Chemistry of Lignocellulosics: Current Trends

Editor

Tatjana Stevanovic
Department of Wood and Forest Sciences
Laval University
Quebec City, Quebec, Canada

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business
A SCIENCE PUBLISHERS BOOK

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2018 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20180626

International Standard Book Number-13: 978-1-4987-7569-4 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Cogress Cataloging-in-Publication Data

Names: Stevanovic, Tatjana, editor.
Title: Chemistry of lignocellulosics : current trends / editor, Tatjana Stevanovic (Department of Wood and Forest Sciences, Laval University, Quebec City, Quebec, Canada).
Description: Boca Raton, FL : CRC Press, [2018] | "A science publishers book." | Includes bibliographical references and index.
Identifiers: LCCN 2018027437 | ISBN 9781498775694 (hardback)
Subjects: LCSH: Lignocellulose. | Botanical chemistry. | Green chemistry. | Hemp. | Wood--Chemistry.
Classification: LCC TP248.65.L54 C4575 2018 | DDC 660.028/6--dc23
LC record available at https://lccn.loc.gov/2018027437

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

3

Near Infrared Spectroscopy, A New Tool to Characterize Wood for Use by the Cooperage Industry

Gilles Chaix,[1,2,3] *Thomas Giordanengo,*[4] *Vincent Segura,*[5] *Nicolas Mourey,*[4] *Bertrand Charrier*[6] and *Jean Paul Charpentier**[,5]

General Introduction

It is important for the industry to be able to quickly measure and/or evaluate the mechanical, physical and chemical properties of wood. Whether it is upstream in the field, on a living tree, when transformed into timber or in industrial product, during and after the material is put into operation. Among the non-destructive measurement techniques that have been developed since the 1980s, spectroscopy based on emission or absorption in the near infrared (NIR spectroscopy), i.e., in the

---

[1] CIRAD, UMR AGAP, 34398 Montpellier, France.
Email: gilles.chaix@cirad.fr

[2] AGAP, Univ Montpellier, CIRAD, INRA, Montpellier SupAgro, Montpellier, France.

[3] ESALQ-USP, Wood Anatomy & Tree-Ring Lab, Piracicaba, Brazil.

[4] R&D Tonnellerie Radoux – Pronektar, 10 Avenue Faidherbe, 17500 Jonzac, France.
Emails: t-giordanengo@sciage-du-berry.fr; n-mourey@radoux.fr

[5] BioForA, UMR INRA-ONF and Wood Analysis Technical Platform GénoBois, INRA Val de Loire, 2163 avenue de la Pomme de Pin 45075 Orléans, France.
Emails: vincent.segura@ inra.fr; jean-paul.charpentier@inra.fr

[6] Université de Pau et des Pays de l'Adour, Xylomat, IUT, 40004 Mont de Marsan, France.

* Corresponding author: jean-paul.charpentier@inra.fr

frequencies between 800 and 2500 nm, offers a new field of possibilities for analysis and evaluation of the quality of materials. While NIR spectroscopy is still not widely used in the wood industry, it is more developed in other industrial sectors such as petrochemicals, pharmaceuticals, agriculture, agrotechnology, food and textiles.

Since the early 1990s, numerous research studies have explored the value of using NIR spectroscopy to estimate the properties of wood material. This represents more than 500 scientific articles published in this sector with an average since the end of the 2000s of about 40 articles published each year (Tsuchikawa 2007, Tsuchikawa and Kobori 2015). This chapter attempts to take stock of the theoretical and practical aspects of SPIR technology and highlights through multiple examples, the wide potential of this measurement tool in the field of wood quality assessment and in the use and processing of wood material.

In the first part, is discussed the general elements of the NIR spectroscopy methodology and present the significant results of the scientific literature. In the second part, we report the first industrial application of NIR spectroscopy in the field of the chemical quality of oak wood for cooperage. We do not seek to be exhaustive but rather to describe some of the most iconic applications, and to make the reader want to go further, such as the examples of durability conferred and cooperage. For an exhaustive view, we recommend reading bibliographic reviews (Tsuchikawa 2007, Tsuchikawa and Schwanninger 2013, Tsuchikawa and Kobori 2015) and specialized works (Osborne et al. 1993, Bertrand and Dufour 2006).

NIR Spectroscopy and Wood Chemistry: Theoretical Approach and Fields of use of the Technology

Principles and theoretical approach of NIR spectroscopy

Spectroscopy can be defined as the study of the interaction of electromagnetic waves with matter. The electromagnetic spectrum is generally divided into various regions as a function of the wavelength of the radiation where the gamma rays are found which are the most energetic, the X-rays, the ultraviolet, the visible, the infrared (IR), microwaves and radio frequency waves. Each region is associated with a type of atomic or molecular transition involving different energies.

The infrared (IR) domain, characterized by vibrational-type energy transitions and comprises three spectral ranges: the near-IR (NIR) between 800 and 2500 nm, the mid IR (MIR) between 2500 and 25000 nm and far IR (FIR), beyond 25000 nm.

NIR spectroscopy is the spectral region of harmonic bands and combination bands (Fig. 1). This region is dominated by the absorption of the bonds of the functional group X-H, where X corresponds to carbon, oxygen or nitrogen atoms, and H denotes the hydrogen atom. An absorption spectrum is most frequently represented by the decimal logarithm of the inverse of the reflectance as a function of wavelengths in nanometers or of the wave number in cm^{-1}. Spectral information is repeated in the regions of the harmonic and combination bands, which facilitates

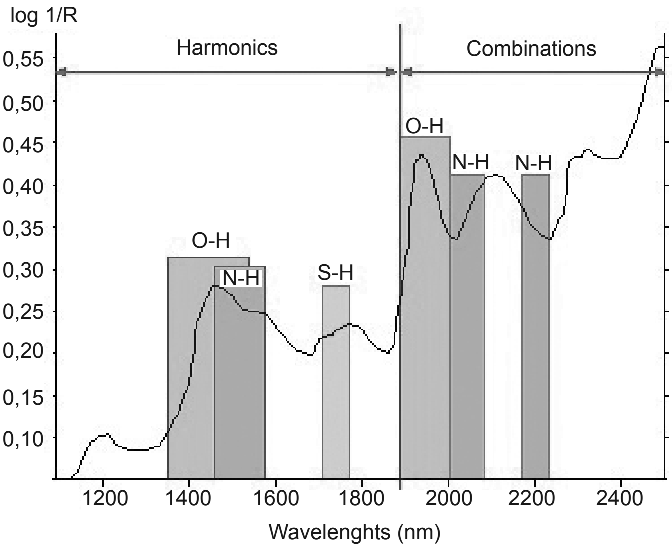

Fig. 1. Near-infrared absorption bands, particularly OH, NH and SH bonds, the C-H bonds are at the origin of the absorption bands throughout the NIR region (after Bertrand 2002).

the construction of the quantitative models. Schwanninger et al. (2011) conducted a review of the absorbance bands of the main wood compounds in the NIR domain.

When light radiation comes into contact with matter, it can be absorbed, transmitted or reflected. The transmittance *T* is defined as the fraction of light energy passing through the sample from one side to the other: $T = IT/I0$ (*IT* being the transmitted light intensity, *I*0 the luminous intensity emitted by the source). The reflectance *R* represents the part of the reflected light. It is defined by the ratio of the intensity reflected on the incident intensity: $R = IR/I0$ (*IR* being the reflected light intensity).

Diffuse reflection contains rich information on the chemical composition of the material. Absorbance *A* is defined as the logarithm of the inverse of the transmittance *T* or the reflectance *R*: $A = \log(1/T)$ or $A = \log(1/R)$

Most molecules are *IR* active and are represented by diverse bands due to different types of molecule vibrations. Band intensities depend on the concentration of the compound on its molar absorption coefficient and on individual properties of the functional group. For complex materials like wood, bands are broad and overlapping and are often not assignable. However, *IR* spectrum could be considered like a “fingerprint” of the analyzed material.

The equipment

Many commercial instruments are specifically dedicated to industrial analytical applications in the NIR region. Their principles differ according to the technical options chosen by the builders; one can classify them into three main technologies:

- **Sequential spectrometers**
  These devices are characterized by recording the light absorptions one after the other, scanning the spectral region in a sequential order. Typical instruments in this group are optical filters or monochromatic spectrometers.
- **Multiplexed spectrometers**
  These spectrometers have a single photosensitive sensor that simultaneously receives information corresponding to several wavelengths. Among the multiplexed devices, Fourier transform (FTNIR) spectrometers are widely used in research and quality control.
- **Multichannel spectrometers**
  Unlike multiplexed spectrometers, multichannel spectrometers have multiple photosensitive sensors that can independently record the absorption of light at specific wavelengths. Examples of devices belonging to this group include diode array systems and hyperspectral cameras.

Chemometrics for NIR spectroscopy analysis

Chemometrics is "the science of using mathematical, statistical and computer methods to improve the extraction of information obtained from analytical data" (Geladi 1995).

NIR spectra provide information on the chemical and physical properties of the samples studied. Obtaining this information is not immediate and requires a mathematical treatment that can be relatively complex.

