Development of Calibration Model for Measuring Stilbene Content of Wood samples by NIRS

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Fast and accurate methods are needed to measure durability related chemical characteristics from wood. In the field of forest tree breeding, the measurements would be performed from increment core samples collected from standing trees. In this study, we have assessed the potential of Near Infrared Spectroscopy (NIRS) for evaluating the content of stilbenes, pinosylvin (PS) and its monomethyl-ether (PSM) from heartwood samples of Scots pine, *Pinus sylvestris* L.

Scots pine wood samples (increment cores) used were collected from a 43-year-old half-sib progeny trial at Leppävirta in eastern Finland in 2009.
Heartwood samples with length of 20-30 mm including the annual rings from 5 to 8 (counted from the pith) were taken from a random side of the increment cores. Each heartwood sample was halved longitudinally. One half was milled for chemical analysis, and the other half was subjected to NIRS measurements.
The concentrations of PS and PSM in milled heartwood samples were analysed by using gas chromatography – mass spectrometry (GC-MS)[1]. The sum of PS and PSM is assimilated to total stilbene amount (**STB**) and was used as reference for NIRS measurements.
The NIRS device used was PerkinElmer Spectrum 400 equipped with NIRA module and INGAAS detector. The resolution of device was 8 cm^{-1}. The heartwood samples were stabilised at 22 RH% at room temperature. Two to five measurements per sample were taken depending on the length of the individual sample. Each measurement consisted of 64 averaged scans within a circle having radius of about 4 mm. Measurements per sample were taken in every 5 millimeters. Resulted spectra ranged between 4000 and 10000 cm^{-1} with a step size of 2 cm^{-1}. Total number of sample measured by NIRS was 474.

Reference data obtained by chemical analyses :

The total stilbenes amount (STB) varied from 1.81 to 23.02 mg/g, with an average of 10.83 mg/g and a standard deviation 4.08 mg/g (Fig. 1).

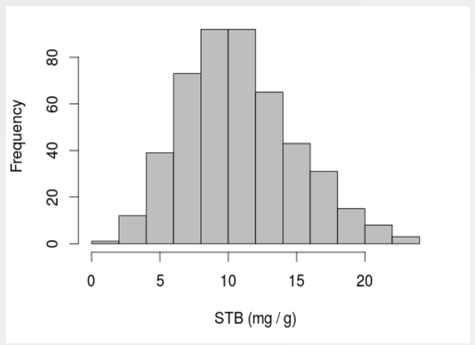

Fig. 1 : Histogram of STB amount in scots pine wood samples

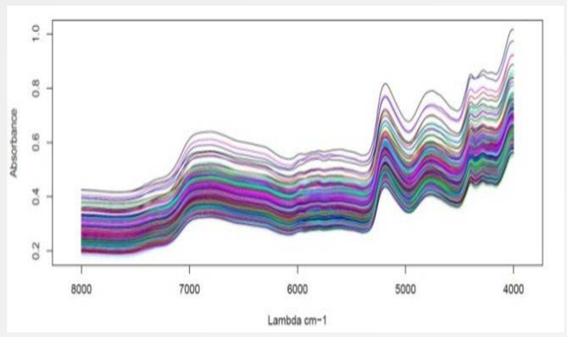

Fig. 2 : Raw spectra from Scots pine heartwood surface measurements by NIRS.

NIRS Models :

Total number of samples measured by NIRS were divided into calibration (212) and test (262) sets.

- First, statistical pretreatments were applied to the spectra to improve the signal quality resulting in 7 spectra modalities: raw (no statistical pre-treatment), norm (normalization), der1 (first derivative on raw spectra), der2 (second derivative on raw spectra), norm_der1 (first derivative on normalized spectra), norm_der2 (second derivative on normalized spectra). Raw spectra are shown in Fig. 2.

- Second, partial-least square (PLS) regressions were carried out for each spectra modality to build the calibration models. The number of components of each PLS regression was optimized in the calibration set using a 4-fold cross-validation sampling scheme repeated 100 times (Monte Carlo Cross Validation, MCCV). The model yielding the lowest root mean square error of prediction was then used to predict the validation set. The corresponding model corresponded to the second derivative. It was characterized by R^2 and Root Mean Square Error (RMSE) of cross-validation of 0.86 and 1.49 mg/g in the calibration set and R^2 and RMSE of 0.86 and 1,54 mg/g in the test set (Fig. 3).

- Additionally, an automatic selection of wavenumbers was carried out using the competitive adaptive reweighted sampling (CARS) approach[2]. With this approach the best model was also obtained with the preatreatment second derivative. This model was based on 204 wavenumbers. Comparatively to the model without selection of wavenumbers, it had a lower rank (9 components) as well as higher R^2 (0.89) and lower RMSE (1.28) in the calibration set, while in the test set model quality statistics were in the range of those obtained with the model without automatic selection of wavenumbers (Fig. 4).

