

Estimation of moisture curves in cork granulate by Vis/NIRS technology

Juan Carlos Sánchez-González¹ · Juan García-Olmo² · Cristina Prades¹

Received: 5 November 2014 / Published online: 9 June 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract The aim of this study was to determine the moisture content of cork granulate between maximum moisture content and equilibrium moisture content and evaluate the potential of Vis/NIR spectroscopy in predicting the moisture content in that range. The study was carried out in a set comprising 118 samples classified into nine granulometric classes (0.5–1, 1–1.5, 1–2, 1.5–2.5, 2–4, 2–5, 2–6, 3–7, and 4–8 mm). Spectra were collected by reflectance in the wavelength range of 400–2500 nm. Approximately 400 spectra were used to develop modified partial least squares calibration equations, while 180 spectra were used for the external validation. The mean maximum moisture content was 661.2 % (range 967.5–271.3 %) after 80 days of saturation, while the mean equilibrium moisture content was 6.2 % (range 5.8–7.5 %) after 58 days of drying depending on the granulometric class. The calibrations achieved excellent accuracy and precision with coefficients of determination in the cross-validation (r_{cv}^2) of 0.99. The best equation showed a coefficient of determination of external validation (r_{EV}^2) of 0.99, similar standard errors of cross-validation (24.22 %) and external validation (26.96 %), a ratio of performance to deviation of 11.7, and a range error ratio of 39.7 in the external validation, thus confirming that Vis/NIRS technology is suitable for quantifying the moisture content of cork granulate in routine analyses.

✉ Cristina Prades
cprades@uco.es

¹ Faculty of Agriculture and Forestry Engineering, University of Cordoba, Cordoba, Spain

² NIR/MIR Spectroscopy Unit, Central Service for Research Support, University of Cordoba, Cordoba, Spain

Introduction

Cork is the outer bark of the cork oak tree (*Quercus suber* L), and cork granulate is defined as cork fragments between 0.25 and 45 mm in dimension (UNE 56911, 1988) obtained by grinding the cork that is not suitable for the production of natural cork stoppers and disks and from the waste generated during cork manufacturing. Granulated cork accounts for 75 % of the raw material at most (Gil 2009).

Cork granulate is the raw material of composites used for the production of stoppers (agglomerated, micro-agglomerated, and technical stoppers) and the manufacture of decorative products (floor and wall coverings), as well as other building and industry applications (Gil 2009). Companies in the cork sector use different granule sizes to manufacture their products as needed in order to obtain the best yield from the raw material and the highest quality end product.

Although the quality requirements of granulated cork depend on its use, moisture content (M) is one of the most important parameters for trading and technological processing, from the field to both solid and granulated cork industries. It is therefore important to predict the M value in a wide range between maximum moisture content (MM) and equilibrium moisture content (EM).

Several authors have studied the evolution of the moisture content of cork from the tree until it reaches the EM with the environment and its mass becomes stationary (Costa and Pereira 2013; Robledano et al. 2009). The EM of cork may vary between 4 and 12 % for wide ranges of temperature (5–40 °C) and relative humidity (20–90 %) (González-Adrados and Haro 1994; Gil and Cortiço 1998). The time required to reach EM depends on environmental conditions, structural properties of the cork, and size of the material. The MM of cork planks reaches 500 % within 330 days at a temperature of 20 °C, or within 4 days at a temperature of 90 °C, when the cell wall and the lumen are saturated with water (Pereira 2007).

The mechanisms underlying the exchange of water with the environment, the sorption and desorption isotherms, and the drying kinetics of the cork in the field and under controlled conditions have been the subject of various studies (González-Adrados and Haro 1994; Gil and Cortiço 1998; Abdulla et al. 2009; Belghit and Bennis 2009; Costa and Pereira 2013; Pintor et al. 2012; Carpintero et al. 2014).

Water absorption follows a characteristic curve with three regions. In the first region, the water is rapidly absorbed with a variation in daily moisture content or constant moisture rate (MR); in the second region, the MR is lower and decreasing, while in the third region, there is scarce water absorption until reaching MM . The absorption ratio varies with the direction. It is clearly higher in the radial direction and increases with temperature (Pereira 2007). The drying surface also affects absorption: the larger the shape, the lower the water activity for the same water content (Abdulla et al. 2010). Desorption follows the same pattern, with hysteresis between the sorption and desorption curves (Lequin et al. 2010).

Near-infrared reflectance spectroscopy (NIRS) is a rapid, clean, and precise non-destructive analytical technique that has proven to be useful in agricultural and forestry industries (Schimleck et al. 2004; So et al. 2004; Tsuchikawa 2007; Gong and Zhang 2008). Numerous studies have demonstrated the potential of NIRS

technology in predicting moisture content in wood (Defo et al. 2007; Jiang and Huang 2006; Mora et al. 2011; Thygesen and Lundqvist 2000a, 2000b; Tsuchikawa et al. 1996) and in predicting mechanical properties on a broad moisture content range (Watanabe et al. 2013; Kothiyal and Raturi 2011).

In the cork industry, recent studies on cork planks and natural cork stoppers support the feasibility of NIRS technology in controlling product quality as it permits to simultaneously obtain reliable information about certain chemical components (extractives), physicochemical parameters (porosity, density, extraction force, and compression), and the origin of the cork (Prades et al. 2010, 2012, 2014; Gómez-Sánchez et al. 2013).

The feasibility of NIRS technology for predicting moisture content has been studied in natural cork planks and stoppers. The first feasibility study was carried out on a set of 167 planks (range 4.75–14.50 % and mean 7.55 %) through cross-validation. The best NIRS equation was obtained in the tangential section, with a coefficient of determination in the cross-validation (r_{cv}^2) of 0.68 and a standard error of cross-validation (SECV) of 0.36 (Prades et al. 2010). Better results were obtained from a set of 150 stoppers stabilized into five hygrothermal classes with an EM of 4.30, 4.78, 5.44, 5.67, and 6.51 % in each class and by external validation. The best NIRS equation was obtained in the transversal section with a r_{cv}^2 of 0.86, a coefficient of determination of external validation (r_{EV}^2) of 0.85, a SECV of 0.34, a standard error of external validation (SEP) of 0.38, and a ratio of performance to deviation (RPD) of 2.65 (Prades et al. 2014). The RPD value, which was close to 3, and the similarity between SECV and SEP showed that the equation was suitable for predicting moisture and improving the speed and efficiency of the traditional method (Williams 2001). The possibility of improving the results suggests that Vis/NIRS technology can be an effective and efficient method for predicting moisture content in cork products. Due to the capacity of cork to absorb water, it is very interesting for industry to have models capable of handling the maximum range of variation in moisture content at different steps of the manufacturing process. Different studies on wood follow this criterion (Watanabe et al. 2011; Cooper et al. 2011; Adedipe and Dawson-Andoh 2008). To the best of the authors' knowledge, however, this technique has not yet been applied to the study of moisture content in cork granulate.