Chemometric methods can be classified according to their linear or non-linear nature (Bertrand 2002). Linear methods assume that useful information can be extracted from linear combinations of predictor variables. In this approach, a spectrum is considered as the sum of pure spectra or underlying signals. Non-linear methods, which are essentially connectionist, are part of the field of artificial intelligence and mainly involve neural networks. Chemometric methods can also be classified according to their supervised (predictive) or unsupervised (descriptive) nature. In supervised methods, NIR spectral data are used to predict a qualitative or quantitative variable. With regard to unsupervised methods (for example, principal component analysis named PCA), spectral data are available only without further information on the nature of the data. The vast majority of NIR spectroscopy applications are based on supervised and linear methods for forecasting quantitative variables.

To calibrate a property by NIR spectroscopy, it is necessary to measure on the same lot of samples the NIR absorbance spectra as well as the values of this property by a reference method. Thanks to chemometrics, a model linking the spectrum and the reference measurement is obtained. If the resulting model is efficient, it can be used to estimate the property of new samples only from the NIR absorbance spectrum. Many methods are available but partial least squares regression (PLS-Regression) is the most used. Via et al. (2014) proposed to assess and compare the performance of PLS and PCR (principal components regression). Their conclusion was that PLS was found to provide better predictive diagnostics but PCR was better for model interpretation and wavenumber selection. Many software programs allow the development and application of these mathematical algorithms and recently a free and shared internet tool was developed by a French team and made available to chemometricians (http://chemproject.org).

Calibration optimization

Limitations and recommendations for a good calibration

The limit detection level of a component on complex products is of the order of 0.5 to 1% of the mass. There is not much hope to use NIR spectroscopy for components in very low concentrations. Moreover, the minerals do not absorb in the NIR, so only the organic matter can be detected.

The penetration depth of IR radiation in solid wood does not generally exceed 1 to 2 mm and only a few millimeters for powdered wood. These penetration depths depend on the characteristics of the emission source, the density and the compaction of the powders.

Attention must also be paid to the quality of the reference measurement. This measurement is the basis of calibration and determines its quality. It is important to perform a repeatability and accuracy analysis of the reference method measurement to determine the Standard Error of Laboratory (SEL). SEL has to be compared to the error of the NIR spectroscopy calibrations. The quality of calibration will depend very much on the quality of the reference measurement. The more noise it contains, the less effective modeling will be. Similarly, the quality of the spectral data and thus the state of the spectrometer will have an influence on the quality of the calibration.

The calibration samples must be numerous (generally between 100 and 300 samples depending on the property to be calibrated), representative of those that will be analyzed later (the selection can be made on the basis of the spectral information measured in advance on the samples) and have a sufficiently large variability of the character of interest to cover the range of variation thereof. Random selection of samples is not desired for calibration: a Gaussian type distribution is usually observed with many values close to the mean and extreme values is infrequent. A selection of samples that balance their distribution well along the gradient of variation is preferable.

Sample preparation must be well defined and repeatable. Sampling conditions, grinding, particle size (for powders), drying, storage, filling (for powders) and presentation for solid wood (ligneous orientation, temperature, surface quality, etc.), must be fixed according to a protocol established by the operator. This protocol will be maintained in the future for the prediction of new samples. In fact, keeping the measuring device in good condition, thanks to the internal tests but also thanks to the regular tests performed on reference samples, is a decisive element for a quality operationality.

Simple calibration does not determine the reliability of the models. In other words, the calibration error (RMSEC: Root Mean Square of Standard Error Calibration) is not sufficient to evaluate the performance of a model. However, it is imperative to validate the models to achieve this goal of reliability. The validation step consists in applying the predictive models to a second set of samples that were not used for calibration. It is considered that the validation is independent (named external validation). It is generally accepted to use a cross-validation, especially when the number of samples is low (100–150), or more simply to check the feasibility of a calibration. The latter consists of successively placing each of the observations available in the validation set (named full cross-validation), or randomly dividing the samples into several validation groups (few is better), and using them successively to validate the model (see Fig. 2). The latter is

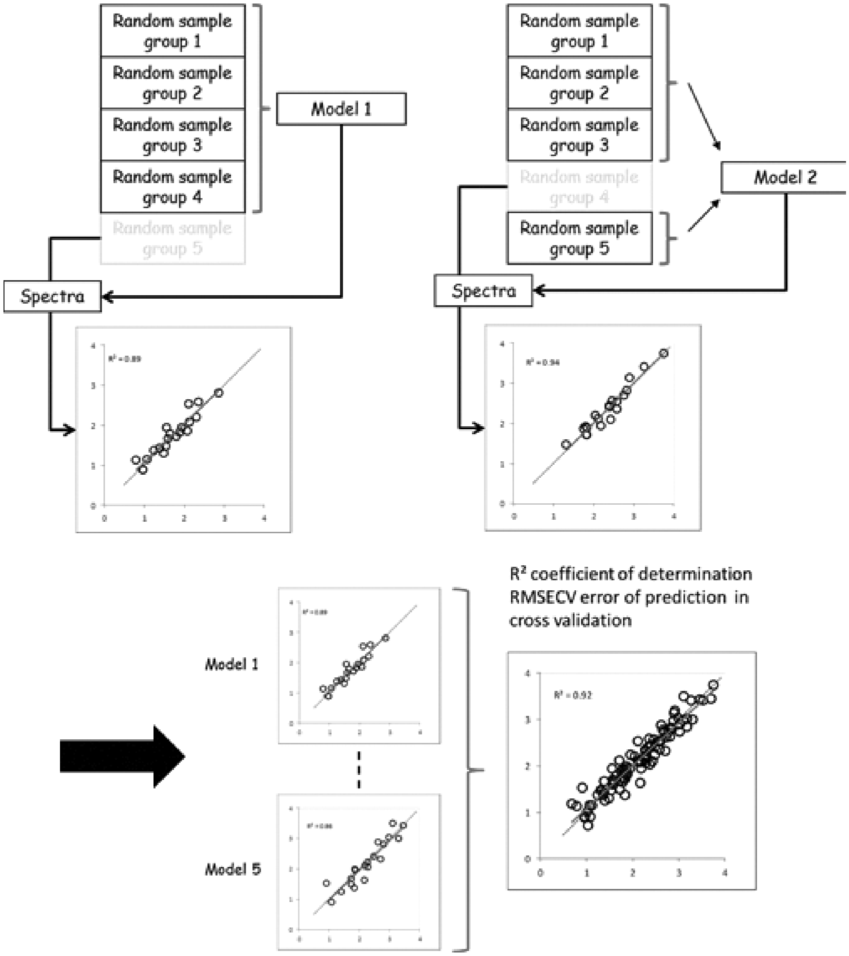

Fig. 2. Cross-validation process for NIR spectroscopy calibration and validation.

recommended and increasingly used. Another option is to divide the sample set into two group and use one for calibration and the other for validation and repeat it several times (minimum of ten times). After this, it is better to use an independent sample set to validate the model.

This set of constraints and recommendations is however essential, as is the dexterity of the operator. Failure to follow them means that costly NIR devices are no longer used, or that the NIR technology is abandoned because it is judged ineffective although many laboratories have shown its efficiency.

Spectral data pretreatments commonly used

Raw spectral data are often spoiled with defects related to surface differences, grain size variation and presence of random noise resulting in deformation of baseline of the NIR spectrum. Spectral pre-treatments can be used before applying a chemometric method to improve the quality of the spectral signal. These pre-treatments are numerous and of several types, and the most common are:

i) *Vector Normalization (SNV)*: The average and the standard deviation are calculated for each spectrum. Then each absorbance value of the spectrum is subtracted with the mean value and the result is divided by the standard deviation of the spectrum. This standardization is very effective in reducing the effect of particle size on absorbance, for example, and any other uncontrollable environmental effect.
ii) *The derivative*: The calculation of a derivative type pre-treatment is characterized by three criteria: the order of the derivative, the segment on which the derivative is calculated and the number of points taken into account for the smoothing preceding the operation of derivation. The derivative is effective in reducing peak overlap problems and large baseline variations (Fig. 3).
iii) *Multiplicative Scatter Correction (MSC)*: It is based on the linear modeling of a spectrum according to the average spectrum of a sample set. The "error" represents effects that cannot be modeled by a constant and multiplier. It therefore reflects spectral variations from "useful" chemical information.

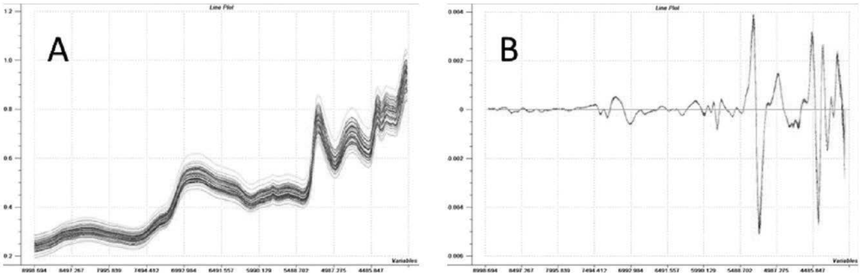

Fig. 3. Example of pretreatment of spectral data of oak wood, (A) raw spectrum, (B) spectra after a second derivative (smoothing on 25 points of polynomial type of order 3 before derivation).