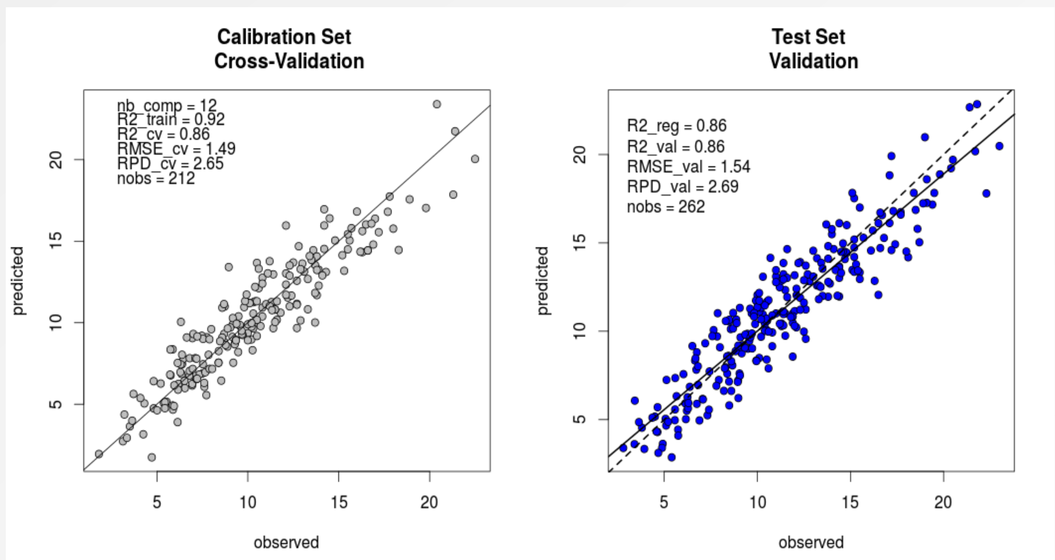

Fig. 3 : NIRS model for STB amount in scots pine wood.

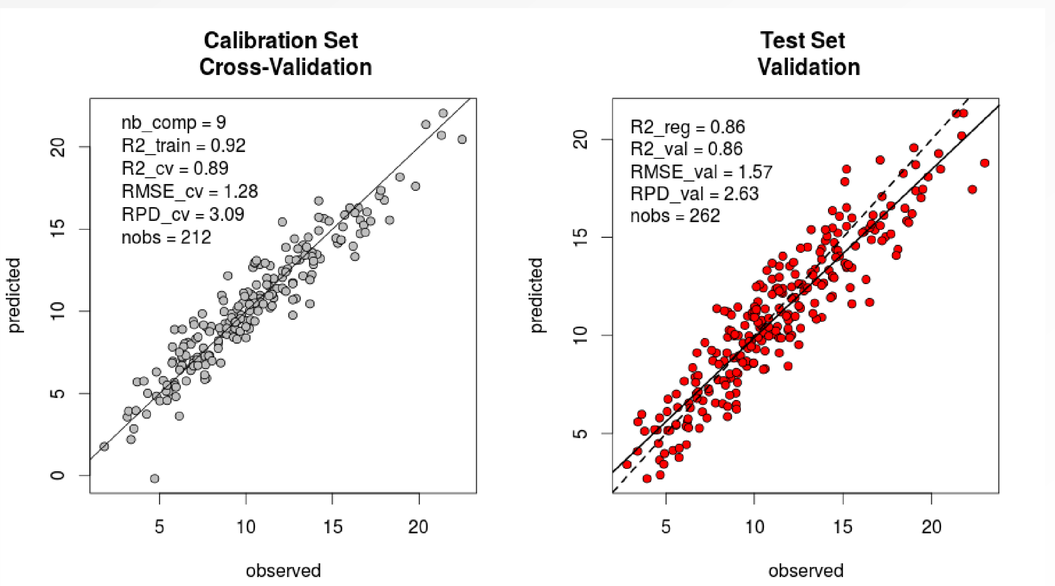

Fig. 4 : NIRS model for STB amount in scots pine wood following an automatic selection of wavenumbers.

This obtained model demonstrates the usefulness of NIRS for evaluating the stilbene content in massif wood. NIRS methodology as non destructive method could be applied to predict concentrations of stilbene amount (PSM, PS, and STB sum) on scots pine solid wood samples. Thanks to the low amount of sample pretreatment steps, NIRS could enable a throughput method for forest tree breeders. A fast and reliable routine-like analysis method to study inheritable traits affecting on wood quality is demanded.
These features are appreciated in breeding the chemical quality of Scots pine heartwood and in controlling of timber quality.

References

1 Partanen *et al.* (2011) Canadian Journal of Forest Research 41: 1993-2000.
2 Li *et al.* (2009) Analytica Chimica Acta 648: 77-84.

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