This study aims firstly to determine and model the behavior of cork granulate in the humidification process until reaching the MM content and in the subsequent drying process until reaching the EM under ambient conditions. Secondly, the study assesses the feasibility of Vis/NIRS technology for determining the moisture content of cork granulate in the range between MM and EM by developing a methodology based on the correlation of analytical reference data and near-infrared spectroscopic measurements.

Methodology

Sample set

The sample set comprised samples of cork granulate of the nine granulometric classes employed in the agricultural and forestry industries: G1 (0.5–1 mm); G2

(1–1.5 mm); G3 (1–2 mm); G4 (1.5–2.5 mm); G5 (2–4 mm); G6 (2–5 mm); G7 (2–6 mm); G8 (3–7 mm); and G9 (4–8 mm). Samples of 0.5 L of cork granulate were obtained from 1 to 10 L bags of each granulometric class. To do so, the granules were homogenized in the bags and subsequently poured into a pipette using a funnel until the established volume was obtained. The samples were then packed in clear plastic containers and weighed.

Moisture content

To determine and model the behavior of the moisture content of the cork granulate in the range between the MM content and the EM under ambient conditions, the samples underwent a saturation process followed by a drying process as described below.

Saturation process 0.5-L samples were saturated in clear plastic containers, where they were kept until reaching the MM. To control the increase in mass, the samples were periodically drained for 10 min in a colander, weighed, and submerged again in the container.

Drying process To remove the water and begin drying the samples, a 80×40 mm opening was cut into the lid of each plastic container, which was then covered with a light-resistant cloth sieve of <0.5 mm, and sealed with a hot silicone sealant. The containers were placed upside down on wooden slats to remove the water. The samples were weighed periodically to monitor mass loss until reaching the EM. The samples were then poured into aluminum containers and placed in an oven at 103 ± 2 °C for drying up to constant weight to obtain the dry mass.

In order to establish the saturation and drying periods of the sample set until reaching MM and EM, respectively, a prior experiment was performed. Two 1-L samples of the G2 and G8 granule sizes were saturated and weighed at weekly intervals. The samples were considered to have reached the MM when the difference in mass between two consecutive weighings was <0.5 %. The samples were then dried until reaching the EM following the same criteria.

The moisture content was calculated on a dry basis according to UNE 56917 (1988).

$$M_o(\%) = \frac{m_1 - m_2}{m_2 - m_3} \cdot 100$$

where m_1 (g) is the wet mass of the container and of the sample, m_2 (g) is the dry mass of the container and of the sample, and m_3 (g) is the mass of the container. The variation in daily moisture content or MR for each granule size was calculated as:

$$MR(\%) = \frac{(M_f - M_i)}{t}$$

where M_f (%) is the final moisture content, M_i (%) is the initial moisture content, and t is the time interval in days.

The equipment comprised a 0.01-g precision scale and drying oven at 103 ± 2 °C. The materials used were 1-L clear plastic containers of $180 \times 140 \times 50$ mm³ with a lid, a cloth sieve of <0.5 mm, silicone sealant, and 1-L aluminum containers without lids.

Data were processed, and the moisture loss models were fitted using Microsoft Office Excel 2007 software.

Vis/NIRS analysis

Instrumentation and collection of spectra

To assess the feasibility of Vis/NIRS technology for determining the moisture content of cork granulate in the range between MM and ME, the samples were scanned in reflectance mode. The reflectance ($\log 1/R$) spectra were collected using a Foss-NIRSystems System II 6500 spectrophotometer (Foss-NIRSystems Inc., Silver Spring, MD, USA) equipped with a transport module and autogain detectors; one from 400 to 1100 nm (known as the VIS region) and another from 1100 to 2500 nm (known as the NIR region). The samples were scanned by reflectance using a 1/4 rectangular cup, and spectra were collected every 2 nm using WinISI 1.50 software (Infrasoft International, Port Matilda, PA, USA).

After homogenizing each sample, part of the granules was poured into the 1/4 cup and one spectrum was obtained per sample under stable temperature conditions (24 °C) on the established days during the drying period. All of the granules were retrieved from the cup, weighed, and returned to the container.

Quantitative chemometric analysis

The moisture content was studied as a quantitative parameter. Spectra were collected, and chemometric analysis was performed using WinISI II software (version 1.5).

Prior to calibration, the CENTER algorithm (Shenk and Westerhaus 1995a) was used to assess the quality of the spectral data. This algorithm performs principal component analysis (PCA) to calculate the distance of each of the spectra from the center of the space defined by the entire population (the Mahalanobis distance) in such a manner that when the distance is >3 for a given sample, the software classifies it as a spectral outlier (Shenk and Westerhaus 1995a).

Multivariate regression was carried out using the modified partial least square regression algorithm (MPLS) described by Shenk and Westerhaus (1991). All spectral data were summarized in a few variables (PLS terms) and showed a higher correlation with the reference values. The residues obtained after calculating each regression term in the MPLS regression were standardized by dividing them by the standard deviation before calculating the next regression term (Shenk and Westerhaus 1991). Scatter correction was accomplished using the standard normal variate and detrending (SNV + DT) algorithm (Barnes et al. 1989). The spectra were transformed using different ranges of the 400–2500 nm spectrum and different combinations of derivative math treatments applied to the spectral data. WinISI

derivative math treatments are referred to by a four-digit notation (a, b, c, d), where a is the derivative order, b is the derivative gap, c is the smoothing segment, and d is the second smoothing segment (Shenk and Westerhaus 1995b).

