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Short Term Scientific Mission

Modelling cork quality and properties by NIRS

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1. Purpose

Cork is the most valuable NWFPs in Mediterranean forests. It has an important role in maintaining a sustainable forest production in a fragile yet rich ecosystem, as well as it is at the base of a relevant social and economic industrial sector. Cork is a natural cellular material characterized by an interesting combination of properties that have been valued in research and in practical utilizations, e.g. low density, reduced permeability to liquids and gases, chemical and biological inertia, mechanical elasticity and insulation properties (Pereira 2007). These properties are at the base of the present known and valued applications i.e. for wine bottling, but can also trigger new applications i.e. as a specialty chemical feedstock (Pereira 2013). Knowledge on the properties, including chemical composition are therefore important, namely their range and variability. However, determinations are complex and labour and time intensive with sample preparation a crucial step to obtain a representative cork material. Therefore development of methods that allow to estimate cork properties may be important tools to pursue the search for new processes and products.

Near-infrared spectroscopy (NIRS) may be such a method. NIRS has been applied for the quantitative assessment of the physical, mechanical, and chemical properties of wood such as lignin and cellulose content, wood density or moisture (Tsuchikawa and Schwanninger 2013, Leblon et al. 2013). As regards cork, quantitative analysis by NIRS has been used to measure the visual quality, porosity, and moisture of cork planks with promising results (Prades et al. 2010). The aim of this STSM was to gain knowledge in NIRS and chemometrics techniques for cork qualitative and quantitative analysis.

2. Work carried out

2.1. Material and reference method

90 cork samples (strips) covering the natural variability of the material was used as the test material. For this cork samples were used for which we already had their chemical characterization by determination of its summative chemical composition. In cork, the determination of the summative chemical composition is more complex than in wood due to

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the occurrence of suberin as principal structural component and to the special topochemistry of the cell wall (Pereira 2007). The chemical analysis was made on granulated material with particle size between 40-60 mesh and started with solvent extraction for quantification of non-structural components of cork and preparation of an extractive-free sample. Subsequently the suberin was quantified by methanolysis of the extractive-free sample and the desuberinised cork sample was used for the determination of lignin and polysaccharides (Pereira 2013). The reference variables were determined as: Dichloromethane extractives, Ethanol extractives, Water extractives, Suberin, Lignin (including soluble and insoluble lignin) and Polysaccharides.

In order to compare with calibration and cross validation errors (SEC and SECV) from NIR the Standard error of laboratory (SEL) was calculated for two replicates and in N samples for each of the reference variables:

$$SEL = \sqrt{\frac{\sum_{i=1}^N (y_{i1} - y_{i2})^2}{2N}}$$

Where N is the number of samples (90) and y_{i1} and y_{i2} are the values obtained for replicates of sample i .

2.2. Spectra collection

During STSM visit the samples were scanned using a remote reflectance fibre optic probe (NR-6539-A) connected to a Foss-NIRSystems 6500 spectrophotometer equipped with autogain detectors: one for 400 to 1100 nm (VIS region) and another for 1100 to 2500 nm (NIR region) and with a Bruker MPA FT-NIR spectrometer with solid fiber optic probe and detector for 1100 to 2500 nm (NIR region). A reference spectrum was recorded before analyzing each sample.

This approach allows to compare differences between the NIR equipment's when analyzing cork samples. With the Foss-NIRSystems 6500 spectrophotometer three spectra were recorded for each sample at 2 nm intervals and stored as $\log(1/R)$, where R is the reflectance, while with Bruker MPA FT-NIR spectrometer the spectra were recorded at 0.5

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nm intervals. The mean spectrum of each sample was used to determine the relationship with the reference variables. The mean spectrum obtained in Bruker MPA FT-NIR spectrometer was averaged to 2 nm intervals in order to allow the comparison of NIR Systems.

Figures 1 and 2 show the mean spectra obtained for one cork sample by the two NIR systems.