Calibration evaluation criteria

Optimizing a calibration requires knowing how to use different statistical criteria to ensure the reliability and quality of the model.

The standard errors of calibration (SEC or RMSEC) corresponds to the standard deviation of the residuals of the modeling. It is representative of the fit quality of the model to the calibration batch.

The standard errors of cross-validation (SECV or RMSECV) is the standard deviation of the residues obtained with cross-validation groups. RMSECV is calculated in the cross-validation process (Wold 1978). The spectra are separated into sets (or groups or segments) of the same number of samples, chosen randomly or systematically. As many models as groups are built and validated by the removed samples.

The standard errors of prediction (SEP or RMSEP) is used to evaluate the quality of the prediction model. A validation test is performed on a group of samples completely independent of that used to create the calibration model. SEP is the standard deviation of the residues obtained with the validation batch.

In addition, the ratio RMSEP/RMSECV was sometime adopted to evaluate the robustness of the model; a model with RMSEP/RMSECV lower than 1.2 was usually considered robust (Alves et al. 2012).

The rank (number of factors, number of latent values) is the number of PLS factors introduced to develop the equation of a model. It is determined during the calibration process by comparing the SEC and SECV curves. Increasing the rank improves the fit of the calibration. However, using too high a rank may result in overfitting.

The ratio of performance to deviation (RPD) is the relationship between population variability (standard deviation) and prediction error (Williams and Sobering 1993, Williams 2014). It is used to judge the quality of the calibration and its potential applications. If the prediction error is close to the standard deviation, calibration can only predict the population mean. There is RPD degrees adapted for wood, forages, feeds, soils (complex materials). For a value less than or equal to 1.9, it is not recommended to use the model. A value between 1.9 and 2.4 generally makes it possible to sort and screen the samples in a few classes. Between 2.5 and 2.9, the sorting will be better and can be used, for example, for breeding programs. Between 3.0 and 3.4, the prediction is satisfactory and can be used in quality control. Between 3.5 and 4.0, the calibration is considered very satisfactory and can be used in process control. Beyond 4.1, the model is considered as excellent and valid for all analytical applications for this type of material (Williams 2014).

The coefficient of determination in calibration (R^2c), in cross-validation: (R^2cv), in validation (r^2) provide information between the NIR model prediction and the reference measurements for the same samples. Its value is between 0 and 1, a value close to 1 indicates a very good fit.

Recently, Williams et al. (2017) report in an exhaustive tutorial almost 40 items essential to show the results on NIR spectroscopy model. These must be reported and explained in a NIR spectroscopy project to allow duplication of the application and methods reported. These items are very important if the final project is to extend it to the level of industrial application.

Application development outside the laboratory

NIR absorbance is sensitive to many parameters such as temperature (Chauchard et al. 2004) or wood moisture content (Giordanengo et al. 2008), and spectrometers are not necessarily suitable for all industrial atmospheres (thermal amplitudes, vibrations, dust, vapors, etc.). When a measurement methodology is developed and validated under controlled laboratory conditions, specific developments are usually necessary in order to obtain a robust measurement methodology for applications in industrial conditions. Sensor design and measurement methodology are critical steps in optimizing application performance. Furthermore, it is also common to use chemometric methods to suppress the influence of NIR signal disturbance factors (Roger et al. 2003, Chauchard et al. 2004, Zeaiter 2004) as well as for calibration transfer between devices.

The development of new miniaturized and portable equipment makes it possible to envisage for the future the deported use on the log parks or the timber stocks or even directly on the field on standing trees.

The main fields of application of NIR spectroscopy to evaluate wood chemical properties and its products

Quantification of wood macromolecules

Cellulose content

The cellulose content of wood is strongly correlated with the yield of kraft pulp (Kube and Raymond 2002). Schimleck et al. (2000) obtained excellent calibration of cellulose content with an r^2 greater than 0.90 for the two eucalyptus species *E. globulus* and *E. nitens*. Raymond and Schimleck 2002 showed the reliability of the NIR spectroscopy to predict the cellulose content for *Eucalyptus globulus*, as did Downes et al. 2010 with *Eucaluptus nitens*. Similar work has been done by Wright et al. 1990 on a series of pine species where a coefficient of determination in cross validation of 0.73 was obtained between the measured cellulose content and that predicted by the NIR spectroscopy. Clarke and Wessels (1995) also measured the cellulose content of a series of eucalyptus species by NIR spectroscopy and the calibrations gave a coefficient of determination equal to 0.73 between the measured value and the predicted value. Schimleck et al. 2000, demonstrated the ability of NIR spectroscopy both in the control of the pulp quality of eucalyptus plantations and in the selection of individuals with the highest pulp yield.

Lignin content and lignin quality

NIR spectroscopy was used to control the delignification process during kraft cooking of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) samples (Lindgren et al. 1998). It has been shown that measurements of NIR spectra made during the various delignification steps can be used in the prediction of pulp yield, kappa index and Klason lignin.

Usually, the quantification of lignin is difficult not only because of the variability of its monomeric composition but also because lignin may be covalently linked with carbohydrates, proteins, phenols and other compounds in the cell wall. These products may interfere with lignin determination leading to over- or under-estimation (Monties 1989). In the works of Brinkmann et al. (2002), the lignin content of 5 different species (*Nicotiana tabacum*, *Populus* x *canescens*, *Fagus sylvatica*, *Quercus robur* and *Picea abies*) was determined using two chemical methods: first a gravimetric method based on acid hydrolysis of polysaccharides (acid detergent fiber technique), and second a spectrophotometric method measuring UV absorbance (thioglycolic acid process). The coefficient of determination between the data obtained by these two methods of analysis and those by the NIR spectroscopy were very high ($R^2 > 0.98$). Yeh et al. (2004) calibrated the lignin level using PIR spectra measured from chips and *Pinus taeda* wood powder. The results obtained in validation between the measured and predicted values were 0.81 for the R^2_{cv} with SECV = 0.73 in crossvalidation for the powders and $r^2 = 0.71$ with a SEP = 0.87 in external validation for the chips.

He and Hu (2013) investigated the feasibility of using FT-NIR spectroscopy to rapidly determine the lignin content of 147 different species of Chinese wood trees species, including softwoods and hardwoods. The automatic selection of relevant wavenumbers combined with the appropriate data pre-processing methods produced satisfactory prediction models (obtained values of R^2 of prediction between 0.9775 and 0.9521).

Hodge and Woodbridge (2004) developed multispecific lignin content calibration for 5 tropical and subtropical pine species (*Pinus caribaea, Pinus maximinoi, Pinus oocarpa, Pinus patula* and *Pinus tecunumanii*) from Brazil and Columbia. Calibrations, developed from the reflectance spectra, gave values of r^2 around 0.90 in validation. Denis et al. (2013) and Chaix et al. (2012) developed calibrations for the main wood chemical compounds (extractives, lignins, holocellulose, cellulose, syringyl/guaiacyl (S/G ratio) with several species of *Eucalyptus*, and obtained relevant results (r^2 of 0.74 to 0.96 and RPD of 2.0 to 4.8). Alves et al. (2011) also proposed a determination of an S/G ratio of *Eucalyptus globulus* wood lignin using analytical pyrolysis as reference method.

To establish the best PLS-R model for prediction of lignin content in wood of Norway spruce, Schwanninger et al. (2011a, 2011b) took care of the influence of the particle size of the wood powder. They also verified several data-processing methods to select wavenumber range in spectra taken with a fiberoptic probe.

Baillères et al. (2002) and Denis et al. (2013) worked on the calibration of the S/G ratio and obtained calibrations for efficient prediction ($r^2 = 0.90$, SEP = 0.28, RPD = 2.4 for Baillères et al. (2002) and $R^2_{cv} = 0.92$, SECV = 0.13, RPD = 2.5 for Denis et al. (2013). Alves et al. (2006) have effectively developed calibrations for another criterion: the ratio H/G in maritime pine.

Holocellulose content

Holocellulose represents all the cellulose and hemicellulose polysaccharides constituting wood. Thus, the hemicellulose and cellulose content was calibrated by NIR spectroscopy in *Liquidambar styraciflua* and *Pinus taeda* (Schultz and Burns 1990). Denis et al. (2013) and Chaix et al. (2012) also investigated the possibility of calibrating holocellulose levels in eucalyptus. They obtained, in cross-validation for holocellulose, $RPD_{cv} = 3.2$, SECV = 2.07% and $R^2_{cv} = 0.90$. Kothiyal et al. (2015) showed multispecific models (*Eucalyptus*, *Dalbergia*, *Leucaena*, and *Populus*) with RMSEP from 0.64 to 1.05% and an r^2 around 0.90

Hemicellulose content and individual sugars

Yao et al. (2010) calibrated hemicelluloses in acacia and observed SEP = 0.55% and an $r^2 = 0.95$. For *Acacia mangium*, Karlinasari et al. (2014) validated a model with an SEP = 1.9, $r^2 = 0.82$ and RPD = 2.38. Chaix et al. (2012), calibrated hemicellulose levels for various eucalyptus species and cross-validation, obtained an $RPD_{cv} = 2.4$, SECV = 1.61% and $R^2_{cv} = 0.82$. All of this work tends to show that one can develop a calibration for hemicelluloses that can be used in the classification of samples.