The calibrations were performed using 0 to a maximum of 9 passes of outlier (T and GH) elimination. T-outliers, or chemical outlier samples, are defined as samples with significant differences between their laboratory and predicted values

Table 1 Moisture content statistics by granulometric class for all samples: pre-saturation (M0), after 2 days following removal of water (M1), after 9 days (M2), after 23 days (M3), after 39 days (M4), and after 58 days (M5)

Moisture content statistics (%)										
G	G1	G2	G3	G4	G5	G6	G7	G8	G9	G1–G9
N	33	1	32	1	15	2	2	31	1	118
M0										
Mean	9.7	8.0	8.6	7.8	8.3	8.8	8.6	7.6	6.5	8.6
Min	7.8	–	7.0	–	7.6	8.2	6.2	6.8	–	6.2
Max	12.0	–	10.1	–	8.9	9.4	11.0	8.6	–	12.0
SD	1.0	–	0.6	–	0.4	0.8	3.4	0.3	–	1.1
M1 = MM										
Mean	96.75	568.4	797.0	524.2	463.0	311.5	325.7	354.9	271.3	661.2
Min	654.8	–	714.7	–	422.2	303.8	305.3	311.7	–	271.3
Max	1134.0	–	904.2	–	512.9	319.2	346.1	409.7	–	1134.0
SD	120.7	–	51.5	–	30.5	10.9	28.8	26.8	–	268.2
M2										
Mean	804.6	475.0	640.8	393.3	334.5	226.3	203.0	231.1	154.4	518.0
Min	515.8	–	504.7	–	293.6	217.8	202.1	197.9	–	154.4
Max	976.1	–	849.2	–	412.3	234.7	203.9	265.8	–	976.1
SD	110.5	–	83.2	–	35.2	12.0	1.3	19.3	–	251.5
M3										
Mean	467.6	262.7	327.1	196.1	143.8	116.8	68.0	86.6	32.6	267.8
Min	311.9	–	203.3	–	98.5	112.1	61.5	48.8	–	32.6
Max	612.9	–	507.5	–	195.1	121.4	74.5	114.0	–	612.9
SD	79.7	–	79.9	–	24.7	6.6	9.2	15.4	–	167.5
M4										
Mean	94.9	17.6	23.9	7.6	7.3	11.5	7.2	7.0	6.7	36.4
Min	20.0	–	6.7	–	7.0	9.7	7.1	6.6	–	6.6
Max	179.3	–	90.0	–	7.6	13.3	7.3	7.3	–	179.3
SD	47.4	–	23.7	–	0.2	2.5	0.2	0.2	–	46.4
M5 = EM										
Mean	6.8	6.4	5.9	6.0	6.2	7.5	6.2	5.9	5.8	6.2
Min	6.0	–	4.5	–	5.9	7.4	6.1	4.7	–	4.7
Max	9.2	–	6.2	–	6.4	7.5	6.3	6.2	–	9.2
SD	0.7	–	0.3	–	0.2	0.1	0.2	0.3	–	0.6

G Granulometric class, N number of samples

(T value higher than 2.5 estimated by the Student's t test), while GH-outliers, or spectral outlier samples, are defined as samples whose spectra show excessive Mahalanobis distance ($GH > 3$) to the spectral center of the training set (Shenk and Westerhaus 1995a).

The SELECT algorithm was used to establish the calibration and validation sets, which comprised approximately two-thirds and one-third of the total spectra sample, respectively.

The best equations were selected taking into account the lowest SECV and SEP values, the highest r_{cv}^2 and r_{EV}^2 values, as well as the values of the ratios of performance to deviation of the cross-validation (RPD_{cv}) and the external validation (RPD_{EV}), and the range error ratio of the cross-validation (RER_{cv}) and the external validation (RER_{EV}), which is considered the best predictive statistic for determining the ability of an equation (Shenk and Westerhaus 1995a).

Results and discussion

Sample set

In accordance with the previous experiment, the saturation and drying periods were set at 80 and 58 days, respectively. Moisture content was obtained prior to saturation (M_0) and during the drying period (M_1, M_2, M_3, M_4 and M_5) at days 2, 9, 23, 39 and 58, respectively (Table 1; Fig. 1). Given that it was not possible to weigh the samples on the first day of the drying period due to an excess of water, it was determined that MM corresponded to M_1 and EM to M_5 .

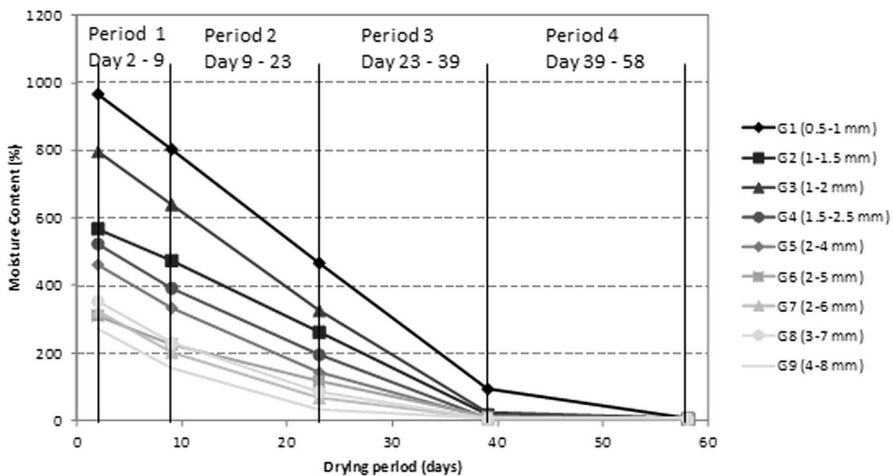


Fig. 1 Evolution of moisture content (%) by granule size in the drying period. Period 1: day 2 to day 9 (MR1). Period 2: day 9 to day 23 (MR2). Period 3: day 23 to day 39 (MR3). Period 4: day 39 to day 58 (MR4)

Moisture content

For a mean ambient temperature of 9 °C during the period, MM varies within a wide range between 967.46 % for the smallest granule size and 271.33 % for the largest granule size (Table 1). The MM of the smallest granule size is greater than the maximum value of the equation as reported by Pereira (2007). Specifically, it is 446 and 545 % for densities of 190 and 160 kg m⁻³, respectively, probably due to the phenomenon of water adhesion between small cork granules.

After 58 days of drying and a relative humidity of 54 % at the end of the period, the EM ranged between 5.77 and 7.46 %, with a mean value for all granule sizes of 6.2 % (Table 1). This is in line with Pereira (2007), who reported an EM of 8, 10, and 16 %, respectively, at a relative humidity of 75, 85 and 95 %, and González-Adrados and Haro (1994), who reported an ME of about 6 % for a temperature of 20 °C and a relative humidity of 65 %.

The variation in daily moisture or MR of the samples shows mean values of +6.1 % (+4.24 to +11.68 %) during saturation and of -8.98 % (-0.06 % to -24.07) during drying, thus indicating hysteresis between the sorption and desorption curves (Lequin et al. 2010). Due to the low diffusion coefficient of cork and the greater surface area per unit of volume, smaller granule sizes show a higher positive (absorption rate) and negative (desorption rate) MR with progressively decreasing values as the granule size increases from -17.2 for G1 to -6.2 for G8 (Table 2) due to the hydrophobic nature of cork and its lack of wettability (Abenojar et al. 2014; Rosa and Fortes 1993). There are also important differences between the MR of the first drying period (between -23.3 and -17.8) and the last drying period (between 4.6 and -0.7) due to a desorption mechanism and the drying kinetics of cork (González-Adrados and Haro 1994; Belghit and Bennis 2009).