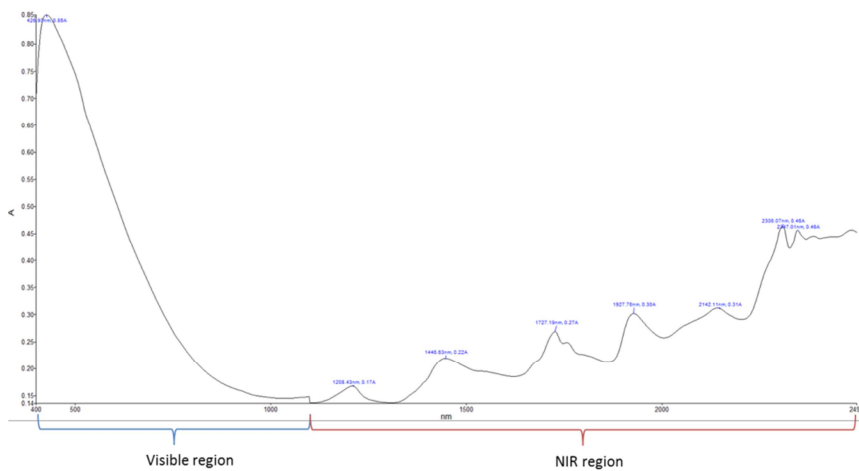


Fig. 1. Mean spectrum obtained with the Foss-NIRSystems 6500 spectrophotometer (VIS and NIR regions).

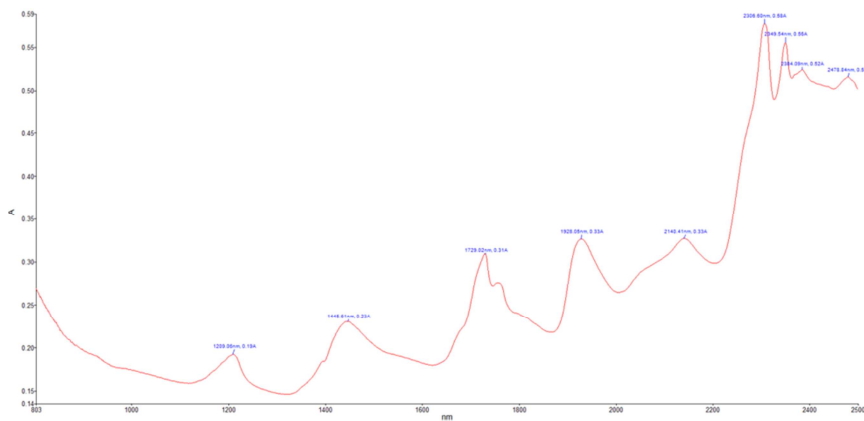


Fig. 2. Mean spectrum obtained with Bruker MPA FT-NIR spectrometer (NIR region).

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2.3. Quantitative chemometric analysis

Because NIR spectra contain information about chemical bonds, compositional information is not directly available from their results, thus, chemometric techniques, such as multivariate models, are necessary for spectra analysis. By reducing the large amount of spectral data (2203 variables for Bruker system and 1050 variables for Foss system) in several latent variables, the statistical methods/models could build a relationship between spectral features and chemical components/bonds (Xu et al., 2013).

All the chemometric analysis was performed using WinISI II software version 1.5 (Infrasoft International Port Matilda, PA, USA). Spectral repeatability was calculated using the root mean square error (RMS statistic) between spectra of the same sample. Principal components analysis (PCA) was used to assess the quality of spectral data with classification as spectral outliers the samples with Mahalanobis distance greater than 3.

Modified partial least-squares (MPLS) method was used to obtain the equations with the references variables. The spectra were transformed by using or not scatter correction by standard normal variate (SNV) and detrend algorithm (Shenk and Westerhaus, 1995) and different combinations of derivative math treatments applied to the spectral data. WinISI derivative math treatments have a four-digit notation (a, b, c, d) where a is a derivative order, b is the derivative gap, c is the smoothing segment and d is the second smoothing segment (Shenk and Westerhaus, 1995).

The calibrations were developed using T and H outlier elimination. T outliers were defined as samples with significant differences between their laboratory and predicted values and H outliers were defined as samples whose spectra showed excessive Mahalanobis distance to the spectral center of the training set. Because 90 samples is not a large sample set for NIR proposes and in order to include all of the spectral and chemical variability of the samples, the equations obtained were validated by means of cross-validation. The best equations were selected taking into account by the software the lowest value of the standard error of cross-validation (SECV) and the highest value of the coefficient of determination (r^2).

Several calibration equations were calculated using different sets of samples.