As part of the *Tree4Joules* project (http://tfj.lrsv.ups-tlse.fr), the first sugar calibration results for eucalyptus and poplar showed the effectiveness of NIR spectroscopy for measuring arabinose, galactose, glucose and xylose.

A recent study by the INRA Orleans team on more than 6,000 samples has highlighted the contribution of NIR spectroscopy for the genetic study of European populations of black poplar to qualify wood quality criteria (lignins, lignin monomers, cellulose, hydrolysed and saccharifiable sugars, and extractives) related to its use for bioenergy (Gebreselassie et al. 2017).

Extractives wood compounds

Extractives content

The methods of analysis used to quantify extractives are complex and destructive. In the early 2000s, Kelley et al. (2004) used NIR spectroscopy to predict the extractive content of *Pinus taeda* solid wood. They obtained coefficients of determination between measured and predicted values between 0.62 and 0.88. The work of Gierlinger et al. (2002) also demonstrated the effectiveness of the NIR spectroscopy technique in assessing the natural durability of larch by determining the level of extractives from solid and powdered heartwood. However, calibrations based on solid wood spectra are less predictive than those constructed from powdered wood spectra. This is probably due to the addition of variable factors such as wood structure, sample geometry or surface properties (Brunner et al. 1996, Tsuchikawa et al. 1998, Zhang et al. 2015). Several studies were then developed to predict the extractive content from wood pulp (Meder et al. 1999, Baillères et al. 2002, Schimleck et al. 2003, Zhari et al. 2008, Alves et al. 2012). The correlations obtained between the quantity of the extracts and the value predicted by the NIR spectroscopy were each time high. These results confirm the effectiveness of the NIR spectroscopy technique in predicting the content of extractives whether from solid wood or sawdust.

The measurement of extractives compounds by NIR spectroscopy has also proved its effectiveness in tropical timber. Ribeiro da Silva et al. (2013) have shown that it is possible to quantify the presence of phenols in mahogany wood with an accuracy of 10% and a minimum concentration of 2.4%. Niamke et al. (2014) also showed it on teak for the total extractives compounds but also on some extractable molecules linked in particular to the natural durability of teak wood.

For Scots pinewood they are stilbene type molecules that give duramen its natural durability. The INRA team in Orléans associated with Finnish researchers has recently shown the feasibility of the indirect measurement of pinosylvine and its monomethyl ether by NIR spectroscopy applied on wood cores with models of sufficient quality to be used for genetic selection (Pulkka et al. 2016).

In the particular case of oak, wood extractives can be up to 10% of the dry wood mass (Scalbert et al. 1989). The work of Zahri et al. (2008) confirmed strong correlations ($R^2 = 0.93$) between chemical analyses of total oak phenols and NIR spectral data, highlighting the low percentage error in the prediction of total phenols (RMSEP = 0.54%). NIR spectroscopy is therefore an effective tool for predicting the amount of phenolic compounds in oakwood (RPD = 5.4). This prediction makes it possible to measure the amount of total phenols irrespective of the variability of the origin of the wood (provenance, species, tree). On solid wood, it can be seen that the prediction of the total phenol content from wood, whether at the axial or radial woody plane, is very satisfactory. From a practical point of view, these two measurement plans could be recommended for a routine implementation of the NIR spectroscopy technique to evaluate the phenol content in a fast, reliable and non-destructive way in industries related to oakwood.

Moreover, other studies have been conducted in France by several teams of cooperage Radoux, Ondalys, IRSTEA, INRA Loire Valley Orleans and CIRAD, and resulted in the establishment of the first European industrial tool for online measurement of the quantity of phenolic compounds in oakwood for the barrel production: *Oakscan*® process (Giordanengo et al. 2009). The approach and the tool are detailed in the next section of this chapter.

Evaluation of Cooperage Oakwood Quality by NIR Spectroscopy

Oak barrels were invented over 2000 years ago during the Gallo-Roman era. They quickly replaced amphora, which was heavier and more fragile. However, an oak barrel is not simply a container. It transmits certain compounds to the liquids it contains and modifies their sensorial properties. Nowadays, oak casks are not just used for the transport of beverages, but have become an essential tool in the production of wines and spirits. Indeed, "cask-matured" wines and spirits have their own complexity and originality.

Quality criteria for oak used in cooperage

In the 1990s, university research studies began to be interested in the use of oak casks in the making of wines and spirits (Chatonnet 1991, Masson 1996, Vivas 1997). Mainly, two physico-chemical phenomena were studied: the extraction of volatile and non-volatile compounds stemming from the oak and dissolution of the dioxygen from the air through the barrel.

The distinctive aroma resulting from oak barrel aging is defined by several descriptors, such as aromatic notes of "vanilla", "coconut", "spicy", "roasted" or "smoked". It is now considered that a hundred or so volatile compounds from wood have an effect on the bouquet of the wine (Boidron et al. 1988, Jarauta et al. 2005). Some compounds having a direct impact on the bouquet of the wine have been identified amongst these molecules: *cis* and trans β-methyl-γ-octalactone ("*boisé*/coconut" aroma), also named whisky lactones as their aroma is similar to that of a whisky, vanillin (aroma of "pastry vanilla") or eugenol and isoeugenol (clove aroma). It can also be remarked that notes of roasted and roasted coffee appear in the wine during aging. The wood's furaldehydes, in particular furfural, are extracted towards the wine and are at the origin of a very fragrant thiol compound, 2-furanemethanethiol (Tominaga et al. 2000).

Furthermore, non-volatile compounds are released during the aging process and contribute to the palate taste and structure of the wine. Amongst these compounds are ellagitannins which influence the astringency and bitterness of the wine (Glabasnia and Hofman 2006), and which are involved in many chemical reactions with wine compounds (Singleton 1987, Quideau et al. 2005, Chassaing et al. 2010). Other compounds, like some lignans, seem to have an impact on the bitterness of the wine. Recent works also highlight an increase in the sweetness of wines aged in barrels, which could be related to a family of compounds: the quercotriterpenosides (Marchal 2010).

Finally, a phenomenon of oxygenation of wines and spirits occurs during the barrel aging (Vivas and Glories 1996). Dissolved dioxygen is involved in the reduction of astringency and softening of red wines, and enables to avoid reduction aromas.

During manufacturing, three stages condition the sensorial typicity of a barrel: selection of the raw material, natural drying of the wood or maturation, and the heat treatment of the oak cask, or toast. Selecting the wood is primordial since it determines the initial chemical composition of the barrel. Natural drying in open yards with influence of weathering, or maturation, generally lasts 24 months and allows the wood to dry, lessens the ellagic tannins content and modifies the aromatic compounds content (Masson and Puech 2000). Traditionally, toasting was used to bend and assemble the casks. This step in manufacture has been widely studied, since thermal processing forms numerous aromatic compounds which give the wine the characteristic aromas of 'roasted', 'spicy' or 'smoked' (Chatonnet 1991). This toasting process is often considered to be the cooper's signature.

The chemical composition of oakwood is highly variable (Mosedale et al. 1996, Snakkers et al. 2000, Dousset et al. 2002, Guilley et al. 2004, Prida et al. 2006). Botanical species, geographic provenance, ecological conditions during growth, forestry, genetic factors or the position of wood in the log are so many parameters influencing this variability. The selection of the wood to be used in the production of the staves therefore plays an essential role in determining the quality of a barrel. For this reason, coopers place a great deal of importance on their supplies of oak.

Originally, geographic provenance was the first criterion for oak selection. Cooperage then turned to a macroscopic anatomical criterion, which was identifiable and which could, to some extent, be correlated with the composition of the wood: the width of annual growth or *grain*. Using grain as a criterion for selecting wood became commonplace within the profession. Nevertheless, wines aged in oak barrels from the same forests, or with the same grains, still present a significant sensorial heterogeneity. The best way to monitor the enological quality of oak wood is to analyze it chemically. However, such analyses are usually carried out on simulated extractions which are time-consuming and not readily compatible with wood selection on a large scale. Moreover, they are complex and costly to set up.

Then, we directed our studies towards the use of fast and non-destructive monitoring tools to assess the quality of oak wood. NIR spectroscopy was used to develop a specific sensor.

Development of NIR sensor to assess chemical quality of cooperage oakwood

In France, Tonnellerie Radoux developed a measurement process of oak polyphenols content, named Oakscan®, in partnership with INRA Val de Loire - Orléans, CEMAGREF, CIRAD and Ondalys Company (Giordanengo et al. 2009). It is the first time that NIR spectroscopy was introduced in the cooperage industry.