According to Pereira (2007), cork planks under natural conditions after boiling in water are dried with an MR of -8.33 % (from 65 to 40 % in 3 days), while small samples dry more quickly with a MR of -11.67 % (from 44 to 9 % in 3 days). For cork granulate, the MR continues to increase until reaching -12.3 %.

Table 2 Moisture rate (MR) for the G1, G3, G5, and G8 granulometric classes for all samples (G1–G9): in the saturation period (MRI), in the drying period from day 2 to day 58 (MRD), and in period 1: day 2–day 9 (MR1). Period 2: day 9–day 23 (MR2). Period 3: day 23–day 39 (MR3). Period 4: day 39–day 58 (MR4)

G	N	Saturation period	Drying period				
		MRI	MR1	MR2	MR3	MR4	MRD
G1	33	11.7	-23.3	-24.1	-23.3	-4.6	-17.2
G3	32	9.6	-22.3	-22.4	-19.0	-1.0	-14.1
G5	15	5.6	-18.4	-13.6	-8.5	-0.1	-8.2
G8	31	4.2	-17.7	-10.3	-5.0	-0.1	-6.2
G1–G9	118	6.1	-17.8	-14.0	-10.5	-0.7	-9.0

G Granulometric class, N number of samples

In fitting the moisture curve in the drying period from MM to EM and omitting the fits that show a negative moisture content, the most accurate model is an exponential model with coefficient of determination (R^2) values between 0.90 and 0.94 depending on the granule size, and of 0.84 for the training set.

$$M_{G1}(\%) = 1855.6e^{-0.089t}; \quad (R^2 = 0.92)$$

$$M_{G2}(\%) = 955.68e^{-0.088t}; \quad (R^2 = 0.92)$$

$$M_{G3}(\%) = 1359.5e^{-0.096t}; \quad (R^2 = 0.91)$$

$$M_{G4}(\%) = 774.67e^{-0.091t}; \quad (R^2 = 0.90)$$

$$M_{G5}(\%) = 622.26e^{-0.087t}; \quad (R^2 = 0.91)$$

$$M_{G6}(\%) = 405.06e^{-0.074t}; \quad (R^2 = 0.93)$$

$$M_{G7}(\%) = 354.57e^{-0.078t}; \quad (R^2 = 0.92)$$

$$M_{G8}(\%) = 416.28e^{-0.082t}; \quad (R^2 = 0.92)$$

$$M_{G9}(\%) = 244.67e^{-0.074t}; \quad (R^2 = 0.92)$$

$$M_{G1-G9}(\%) = 921.52e^{-0.088t}; \quad (R^2 = 0.84)$$

where M is the moisture content on a dry basis, and t is the time in days from MM.

Vis/NIRS analysis

Spectral study

One spectrum was obtained per sample for each moisture content (M1, M2, M3, M4, and M5) using a Foss-NIRSystems SY II 6500 spectrophotometer and the 1/4 cup during the drying period. The spectral set consisted of 590 spectra (one spectrum for each of the 118 samples and for each of the five drying times M1–M5), which were subsequently measured to obtain the mean spectrum of the spectral set and the mean spectrum of each moisture content (Fig. 2).

Nine spectral outliers were detected and eliminated in the calibration, six corresponding to the first spectra obtained (M1) and three corresponding to the fifth and final spectra obtained (M5). The three outliers corresponding to the fifth measurement (M5) were detected by the CENTER algorithm: a T-spectral outlier, which was due to an error when obtaining the spectrum of the sample G9-1 and two GH-outliers (samples G1-1 and G8-30). Sample G1-1 showed higher absorbance in the entire spectrum (GH 6.3), while sample G8-30 showed an anomalous spectrum in the visible region (GH 9.8). The six spectral outliers corresponding to the first measurement (M1), belonging to the G6 (1 outlier) and G8 (five outliers) granule

classes, had $\text{GH} \approx 3$. They were revised and eliminated; therefore, the final spectral set comprised 581 spectra.

The mean spectra exhibit the same profile in the visible region and in the NIR region as reported in previous studies on solid cork with absorption bands corresponding to the $-\text{NH}$ and $-\text{OH}$ groups (1450 and 1930 nm), and others due to $-\text{CH}$ groups (1215, 1730, 2146, 2310, and 2354 nm) (Prades et al. 2010, 2012, 2014; Gómez-Sánchez et al. 2013). The two main peaks around 1450 and 1940 nm correspond to the overtone and combination bands of the hydroxyl ($-\text{OH}$) group. Although the absorption bands coincide, the absorption peaks are higher with increasing moisture content, thus shifting the profile of the mean spectra (Fig. 2). The profile obtained for the granulate in M5 ($M = 6.2\%$) is very similar to the profile obtained for natural cork stoppers ($M = 6\%$) (Prades et al. 2012), since the characteristics of the raw material are not altered in the manufacturing process. However, small differences are observed in the visible region due to the tonality (around 500–550 nm) and in the NIR region due to the gaps between the granules and the scatter effect.

The study of the first derivative of the raw spectra amplifies the regions without the scatter effect and permits identifying very marked minimums in the 1450 and 1930 nm bands (associated with $-\text{OH}$ groups), thus reflecting the relationship between absorbance and moisture content, and much lower minimums in the 2300 nm band (associated with $-\text{CH}$). The change in detector can be observed in the 1100 nm band (Fig. 3).

