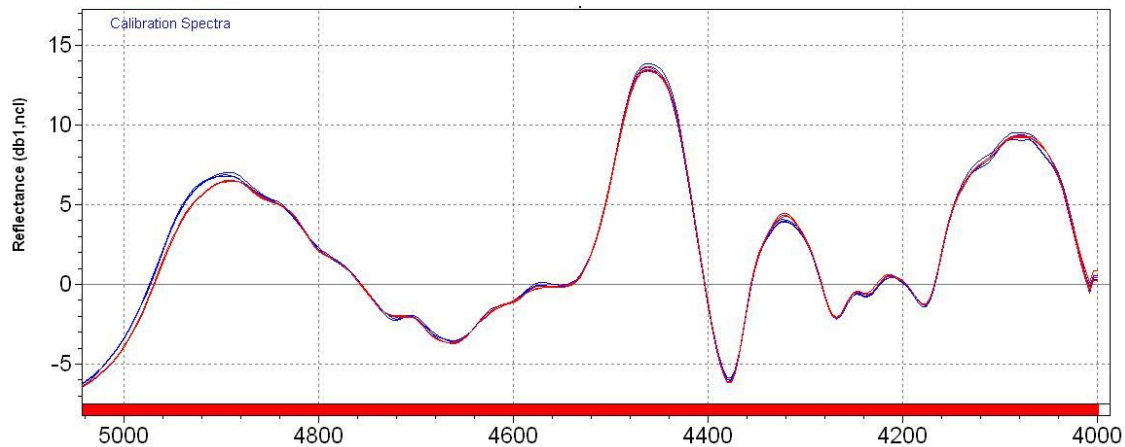


Figure 7. Zoom of the Figure 6 in the region 4000 cm^{-1} to 5000 cm^{-1} .

CONCLUSIONS

- 1) In this study, samples of Uruguayan *Eucalyptus spp.* were used to develop adequate NIRS calibrations for the three chemical properties, acetone extractives, Klason lignin and one percent sodium hydroxide solubility, regardless where they grew up or the species.
- 2) These new calibration models, together with two previously studied properties, yield and basic density, were included in a NIRS application, providing useful data to get a more complete characterization of wood samples in brief time.
- 3) It may be possible to improve these calibrations, adding samples in the weaker zones of each curve.
- 4) Considering the satisfactory results of the previous and present works, as well as the several advantages of the NIRS method, it could be interesting to include other properties in this application.

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