A collection of oak samples was prepared in order to build the NIR calibrations. Four hundred pieces of French oak were selected from the cooper's maturation stock with the aim of including the largest possible variation of wood composition. These samples were taken from 33 different batches of wood and were selected according to geographic provenance and their grain. First, the samples were characterized by chemical analysis, then measured by NIR spectroscopy.

Chemical analysis of the polyphenols was carried out in a laboratory by several 80% acetone extractions on wood powders. The amount of polyphenols present in the extracts was quantified by four methods:

- The extract rate is determined by measuring the loss of mass in the wood powders after extraction and drying.
- The optical density at 280 nm is measured in the final extract.
- The total phenols present in the extracts are dosed by a colorimetric method using the Folin-Ciocalteu reagent (Boizot and Charpentier 2006).
- The concentrations of eight oak ellagitannins in the extracts are determined by high performance liquid chromatography.

These reference analyses provide a rich information about the polyphenolic content of the oak samples and allow to build four NIR calibrations.

Figure 4 presents the correlations obtained for the four calibrations of the reference analyses characterizing the polyphenolic content of oakwood. These calibrations were built by Partial Least Squares regression, in controlled laboratory conditions. The NIR calibrations of optical density at 280 nm, total phenols measured by Folin-Ciocalteu and of ellagitannins are efficient (Table 1), and the NIR estimations are well correlated to the reference chemical analyses.

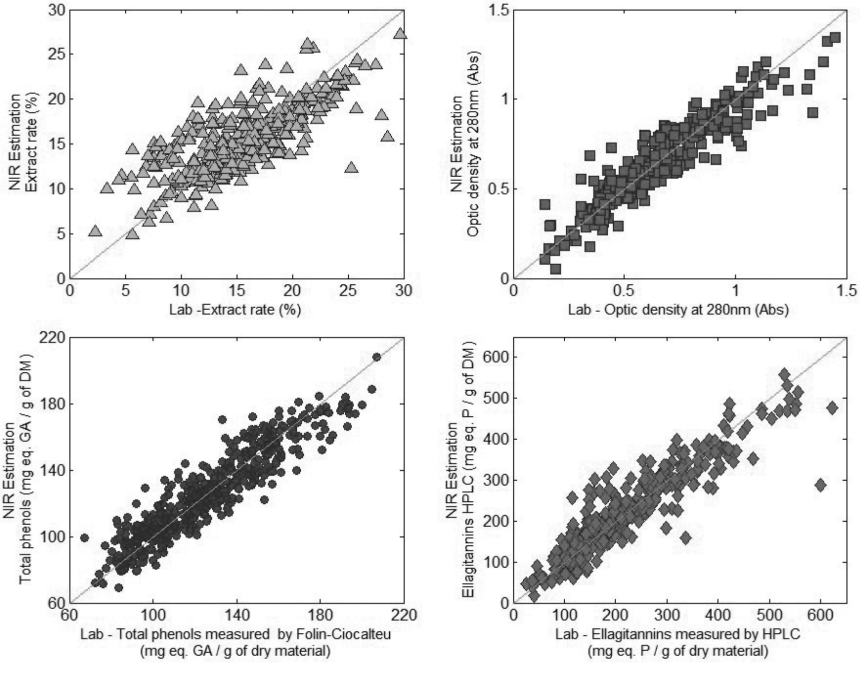

Fig. 4. Results of NIR calibrations for the extract rate, for the optical density at 280 nm, for the total phenols in the wood extracts measured by the Folin-Ciocalteu method and for the ellagitannins content measured by HPLC (cross validation).

Table 1. NIR calibrations results of the four reference chemical analyses of oakwood.

Analysis	Unit	Reference analyses			NIR Calibrations				
		Mean	Standard deviation	SEL	Rank	SECV	R^2_{CV}	bias $_{CV}$	SECV / SEL
Extract rate	%	15,4	4,9	2,1	6	3,3	0,56	-0,004	1,6
Optic density at 280nm	Absorbancy	0,64	0,24	0,05	5	0,09	0,85	-0,0008	1,9
Total phenols	mg equivalent gallic acid / g of dry material	122	24	6,9	4	10,7	0,86	-0,2	1,5
Ellagitannins	mg equivalent pyrogallol / g of dry material	223	116	21	10	49	0,82	-0,08	2,4

SEL: *Standard Error of Laboratory*; Rank: number of PLS latent variables used in the model; SECV: *Standard Error of Cross Validation*; R^2_{cv}: determination coefficient obtained in cross validation; bias$_{cv}$: bias of the results obtained in cross validation.

The prediction models of optical density at 280 nm, of total phenols and of ellagitannins content obtained are enough efficient to consider an industrial application aimed at measuring the polyphenols content of oak wood by NIR spectroscopy.

Industrialization of Oakscan® process

At the cooperage workshop, an NIR sensor was designed to function on the stave machining line. Adaptation on the line proved to be a difficult task, particularly to succeed in making the measurement reliable in the face of disrupting parameters such as temperature, variations in working conditions or the moisture content of the wood. Various methods were applied in order to obtain a robust spectral acquisition, by optimizing the physical conditions of the measurement and by processing the spectral information data with chemometric methods (Roger et al. 2003, Giordanengo et al. 2008).

In practice, the measurement process is used to create different selections of wood. The body of a barrel is composed of about 30 oak staves. Each machined stave is scanned in under one second. The three characteristics of polyphenolic content are estimated from the NIR calibrations, then an *Index of Polyphenols* between 0 and 100 is calculated and attributed to the piece. Figure 5 represents a control chart of the staves analyzed by Oakscan® process during one morning's production, and illustrates the variability of oak polyphenol content.

The oak staves are sorted into three classes with this *Index of Polyphenols* and then marked (Plate 1). Sorting wood according to this chemical criterion allow to improve the homogeneity of the raw material within each selection and thus favorize the reproducibility of wine aging in barrel over the years. Furthermore, it is possible to adapt the tannic potential of oak wood to the specifications of aging needed for each wine.

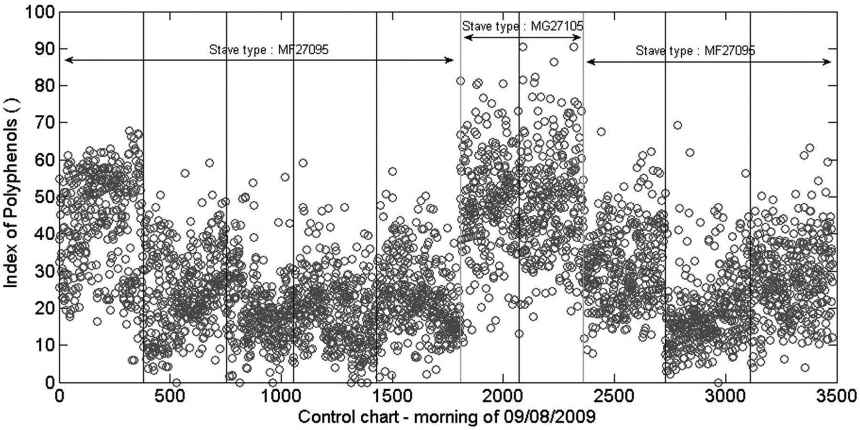

Fig. 5. Example of an Index of Polyphenols control chart, measurements realized on ten pallets of staves. Each point represents the Index of Polyphenols of one scanned stave. The vertical lines represent a change of pallet. Two types of staves are produced: MF27095–Fine Grain French oak stave for the production of 225 Li barrels and MG27105–Large Grain French oak stave for the production of 400 Li barrels.

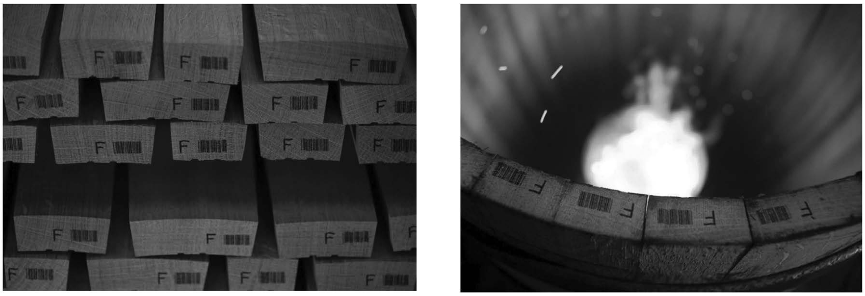

Plate 1. Stock of Oakscan® sorted staves and barrel during the toasting process.

The first comparative trials on wine began with the 2006 vintage. They were carried out in several appellations of the French regions of Bordeaux, Burgundy, Rhône Valley and Languedoc-Roussillon, as well as in Spain, Chile and California. The influence of the oak selection process has thus been studied for the production of red and white wines of different specifications from these regions and from different grape varieties (Merlot, Cabernet Sauvignon, Pinot Noir, Syrah, Grenache, Sauvignon Blanc, etc.). These trials have confirmed the importance of selecting oak wood according to its polyphenol content, and its value in order to monitor oak impact on wines and spirits.