Quantitative chemometric analysis

Calibrations were performed with approximately two-thirds of the total sample, and the best equation was validated with the remaining one-third of the sample. The

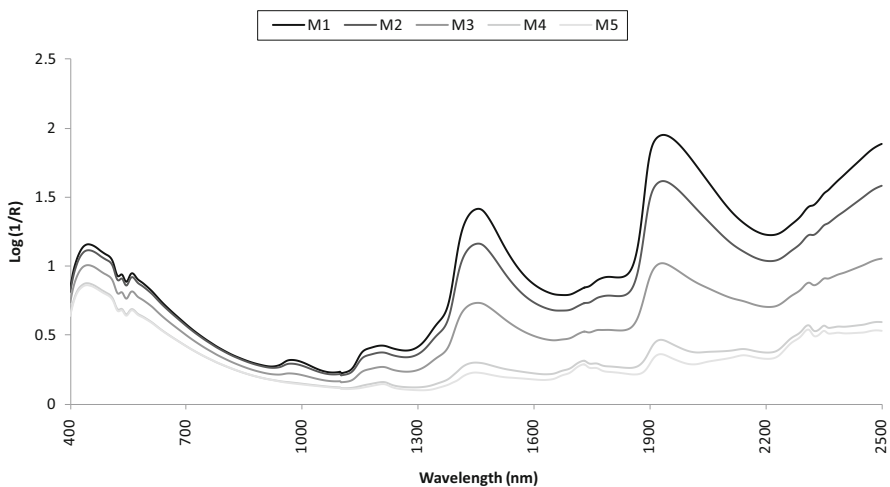


Fig. 2 Mean spectrum obtained for cork granulate for each drying period: after 2 days following removal of water (M1), after 9 days (M2), after 23 days (M3), after 39 days (M4), and after 58 days (M5) in the Vis/NIR region (400–2500 nm)

calibration and validation sets obtained from the SELECT algorithm (Shenk and Westerhaus 1995a) were structured to cover all the ranges, checking that the mean M and SD were of the same order of magnitude. The calibration set comprised 401 samples with a mean M of 322.5 % (between 4.5 and 1135.0 %) and a SD of 316.3 %. The validation set comprised 180 samples, with a mean M of 245.7 % (4.7–1075.5 %) and a SD of 315.6 %.

Models were developed for the entire spectral range, the Vis/NIR region (400–2500 nm), and using only the NIR region (1100–2500 nm). Although the results were similar, the best models were obtained in the 400–2500 nm region for all cases. With just one exception, the best pre-treatment was (SNV + DT), while it was possible to use different mathematical treatments (0, 0, 1, 1, 1), (1, 4, 4, 1), (1, 10, 10, 1), (2, 10, 5, 1) (Table 3).

The coefficients of the best model provide more in-depth information about this analysis and show that they have more weight in the 400–750 nm range and in the 800–1100 nm range (Fig. 4a). The spectral region (400–750 nm) is associated with the color of the samples; however, the regression coefficients associated with these bands are not high. Upon recalibrating the equations with only the Vis region (400–1100 nm), the statistics are poorer. The spectral region (750–1100 nm) is associated with the presence of overtones and combination bands of the organic bonds (Schwanninger et al. 2011) and was found to have a clear influence on predicting moisture in the samples of cork granulate (Fig. 4b). The coefficients of the equation with better statistics (Table 3 bottom part) are shown in Fig. 4b. As can be seen, in this case the values of the regression coefficients in the region associated with the –OH absorption band (over 1450 and 1930 nm) are high in absolute value. This confirms that the NIR region—where the bands associated with the –OH groups and the moisture content are located—is necessary in the calibration. The

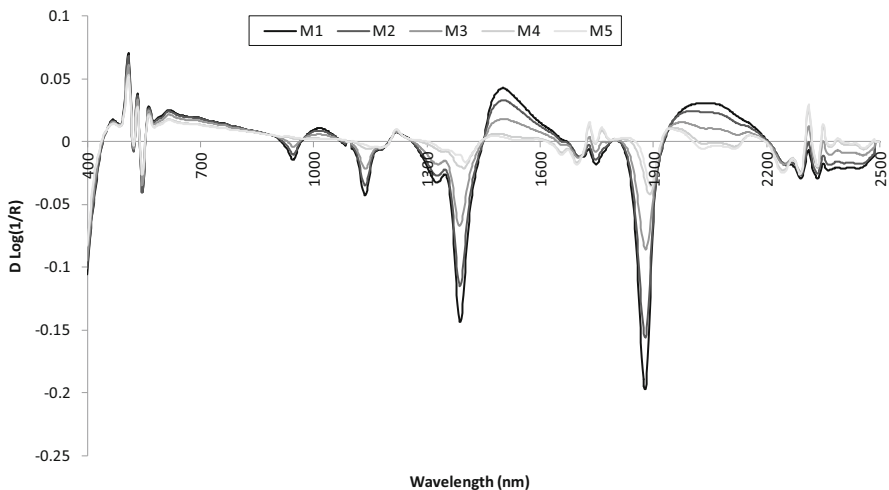


Fig. 3 Mean value of the first derivative of the spectra obtained for cork granulate at the five moisture points (M1, M2, M3, M4, M5) in the Vis/NIR region (400–2500 nm)

Table 3 Equations to predict moisture content of cork granulate with the best statistical values for the master instrument in the cross-validation