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3. Main results

The mean spectrum obtained for each sample and NIR system by means of remote reflectance fiber-optic probes shows the same profile reported in previous studies on cork using NIR absorption bands corresponding to the –CH groups (around 1750, 2150, 2300 and 2360 nm) and others due to the –NH and –OH groups (1450 and 1930 nm) (Fig. 1 and 2). Bands nearby 1750 nm correspond to –CH groups in the first overtone and are associated to a CH₂ structure. Bands 1450 and 1930 nm corresponds to the first overtone and combination bands of the –OH groups mostly due to water. Bands close to 2150 nm are usually associated with CH and C=O combination band (Prades et al. 2012, 2014). The mean spectrum obtained with the Foss-NIRSystems 6500 spectrophotometer shows absorption maximum in the visible region at 450 nm (Prades et al. 2012, 2014).

Table 1 shows the results obtained for the best NIRS equations developed to determine the chemical reference variables selected.

Table 1. Number of samples used in the model, mean, standard deviation (SD), the standard error of cross-validation (SECV), coefficient of determination (r^2) and coefficient of variation (CV) of the best NIRS equations for the two systems

	Dichloromethane extractives	Ethanol extractives	Water extractives	Suberin	Lignin	Polysaccharides
Foss-NIRSystems 6500 spectrophotometer						
N	50	43	47	50	48	35
Mean	5.87	5.12	4.30	41.09	21.40	11.01
SD	0.76	1.47	1.11	5.01	2.57	2.91
SECV	0.59	1.14	1.06	4.47	2.55	2.58
r^2	0.40	0.35	0.11	0.21	0.07	0.28
CV (%)	10.0	21.9	24.6	10.9	11.9	23.4
Math pretreatments	SNV+DT (1,10,5,1)	SNV+DT (2,10,5,1)	SNV+DT (2,10,5,1)	SNV+DT (2,10,5,1)	none (2,10,5,1)	SNV+DT (1,4,4,1)
Bruker MPA FT-NIR spectrometer						
N	87	78	84	89		
Mean	5.85	5.01	4.36	41.15	-	-
SD	0.62	1.41	1.12	4.76	-	-
SECV	0.57	1.22	1.02	4.69	-	-
r^2	0.15	0.29	0.18	0.03	-	-
CV (%)	9.80	24.0	23.4	11.4	-	-
SEL	0.32	0.53	0.72	2.44	1.57	3.04

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Equations were obtained for each chemical reference variable using the total spectral range totaling 2203 variables for Bruker system and 1050 variables for Foss system. The best calibration results differed in the preprocessing methods depending on the chemical variable. The spectral range provided by Foss-NIRSystems 6500 spectrophotometer that include VIS and NIR region provided the best results. With exception of lignin the best preprocessing method was SNV+DT combined with different pretreatments (Table 1).

The calibration generated unequal results, with the r^2 ranging from 0.07 for lignin to 0.40 for dichloromethane extractives. Despite our worst results, they are in accordance with the ones published by Prades et al. (2014).

Based on these results, we can conclude that although these equations do not have a high degree of accuracy and precision they are suitable for estimating low and high values with SECV near 2xSEL, one of the criteria used to evaluate equations.

For all the other equations the r^2 value obtained is very low; this could be explained by the fact that the NIR spectra were acquired using a cork strip (sample) that was not the same used for the chemical summative analysis. Moreover, the chemical summative analysis uses only the 40-60 mesh fraction that contains only cork (e.g. without lenticular filling material) while the spectra considered the high physical heterogeneity of the cork strip, namely, considering lenticular channels.

We would expect that the Bruker MPA FT-NIR spectrometer would present better results because the area of analysis was very small and we tried to scan only the cork tissue, and the resolution is much better, however the comparison did not show that one NIR system was better than the other for the analysis of cork samples.

Bearing in mind these sources of error, the results obtained in this STSM can be seen as very promising and we expect that with a new experimental design the NIR technique will be capable to predict more accurately cork chemical composition and therefore be an important tool to pursue the search for new processes and products.

The aim of this STSM was achieved and I have gain knowledge in NIRS and chemometrics techniques for cork qualitative and quantitative analysis.

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4. Future collaboration with host institution

It is expected future collaborative work with the host institution. This collaboration can be carried through new NIRS analysis potentiating the facilities available at Servicio Central de Apoyo a la Investigación and/or through international projects with collaboration of both institutions.

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