In order to study deeply the interactions between oak and wine, this novel criterion for wood selection was studied during a Ph.D. thesis (Institut des Sciences de la Vigne et du Vin, Bordeaux, Michel 2012). The conducted research validated the correlation between the richness in tannins of the oak selections and the concentration of ellagitannins released in wine, as well as the influence of Oakscan® selections on sensorial descriptors such as roundness, fullness, bitterness or astringency.

Following on this experience, the technology has been applied to other activities in the industry. A similar process has been applied on stave milling, when the oak logs are first transformed into "merrain" (rough barrel stave). An NIR sensor allows the measurement of the level of tannins of oak wood before the natural drying, and thus characterize the distinctive types of stocked wood. Furthermore, the process has also been introduced into the manufacture of *Oak for Enology* (Giordanengo et al. 2012). Oak chips or tank staves provide an economical solution for producing oaked wines. New selections of *Oak for Enology* that have been sorted according to their richness in polyphenols exist since 2012.

Conclusions and perspectives

The entire production of French oak barrels manufactured by Tonnellerie Radoux has been measured and sorted according to the NIR spectroscopy process Oakscan®, since the summer of 2009. This technology has been introduced into the first transformation of wood, when oak logs are transformed into *merrain*, as well as in production of *Oak for Enology*. NIR analysis of the richness in polyphenols of oakwood ensures a better monitoring of oak tannic impact than that offered by traditional selection methods. This new sorting criterion allows to adapt the oak to the desired enological objectives and also contributes to improving the reproducibility of wine aging in the barrel. Furthermore, Tonnellerie Radoux constitutes a large data base of analyses, thus leading to improved knowledge about the oak-supplying regions.

General Conclusion

Research on NIR spectroscopy technology since the 1980s has demonstrated the effectiveness of this method in the non-destructive testing of wood. Today, multiple parameters related to the chemical composition but also to the anatomical organization of wood as well as certain mechanical properties can be characterized using NIR spectroscopy methods. Following the example of the first industrial use of NIR spectroscopy in a company in the wood industry with Oakscan® process on oakwood of the French cooperage Radoux, other systems could have a significant benefit to this sector. Thus, the feasibility of measuring the natural or conferred durability by NIR spectroscopy has been possible too. The technique can be used for timber grading, identification of species or origin and quality control in processing units. Research shows that these results can be used for both temperate and tropical wood species.

The development of rapid, non-destructive and cost-effective tools such as NIR spectroscopy allowed the assessment of large populations needed to provide genetic parameter estimates such as chemical properties of wood, in a short time at lower costs (Perez et al. 2007, Gaspar et al. 2011). Today, NIR spectroscopy method can be used in genetic improvement programs and in genetic studies of forest species thanks to its capacity to phenotype a large number of samples in a short time (Lepoittevin et al. 2011, Gebresselassie et al. 2017). Thus, as for growth, genetic control of wood chemicals properties can be estimated (Raymond and Schimleck 2002, Hein et al. 2012) and when this is proved, certain traits can be included as the selection criteria in the breeding programs (Estopa et al. 2017). It is one of the few technologies that has made possible the production of selected varieties on the characteristics of wood interests, the main objective of production forests (Resende et al. 2012). With the increasing improvement in the quality of portable equipment of a smaller and smaller size, applications with spectra taken directly in the field on standing trees are conceivable and would bring an additional evolution towards high-throughput phenotyping for this type of genetic research. Similarly, NIR spectroscopy is used for the mass phenotyping of samples used in quantitative genetic studies (Raymond and Schimleck 2002, Hein et al. 2012), association genetics (Wegrzyn et al. 2010, Gebresselassie et al. 2017), genetic mapping (Gion et al. 2015) and genomic studies for various forest species (Denis et al. 2013). Studies conducted by the forest tree genetic team at the INRA VDL in Orleans (France) and other teams (Posada et al. 2009, O'Reilly-Wapstra et al. 2013) show the opportunity to use the NIR spectrum as a variable (biological marker) and usable as such to explore genetic diversity in the selection programs, it is called "phenome". Other authors showed the heritability map of NIR spectrum wavelength (Hein and Chaix 2014).

In view of all the work carried out since the late 1980s, NIR spectroscopy is therefore a non-destructive testing technology, which has shown its interest in wood analysis. With the evolution of technologies and in particular measuring devices and signal processing capacities, it should increase its level of efficiency in the years to come and thus be more present in the production chains of the companies in the wood industry.

References

Alves, A., M. Schwanninger, H. Pereira and J. Rodrigues. 2006. Calibration of NIR to assess lignin composition (H/G ratio) in maritime pinewood using analytical pyrolysis as the reference method. Holzforschung 60: 29–31.

Alves, A., R.F.S. Simões, J.S. Desmond, R.E. Vaillancourt, B.M. Potts, M. Schwanninger and J. Rodrigues. 2011. Determination of syringyl/guaiacyl ratio of *Eucalyptus globulus* wood lignin by near infrared-based partial least squares regression models using analytical pyrolysis as the reference method. Journal of Near Infrared Spectroscopy 19: 343–348.

Alves, A., A. Santos, P. Rozenberg, L.E. Pâques, J.P. Charpentier, M. Schwanninger and J.C. Rodrigues. 2012. A common near infrared based partial least squares regression model for the prediction of wood density of *Pinus pinaste*r and *Larix* × *eurolepis*. Wood Science & Technology 46(13): 157–175.

Alves, A., A. Santos, R.F.S. Simões, C.A. Santos, B.M. Potts, J. Rodrigues and M. Schwanninger. 2012. Determination of *Eucalyptus globulus* wood extractives content by near infrared-based partial least squares regression models: comparison between extraction procedures. Journal of Near Infrared Spectroscopy 20(2): 275–285.

Baillères, H., F. Davrieux and F. Ham-Pichavant. 2002. Near infrared analysis as a tool for rapid screening of some major wood characteristics in a eucalyptus breeding program. Annals of Forest Sciences 59: 479–490.

Bertrand, D. 2002. La spectroscopie proche infra-rouge et ses applications dans les industries de l'alimentation animale. INRA Productions Animales 15(3): 209–220.

Bertrand, D. and E. Dufour. 2006. La spectroscopie infrarouge et ses applications analytiques. Collection Sciences et Techniques Agroalimentaires. Paris, FRA: Lavoisier, 660 p.

Boidron, J.N., P. Chatonnet and M. Pons. 1988. Influence du bois sur certaines substances odorantes des vins. Connaissance de la Vigne et du Vin 22: 275–294.

Boizot, N. and J.-P. Charpentier. 2006. Méthode rapide d'évaluation du contenu en composes phénoliques des organes d'un arbre forestier. Le Cahier des Techniques de l'INRA, n° spécial 2006, Méthodes et outils pour l'observation et l'évaluation des milieux forestiers, prairiaux et aquatiques, pp. 79–82.

Brinkmann, K., L. Blaschke and A. Polle. 2002. Comparison of different methods for lignin determination as a basis for calibration of near-infrared reflectance spectroscopy and implications of lignoproteins. Journal of Chemical Ecology 28(12): 2483–2501.

Brunner, M., E. Eugster, E. Trenka and L. Bergamin-strotz. 1996. FT-NIR spectroscopy and wood identification. Holzforschung 50(2): 130–13.

Chaix G., F.M. Tomazello, S. Nourissier and A. Diombokho. 2012. Global Nirs models to predict main chemical compounds of eucalyptus woods. *In*: Forests and forest products – International Union Of Forest Research Organizations (IUFRO) Division 5, Estoril, Portugal, 8–13 July 2012.

Chassaing, S., D. Lefeuvre, R. Jacquet, M. Jourdes, L. Ducasse, S. Galland, A. Grelard, C. Saucier, P.-L. Teissedre, O. Dangles and S. Quideau. 2010. Physicochemical studies of new anthocyano-ellagitannin hybrid pigments: about the origin of the influence of oak C-glycosidic ellagitannins on wine color. European Journal of Organic Chemistry 1: 55–63.

Chatonnet, P. 1991. Incidence du bois de chêne sur la composition chimique et les qualités organoleptiques des vins. Thèse DER. Université de Bordeaux II.

Chauchard, F., J.-M. Roger and V. Bellon-Maurel. 2004. Correction of the temperature effect on near infrared calibration—application to soluble solid content prediction. Journal of Near Infrared Spectroscopy 12-3: 199–205.

Clarke, C.R.E. and A.M. Wessels. 1995. Variation and measurement of pulp properties in eucalypts. pp. 93–100. *In*: Potts, B.M. and N.M.G. Vienna (eds.). Eucalypt Plantations: Improving Fibre Yield and Quality. Proceedings of the CRCTHF-IUFRO Conference, Feb. 1995, Hobart, Australia.

Denis, M., B. Favreau, S. Ueno, L. Camus-Kulandaivelu, G. Chaix, J.-M. Gion, S. Nourrisier-Montou, J. Polidori and J.-M. Bouvet. 2013. Genetic variation of wood chemical traits and association with underlying genes in *Eucalyptus urophylla*. Tree Genetics & Genomes 9: 927–942.