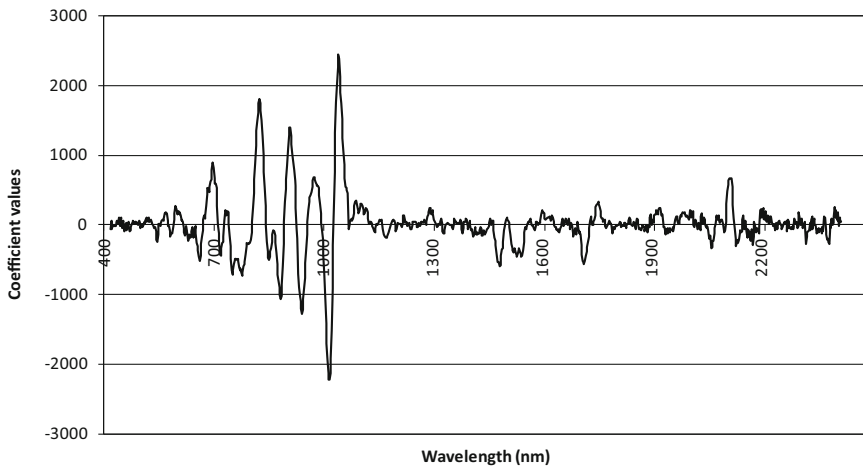
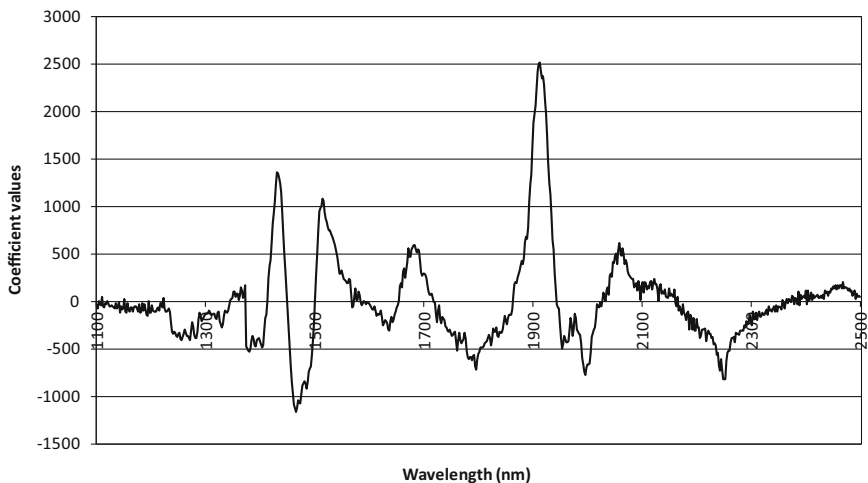
Moisture content (%)						
Equation	1	2	3	4	5	6
Vis/NIR region (400–2500 nm)						
Pre-treatment	(1, 4, 4, 1) SNV + DT	(0, 0, 1, 1) none	(0, 0, 1, 1) SNV-DT	(1, 10, 10, 1) SNV + DT	(2, 5, 5, 1) SNV + DT	(2, 10, 5, 1) SNV + DT
PLS factors	12	10	9	10	9	8
<i>N</i>	373	377	365	378	372	356
Mean	304.1	308.7	306.8	309.0	310.3	294.8
SD	307.8	310.6	319.8	314.8	315.3	306.2
Min	4.50	4.54	4.52	4.50	4.58	4.52
Max	1227.4	1240.5	1266.2	1253.3	1256.3	1213.5
SECV	27.52	36.85	34.76	35.87	27.15	24.22
r_{cv}^2	0.99	0.99	0.99	0.99	0.99	0.99
RPD _{cv}	11.2	8.4	9.2	8.8	11.6	12.6
RER _{cv}	41.0	30.6	32.5	31.5	41.6	46.6
NIR region (1100–500 nm)						
Pre-treatment	(1, 4, 4, 1), SNV + DT	(0, 0, 1, 1), NONE	(0, 0, 1, 1), SNV-DT	(1, 10, 10, 1), SNV + DT	(2, 5, 5, 1), SNV + DT	(2, 10, 5, 1), SNV + DT
PLS factors	10	9	9	10	9	9
<i>N</i>	384	364	382	384	358	376
Mean	311.2	286.5	310.7	310.4	278.2	285.5
SD	304.2	290.4	304.2	303.8	280.3	280.3
Min	4.51	4.5	4.51	4.53	4.56	4.52
Max	1223.9	1157.6	1223.3	1221.9	1119.2	1126.3
SECV	55	34.9	67.9	58.5	47.6	51.3
r_{cv}^2	0.97	0.99	0.95	0.96	0.97	0.97
RPD	6.3	7.5	4.6	5.7	5.1	6.1
RER	21.3	25.4	15.5	19.4	17.2	20.5

Equations 6 and 2 have better results (indicated in bold)

high values of the coefficients in the 800–1100 nm region may be due to the higher gain of the instrument in that region.

All the selected equations in the Vis/NIR region exhibited excellent accuracy and precision with a r_{cv}^2 value of 0.99. Equation 6 was selected for the external validation as it showed a lower SECV and higher RPD_{cv} and RER_{cv} (Table 3 top part). The external validation of Eq. 6 was performed on 180 samples, yielding the following statistics: mean (245.7 %), SD (315.7 %), SEP (26.96 %), r_{EV}^2 (0.99), RPD_{EV} (11.7) and RER_{EV} (39.7).

SECV (24.22 %) and SEP (26.96 %) show values of the same order of magnitude. Analogously, RPD_{cv} (12.6) and RPD_{EV} (11.7), as well as RER_{cv} (46.6) and RER_{EV} (39.7), show similar and high values, thus supporting the consistency of the equation (Table 3 top part). The linear fit between the moisture content values

a Vis/NIR region (400–2500 nm)**b** NIR region (1100–2500 nm)**Fig. 4** Weights of the bands of the best model obtained for moisture content (%)

obtained in the assay and predicted in the external validation produces a straight line with a slope practically equal to one (0.998) and a bias of 1.44 (Fig. 5a).

The RPD and RER statistics of both the cross-validation and the external validation far exceed the minimum values recommended by Williams (2001) (three and ten, respectively). However, thresholds provided for the RPD value can be subjected to manipulation depending on how the sample set is constructed. Fearn (2002) considered that the RER value is a better test for the quality of the model, providing that there are no concentration outliers to inflate the value and that the concentration range of the constituent is well represented. According to the AACC

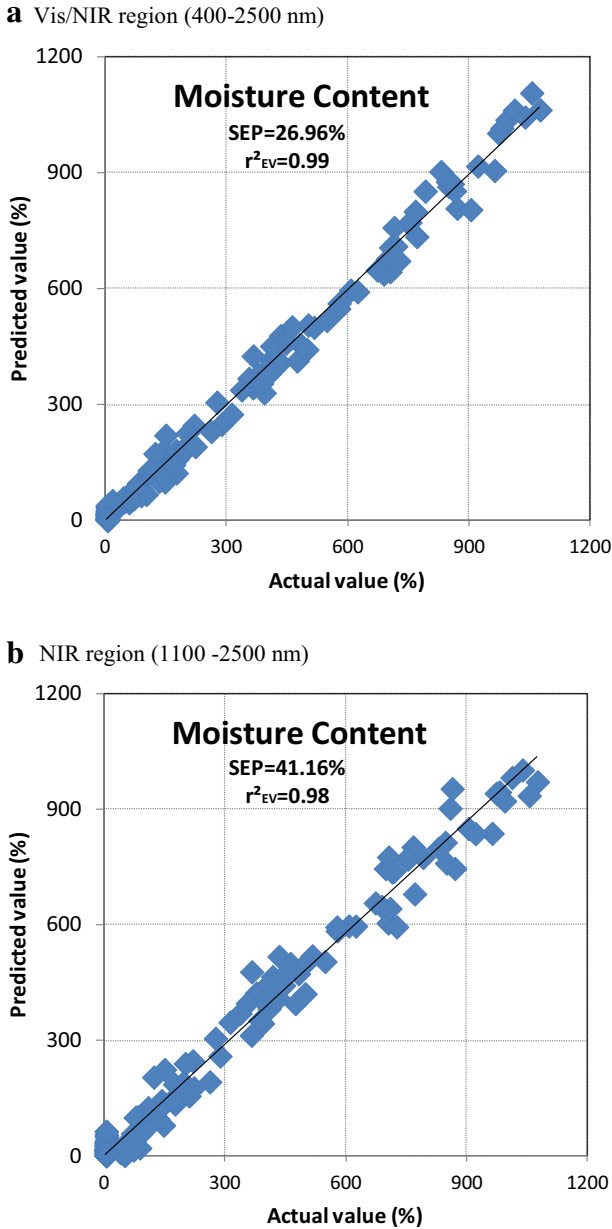


Fig. 5 Comparison of values obtained in moisture content assay (actual value) and predicted values by Vis/NIR (predicted value) for cork granulate in the validation step

method (AACC 1999), quality thresholds for model performance based on RER values provide that for $RER \geq 15$ the calibration is good for quantification.

To analyze the influence of the Vis region and the potential of the NIR region in the estimation, the equations were developed in the NIR region (1100–2500 nm).

The best equation was obtained without scatter pre-treatment or (0, 0, 1, 1) mathematical treatment, thus confirming the importance of the 1450 nm and 1930 wavelengths in the estimate. The predictive ability of the equations is lower (SECV values increase and the RER, RPD and r^2 statistics decrease) than that obtained for the full range of 400–2500 nm (Table 3 bottom part). However, the RER and RPD values, which are above 15 in all cases, are still good for quantifying moisture content (AACC 1999) and the r_{cv}^2 are always >0.95 . Therefore, it cannot be established that the color is responsible for the discrimination, although the wavelengths below 1000 nm do contribute to the predictive ability of the model.

Although there are significant differences between the chemical composition and anatomical structure of wood and cork, results obtained using Vis/NIR spectroscopy models to measure moisture content in solid wood (Leblon et al. 2013) can be compared with cork models, considering the variations in the range of the different studies. The r^2 values in wood (up to 0.99) are also reached in cork. The RMSE values in wood (2.2–30 %) are highly variable and increase with the range, producing the largest error (30 %) for the widest moisture range (0–250 %). Errors in cork granulate reach 24.22 % for a range of 4.52–1213.5 % in the Vis/NIR model (Table 3 top part) and 34.9 % for a range of 4.5–1157.6 % in the NIR model (Table 3 bottom part). However, the reliability of the equations must be compared using statistics such as RER and/or RPD. The RER values calculated from the error and range values in Leblon et al. (2013) vary from 8 to 12, with the highest RER value (12.2) reported in Watanabe et al. (2011). The RER values obtained for the cork granulate are clearly higher than those described for the determination of moisture in wood, when using either the Vis + NIR region (RER: 46.6; Table 3 top part) or only the NIR region (RER: 25.4; Table 3 bottom part).

The results obtained for the granulate show an improvement over previous results in cork planks (r_{cv}^2 0.66 and SECV 0.36) and stoppers (r_{cv}^2 0.86; r_{EV}^2 0.85; SECV 0.34; SEP 0.38; RPD_{EV} 2.65; RPD_{EV} 2.51). The moisture range of the granulate training set (271.3–967.5 %) is much higher than the moisture range found in previous studies in cork planks (4.74–14.5 %) and stoppers (3.47–8.14 %) (Prades et al. 2010, 2014). The RPD and RER values obtained in the granulate are substantially better than the values for cork planks and stoppers due to the higher range, the smaller error as a result of how the spectra was obtained, and the greater homogeneity of the granulated product compared to intact products such as cork planks and natural cork stoppers. The calibrations developed and described in Table 3 are in line with those of the AACC (1999) and Fearn (2002), thus indicating that they are suitable for quantifying the moisture content of cork granulate in both the VIS/NIR and NIR region.

Conclusion

The MM of cork granulate was reached after 80 days of saturation, with a mean MM of 661.1 (ranging from 967.5 % for the smallest granule size to 271.3 % for the largest). The EM under ambient conditions was reached after 58 days of drying, with a mean EM of 6.2 % (ranging from 5.8 % for the smallest granule size to

7.5 % for the largest). The most accurate model to estimate the moisture content as a function of days elapsed since the start of the drying period was exponential with coefficient of determination (R^2) values between 0.90 and 0.94 depending on the granule size, and of 0.84 for the training set.

The quantitative calibrations achieved excellent accuracy and precision, with r_{cv}^2 and r_{EV}^2 values of 0.99. The equation with the lowest SECV and SEP values (24.22 and 26.96 %, respectively) and the highest RPD and RER values in both the calibration (12.6 and 46.6, respectively) and the external validation (11.7 and 39.7, respectively) was selected. The equation has a high predictive capacity in line with Williams (2001) and is suitable for use in routine quantification according to AACC (1999).

No previous studies have estimated the moisture content of cork granulate between MM content and EM using Vis/NIRS technology. The results confirm that Vis/NIRS technology can be used to quantify the moisture content of cork granulate in routine analysis in an easy and inexpensive manner.

Acknowledgments NIR data were obtained using NIRS hardware and software provided by the NIR/MIR Spectroscopy Unit of the SCAI at the University of Cordoba (Spain). The authors acknowledge Morell and Samec for supplying the cork granulate used in the study.

References

- AACC (1999) Near-infrared methods: guidelines for model development and maintenance—AACC method 39–00. Approved methods of the American association of cereal chemists. St. Paul MN, AACC Press, Washington, D.C.
- Abdulla G, Belghit A, Allaf K (2009) Impact of instant controlled pressure drop treatment on moisture adsorption isotherm of cork granules. *Dry Technol* 27(2):237–247
- Abdulla G, Belghit A, Allaf K (2010) Impact of the instant controlled pressure drop treatment on hot air drying of cork granules. *Dry Technol* 28(2):180–185
- Abenojar J, Barbosa AQ, Ballesteros Y, del Real JC, da Silva LFM, Martínez MA (2014) Effect of surface treatment on natural cork: surface energy, adhesion and acoustic insulation. *Wood Sci Technol* 48(1):207–224
- Adedipe OE, Dawson-Andoh B (2008) Predicting moisture content of yellow-poplar (*Liriodendron tulipifera*) veneer using near-infrared Spectroscopy. *For Prod J* 58:28–33
- Barnes RJ, Dhanoa MS, Lister SJ (1989) Standard normal variate transformation and de-trending of near-infrared diffuse reflectance spectra. *Appl Spectrosc* 43(5):772–777
- Belghit A, Bennis A (2009) Experimental analysis of the drying kinetics of cork. *Energy Convers Manag* 50(3):618–625
- Carpintero E, Jurado M, Prades C (2014) Application of a kiln drying technique to *Quercus Suber L.* cork planks. *Food Bioprod Process* 93:176–185
- Cooper PA, Jeremic D, Radivojevic S, Ung YT, Leblon B (2011) Potential of near-infrared spectroscopy to characterize wood products. *Can J For Res* 41:2150–2157
- Costa A, Pereira H (2013) Drying kinetics of cork planks in a cork pile in the field. *Food Bioprod Process* 91:14–22
- Defo M, Taylor AM, Bond B (2007) Determination of moisture content and density of fresh-sawn red oak lumber by near infrared spectroscopy. *For Prod J* 57(5):68–72
- Fearn T (2002) Assessing calibrations: SEP, RPD, RER and R2. *NIR News* 13(6):12–14
- Gil L (2009) Cork composites: a review. *Materials* 2(3):776–789
- Gil L, Cortiço P (1998) Cork hygroscopic equilibrium moisture content. *Holz Roh Werkst* 56:35–358
- Gómez-Sánchez I, García de Ceca JL, García-Olmo J, Lara-Buil L, López-Luque R, Prades C (2013) Application of image analysis and NIRS technology for the evaluation of the porosity of planks,