Dousset, F., B. De Jeso, S. Quideau and P. Pardon. 2002. Extractives content in cooperage oak wood during natural seasoning and toasting; influence of tree species, geographic location, and single-tree effects. Journal of Agricultural and Food Chemistry 50: 5955–5961.

Downes, G.M., R. Meder, N. Ebdon, H. Bond, R. Evans, K. Joyce and S.G. Southerton. 2010. Radial variation in cellulose content and Kraft pulp yield in *Eucalyptus nitens* using near infrared spectral analysis of air-dry wood surfaces. Journal of Near Infrared Spectroscopy 18(2): 147–155.

Estopa, R.A., F.R. Milagres, R.A. Oliveira and P.R.G. Hein. 2017. NIR spectroscopic models for phenotyping wood traits in breeding programs of *Eucalyptus benthamii*. Cerne 22: 367–375. https://doi.org/10.1590/0104776020172303231 9.

Gaspar, M.J., A. Alves, J.L. Louzada, Morais, A. Santos, C. Fernandes, M.H. Almeida and J.C. Rodrigues. 2011. Genetic variation of chemical and mechanical traits of maritime pine (*Pinus pinaster* Aiton). Correlations with wood density components. Annals of Forest Science 68: 255–265.

Gebreselassie, M.N., K. Ader, N. Boizot, F. Millier, J.P. Charpentier, A. Alves, R. Simões, J.C. Rodrigues, G. Bodineaud, F. Fabbrinie, M. Sabattie, C. Bastien and V. Segura. 2017. Near-infrared spectroscopy enables the genetic analysis of chemical properties in a large set of wood samples from *Populus nigra* (L.) natural populations. Industrial Crops & Products 107: 159–171.

Geladi, P. 1995. An Overview of Multivariate Spectral Data Analysis Spectral Data Analysis in Infra Red Spectroscopy: The Future Waves, edited by Davies A.M.C and Willamp. NIR Publications, Chichester, UK.

Gierlinger, N., M. Schwanninger, B. Hinterstoisser and R. Wimmer. 2002. Rapid determination of heartwood extractives in *Larix* sp. by means of Fourier transform near infrared spectroscopy. Journal of Near Infrared Spectroscopy 10: 203–214.

Gion, J.M., P. Chaumeil and C. Plomion. 2015. EucaMaps: linking genetic maps and associated QTLs to the *Eucalyptus grandis* genome. Tree Genetics & Genomes 11: 1–7.

Giordanengo, T., J.-P. Charpentier, J.-M. Roger, S. Roussel, L. Brancheriau, G. Chaix and H. Baillères. 2008. Correction of moisture effects on near infrared calibration for the analysis of phenol content in eucalyptus wood extracts. Annals of Forest Science 65(8): 803.

Giordanengo, T., J.-P. Charpentier, N. Boizot, S. Roussel, J.-M. Roger, G. Chaix, C. Robin and N. Mourey. 2009. *OAKSCAN*™: Procédé de mesure rapide et non destructif des polyphénols du bois de chêne de tonnellerie. Revue Française d'Œnologie 234: 10–15.

Giordanengo, T., J. Michel, P. Gauthier, J.-P. Charpentier, M. Jourdes, P.-L.Teissedre and N. Mourey. 2012. Application du procédé *OakScan*® aux Bois pour l'Œnologie : Sélection et influence de la teneur en polyphénols du chêne sur le profil aromatique et structurant du vin. Revue Française d'Œnologie 255 : 16–24.

Glasbania, A. and T. Hofmann. 2006. Sensory-directed identification of taste-active ellagitannins in ethanol/water extracts of American white oak wood (*Quercus alba* L.) and European oakwood (*Quercus robur* L.) and quantitative analysis in bourbon whiskey and oak matured red wines. Journal of Agricultural and Food Chemistry 54: 3380–3390.

Guilley, E., J.P. Charpentier, N. Ayadi, G. Snakkers, G. Nepveu and B. Charrier. 2004. Decay resistance against *Coriolus versicolor* in Sessile oak (*Quercus petraea* Liebl.): analysis of the between-tree variability and correlations with extractives, tree growth and other basic wood properties. Wood Science and Technology 38: 539–554.

He, W. and H. Hu. 2013. Rapid prediction of different wood species extractives and lignin content using near infrared spectroscopy. Journal of Wood Chemistry and Technology 33(1): 52–64. DOI: 10.1080/02773813.2012.731463.

Hein, P.R.G., J.M. Bouvet, E. Mandrou, B. Clair, P. Vigneron and G. Chaix. 2012. Age trends of microfibril angle inheritance and their genetic and environmental correlations with growth, density and chemical properties in *Eucalyptus urophylla* S.T. Blakewood. Annals of Forest Science 69: 681–691.

Hein, P.R.G. and G. Chaix. 2014. NIR spectral heritability: a promising tool for wood breeders? Journal of Near Infrared Spectroscopy 22: 141–147.

Hodge, G.R. and W.C. Woodbridge. 2004. Use of near infrared spectroscopy to predict lignin content in tropical and sub-tropical pines. Journal of Near Infrared Spectroscopy 12: 381–390.

Jarauta I., J. Cacho and V. Ferreira. 2005. Concurrent phenomena contributing to the formation of the aroma of wine during aging in oak wood: an analytical study. Journal of Agricultural and Food Chemistry 53: 4166–4177.

Karlinasari, L., M. Sabed, I.N.J. Wistara and Y.A. Purwanto. 2014. Near infrared (NIR) spectroscopy for estimating the chemical composition of (*Acacia mangium* Willd.) wood. J. Indian Acad. Wood Sci. 11(2): 162–167.

Kelley, S.S., T.G. Rials, L.R. Groom and C.L. So. 2004. Use of near infrared spectroscopy to predict the mechanical properties of six softwoods. Holzforschung 58: 252–260.

Kothiyal, V., Jaideep, S. Bhandari, H.S. Ginwal and S. Gupta. 2015. Multi-species NIR calibration for estimating holocellulose in plantation timber. Wood Sci. Technol. 49: 769–793.

Kube, P.D. and C.A. Raymond. 2002. Prediction of whole tree basic density and pulp yield using wood core samples in *Eucalyptus nitens*. APPITA J. 55: 43–48.

Lepoittevin, C., J.P. Rousseau, A. Guillemin, C. Gauvrit, F. Besson, F. Hubert, D. da Silva Perez, L. Harvengt and C. Plomion. 2011. Genetic parameters of growth straightness and wood chemistry traits in *Pinus pinaster*. Ann. For. Sci. 68: 873–884. https://doi.org/10.1007/s13595-011-0084-0.

Lindgren, T. and U. Edlund. 1998. Prediction of lignin content and pulp yield from black-liquor composition using near infrared spectroscopy and partial least squares. Nord. Pulp Pap. Res. J. 13: 76–80.

Marchal, A. 2010. Recherches sur les bases moléculaires de la saveur sucrée des vins secs, Approches analytique et sensorielle. Thèse DER. Université de Bordeaux II, 300 p.

Masson, G. 1996. Composition chimique du bois de chêne de tonnellerie. Essai de discrimination des espèces et des forêts. Thèse DER. Université de Montpellier II, 150 p.

Masson, E. and J.L. Puech. 2000. Les méthodes de séchage du bois: 1-influence du séchage en étuve sur les teneurs en ellagitannins et en composés volatils de merrains de chêne sessile (*Quercus petraea* (Matt.) Liebl.) V^e Colloque des Sciences et Techniques de la Tonnellerie, Bordeaux, France.

Meder, R., S. Gallagher, K.L. Mackie, H. Bohler and R.R. Meglen. 1999. Rapid determination of the chemical composition and density of *Pinus radiata* by PLS modelling of transmission and diffuse reflectance FTIR spectra. Holzforschung 53: 261–266.

Michel, J. 2012. Classification et influences des polyphénols du bois de chêne sur la qualité sensorielle des vins (Application du procédé *Oakscan*®). Thèse DER. Université de Bordeaux II, 226 p.

Monties, B. 1989. Molecular structure and biochemical properties of lignins in relation to possible self-organization of lignin networks. Annales des sciences forestières. INRA/EDP Sciences 46 (Suppl), pp. 848s–855s.

Mosedale, J., B. Charrier, N. Crouch, G. Janin and P. Savill. 1996. Variation in the composition and content of ellagitannins in the heartwood of European oaks (*Quercus robur* and *Quercus petraea*). A comparison of two French forests and variation with heartwood age. Annals of Forest Science 53: 1005–1018.

Niamké, F.B., N. Amusant, A.A. Kadio, M.F. Thevenon, S. Nourissier, A.A. Adima, C. Jay-Allemand and G. Chaix. 2014. Rapid prediction of phenolic compounds as chemical markers for the natural durability of teak (*Tectona grandis* Linn f.) heartwood by near infrared spectroscopy. Journal of Near Infrared Spectroscopy 22(1): 35–43.

O'Reilly-Wapstra, J.M., J.S. Freeman, R. Barbour, R.E. Vaillancourt and B.M. Potts. 2013. Genetic analysis of the near-infrared spectral phenome of a global Eucalyptus species. Tree Genetics & Genomes 9: 943–959.