- sheets and cork stoppers, and its relation with the industrial quality (in Spanish). *Maderas-Cienc Tecnol* 15(3):293–309
- Gong YM, Zhang W (2008) Recent progress in NIR spectroscopy technology and its application to the field of forestry. *Spectrosc Spect Anal* 28(7):1544–1548
- González-Adrados JR, Haro R (1994) Variation in the equilibrium moisture content of raw cork with relative humidity. Nonlinear regression models for sorption isotherms (in Spanish). *For Syst* 3:199–209
- Jiang ZH, Huang AM (2006) Water in wood and its near infrared spectroscopic analysis. *Spectrosc Spect Anal* 26(8):1464–1468
- Kothiyal V, Raturi A (2011) Estimating mechanical properties and specific gravity for five-year-old *Eucalyptus tereticornis* having broad moisture content range by NIR spectroscopy. *Holzforschung* 65(5):757–762
- Leblon B, Adedipe O, Hans G, Haddadi A, Tsuchikawa S, Burger J, Stirling R, Pirouz Z, Groves K, Nader J, LaRocque A (2013) A review of near-infrared spectroscopy for monitoring moisture content and density of solid wood. *For Chron* 89(5):595–606
- Lequin S, Chassagne D, Karbowski T, Gougeon R, Brachais L, Bellat JP (2010) Adsorption equilibria of water vapor on cork. *J Agr Food Chem* 58(6):3438–3445
- Mora CR, Schimleck LR, Clark IIIA, Daniels RF (2011) Determination of basic density and moisture content of merchantable loblolly pine logs by near infrared spectroscopy. *J Near Infrared Spectrosc* 19(5):391–399
- Pereira H (2007) *Cork: Biology, Production and Uses*. Elsevier, Amsterdam
- Pintor AMA, Ferreira CIA, Pereira JC, Correia P, Silva SP, Vilar VJP, Botelho CMS, Boaventura RAR (2012) Use of cork powder and granules for the adsorption of pollutants: a review. *Water Res* 46(10):3152–3166
- Prades C, García J, Romero T, García JL, López R (2010) Methodology for cork plank characterization (*Quercus suber L.*) by near-infrared spectroscopy and image analysis. *Meas Sci Technol* 21(6):065602
- Prades C, Gómez I, García J, González JR (2012) Discriminant analysis of geographical origin of cork planks and stoppers by near infrared spectroscopy. *J Wood Chem Technol* 32(1):54–70
- Prades C, Gómez I, García J, González F, González JR (2014) Application of VIS/NIR spectroscopy for estimating chemical, physical and mechanical properties of cork stoppers. *Wood Sci Technol* 48(4):811–830
- Robledano MD, Prades C, González JA (2009). Evolution of cork moisture content after extraction in Sierra de Jerez de los Caballeros (Extremadura) (in Spanish) In: Zapata, s. (Ed.), *Cork Oak Woodlands and Cork Industry: Present, Past and Future*. Palafrugell, pp. 266–275
- Rosa ME, Fortes MA (1993) Water absorption by cork. *Wood Fiber Sci* 25:339–348
- Schimleck LR, Stürzenbecher R, Jones PD, Evans R (2004) Development of wood property calibrations using near infrared spectra having different spectral resolutions. *J Near Infrared Spectrosc* 12:55–61
- Schwanninger M, Rodrigues JC, Fackler K (2011) A review of band assignments in near infrared spectra of wood and wood components. *J Near Infrared Spectrosc* 19(5):287–308
- Shenk JS, Westerhaus MO (1991) Population definition, sample selection and calibration procedures for near infrared reflectance spectroscopy. *Crop Sci* 31(2):469–474
- Shenk JS, Westerhaus MO (1995a) Routine operation, calibration, development and network system management manual. NIRSystem Inc., Silver Spring, USA
- Shenk JS, Westerhaus MO (1995b) Analysis of agriculture and food products by near infrared reflectance spectroscopy. Moograph. NIRSystem Inc., Silver Spring, USA
- So CL, Via BK, Groom LH, Schimleck LR, Shupe TF, Kelley SS, Rials TG (2004) Near infrared spectroscopy in the forest products industry. *For Prod J* 54(3):6–16
- Thygesen LG, Lundqvist SO (2000a) NIR measurement of moisture content in wood under unstable temperature conditions. Part 1: thermal effects in near infrared spectra of wood. *J Near Infrared Spectrosc* 8:183–189
- Thygesen LG, Lundqvist SO (2000b) NIR measurement of moisture content in wood under unstable temperature conditions. Part 2: handling temperature fluctuations. *J Near Infrared Spectrosc* 8:191–199
- Tsuchikawa S (2007) A review of recent near infrared research for wood and paper. *Appl Spectrosc Rev* 42(1):43–71
- Tsuchikawa S, Torii M, Tsutsumi S (1996) Application of near infrared spectrophotometry to wood. 4. Calibration equations for moisture content. *Mokuzai Gakkaishi* 42:743–754

- UNE 56917 (1988). Cork granulate. Determination of moisture content (in Spanish). AENOR. Madrid
- UNE 56911 (1998). Cork. Vocabulary (in Spanish). AENOR. Madrid
- Watanabe K, Mansfield SD, Avramidis S (2011) Application of near-infrared spectroscopy for moisture-based sorting of green hem-fir timber. *J Wood Sci* 57:245–258
- Watanabe K, Kobayashi I, Saito S, Kuroda N, Noshiro S (2013) Nondestructive evaluation of drying stress level on wood surface using near-infrared spectroscopy. *Wood Sci Technol* 47(2):299–315
- Williams PC (2001) Implementation of near-infrared technology. In: Williams PC, Norris KH (eds) *Near infrared technology in the agricultural and food industries*. AACC Inc, St. Paul, pp 145–171