Osborne, B.G., T. Fearn and P.T. Hindle. 1993. Practical NIR spectroscopy with applications in food and beverage analysis. (2nd Ed.). Addison-Wesley Longman Ltd: Harlow UK.

Perez, D.D., A. Guillemain, P. Alazard, C. Plomion, P. Rozenberg, J.C. Rodrigues, A. Alves and G. Chantre. 2007. Improvement of Pinus pinaster Ait. elite trees selection by combining near infrared spectroscopy and genetic tools. Holzforschung 61: 611–622.

Posada, H., M. Ferrand, F. Davrieux, P. Lashermes and B. Bertrand. 2009. Stability across environments of the coffee variety near infrared spectral signature. Heredity 102: 113–119.

Prida, A., J.C. Boulet, A. Ducousso, G. Nepveu and J.L. Puech. 2006. Effect of species and ecological conitions on ellagitannin content in oak wood from an even-aged and mixed stand of *Quercus robur* L. and *Quercus petraea* Liebl. Annals of Forest Science 63: 415–424.

Pulkka, S., V. Segura, A. Harju, T. Tapanila, J. Tanner, L. Pâques and J.P. Charpentier. 2016. Prediction of stilbene content from heartwood increment cores of scots pine using NIRS methodology. Journal of Near Infrared Spectroscopy 24: 517–528.

Quideau, S., M. Jourdes, D. Lefeuvre, D. Montaudon, C. Saucier, Y. Glories, P. Pardon and P. Pourquier. 2005. The chemistry of wine polyphenolic C-glycosidic ellagitannins targeting human topoisomerase *II*. Chemistry—A European Journal 11: 6503–6513.

Raymond, C.A. and L.R. Schimleck. 2002. Development of near infrared reflectance analysis calibrations for estimating genetic parameters for cellulose content in *Eucalyptus globulus*. Can. J. For. Res. 32: 170–176.

Resende, M.D.V., M.F.R. Resende Jr., C.P. Sansaloni, C.D. Petroli, A.A. Missiaggia, A.M. Aguiar, J.M. Abad, E.K. Takahashi, A.M. Rosado, D.A. Faria, G.J. Pappas Jr., A. Kilian and D. Grattapaglia. 2012. Genomic selection for growth and wood quality in Eucalyptus: capturing the missing heritability and accelerating breeding for complex traits in forest trees. New Phytologist 194: 116–128.

Ribeiro da Silva, A.R., T.C.M. Pastore, J.W.B. Braga, F. Davrieux, E.Y.A. Okino, V.T.R. Coradin, J.A.A. Camargos and A.G.S. Soares do Prado. 2013. Assessment of total phenols and extractives of mahogany wood by near infrared spectroscopy (NIRS). Holzforschung 67: 1–8.

Roger, J.-M., F. Chauchard and V. Bellon-Maurel. 2003. EPO-PLS external parameter orthogonalisation of PLS application to temperature-independent measurement of sugar content of intact fruits. Chemometrics and Intelligent Laboratory Systems 66: 191–204.

Scalbert, A., B. Monties and G. Janin. 1989. Tannins in wood: comparison of different estimation methods. Journal of Agriculture and Food Chemistry 37: 1324–1329.

Schimleck, L.R., C.A. Raymond, C.L. Beadle, G.M. Downes, P.D. Kube and J. French. 2000. Applications of NIR spectroscopy to forest research. Appita Journal 53: 458–464.

Schimleck, L.R. and Y. Yazaki. 2003. Analysis of *Pinus radiata* D. don bark by near infrared spectroscopy. Holzforschung 57: 520–526.

Schultz, T.P. and D.A. Burns. 1990. Rapid secondary analysis of lignicellulose: comparison of near infrared and fourier transform infrared (FTIR). Tappi J. 73(5): 209–212.

Schwanninger, M., J.C. Rodrigues and K. Fackler. 2011. A review of band assignments in near infrared spectra of wood and wood components. Journal of Near Infrared Spectroscopy 19(5): 287–308.

Schwanninger, M., Rodrigues, N. Gierlinger and B. Hinterstoisser. 2011a. Determination of lignin content in Norway spruce wood by Fourier Transformed near infrared spectroscopy and partial least square regression. Part 1: Wavenumber selection and evaluation of selected range. Journal of Near Infrared Spectroscopy 19: 319–329.

Schwanninger, M., Rodrigues, N. Gierlinger and B. Hinterstoisser. 2011b. Determination of lignin content in Norway spruce wood by Fourier Transformed near infrared spectroscopy and partial least square regression. Part 2: Development and evaluation of the final model. Journal of Near Infrared Spectroscopy 19: 331–341.

Singleton, V.L. 1987. Oxygen with phenols and related reactions in musts, wines and model systems. Observations and practical implications. American Journal of Enology and Viticulture 38: 69–77.

Snakkers, G., G. Nepveu, E. Guilley and R. Cantagrel. 2000. Variabilité géographique, sylvicole et individuelle de la teneur en extractibles de chênes sessiles français (*Quercus petraea* Liebl.): polyphénols, octalactones et phénols volatils. Annals of Forest Science 57: 251–260.

Tominaga, T., L. Blanchard, P. Darrier and D. Dubourdieu. 2000. A powerful aromatic volatile thiol, 2-Furanmethanethiol, exhibiting roast coffee aroma in wines made from several *Vitis vinifera* grape varieties. Journal of Agricultural and Food Chemistry 48: 1799–1802.

Tsuchikawa, S., M. Torii and S. Tsustumi. 1998. Directional characteristics of near infrared light in the process of radiation and transmission from wood. Journal of Near Infrared Spectroscopy 6: 47–53.

Tsuchikawa, S. 2007. A review of recent near infrared research for wood and paper. Applied Spectroscopy Review 42: 43–71.

Tsuchikawa, S. and M. Schwanninger. 2013. A review of recent near infrared research for wood and paper-Part 2. Applied Spectroscopy Review 48: 560–587.

Tsuchikawa, S. and H. Kobori. 2015. A review of recent application of near infrared spectroscopy to wood science and technology. J. Wood Sci. 61: 213–220.

Via, B.K., C. Zhou, G. Acquah, W. Jiang and L. Eckhardt. 2014. Near infrared spectroscopy calibration for wood chemistry: Which chemometric technique is best for prediction and interpretation? Sensors 14: 13532–13547; doi:10.3390/s140813532.

Vivas, N. and Y. Glories. 1996. Role of oak wood ellagitannins in the oxidation process of red wines during aging. American Journal of Enology and Viticulture 47(1): 103–107.

Vivas, N. 1997. Recherches sur la qualité du chêne français de tonnellerie (*Q. Petraea* Liebl., *Q. robur* L.) et sur les mécanismes d'oxydoréduction des vins rouges au cours de leur élevage en barriques. Thèse DER. Université de Bordeaux II.

Wegrzyn, J.L., A.J. Eckert, M. Choi, J.M. Lee, B.J. Stanton, R. Sykes, M.F. Davis, C.-J. Tsai and D.B. Neale. 2010. Association genetics of traits controlling lignin and cellulose biosynthesis in black cottonwood (*Populus trichocarpa*, Salicaceae) secondary xylem. New Phytologist 188: 515–532.

Williams, P. and D. Sobering. 1993. Comparison of commercial near infrared transmittance and reflectance instruments for analysis of whole grains and seeds. Journal of Near Infrared Spectroscopy 1: 25–32.

Williams, P. 2014. The RPD statistic: a tutorial note. NIR News 25: 22–26.

Williams, P., P. Dardenne and P. Flinn. 2017. Tutorial: Items to be included in a report on a near infrared spectroscopy project. Journal of Near Infrared Spectroscopy 25(2): 85–90. DOI: 10.1177/0967033517702395.

Wold, S. 1978. Cross-validatory estimation of the number of components in factor and principal component model. Technometrics 20: 397–405.

Wright, J., M. Birkett and M. Gambino. 1990. Prediction of pulp yield and cellulose content from wood using near infrared reflectance spectroscopy. Tappi J. 73: 164–166.

Yeh, T.F., H.M. Chang and J.F. Kadla. 2004. Rapid prediction of solid wood lignin content using transmittance near-infrared spectroscopy. Journal of Agricultural and Food Chemistry 52(6): 1435–1439.

Zahri, S., A. Moubarik, F. Charrier, G. Chaix, H. Baillères, G. Nepveu and B. Charrier. 2008. Quantitative assessment of total phenols content of European oak (*Quercus petraea* and *Quercus robur*) by diffuse reflectance NIR spectroscopy on solid wood surfaces. Holzforschung 62(6): 679–687.

Zhang, M., Y. Liu and Z. Yang. 2015. Correlation of near infrared spectroscopy measurements with the surface roughness of wood. BioResources 10: 6953.

Zeaiter, M. 2004. Mesures robustes en ligne des solutés organiques par spectrométrie infrarouge et étalonnages multivariés. Ph.D. thesis, Montpellier 2 University, 158p.