Chemometrics for monitoring the structure of modified wood and the interaction with water molecules

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Scope

To apply spectral techniques in order to better understand

- ✓ the structural modifications induced by different tratments
- ✓ the monitor the moisture content in the wood

Materials

Thermal treatment (spruce wood):
T = 150 °C
RH = 0, 10, 25%
t = 0, 5, 11, 26 days

Thermal treatment (lime wood):
T = 140 °C
RH = 10%
t = 0, 4, 7, 12, 21 days

Chemical modification (acetylation of birch wood):
WPG = 0, 4, 9, 13%

Methods

PCA – principal component analysis

PLS – partial least square

2D-COS – two dimensional correlation spectroscopy

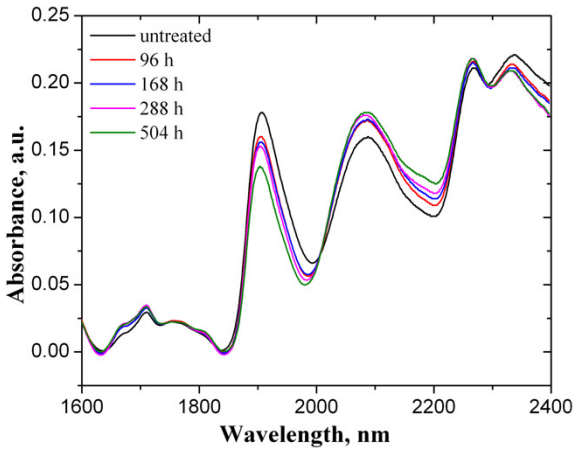
PCA

Convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables.

Reduces multidimensional data to lower dimensions while retaining most of the information.

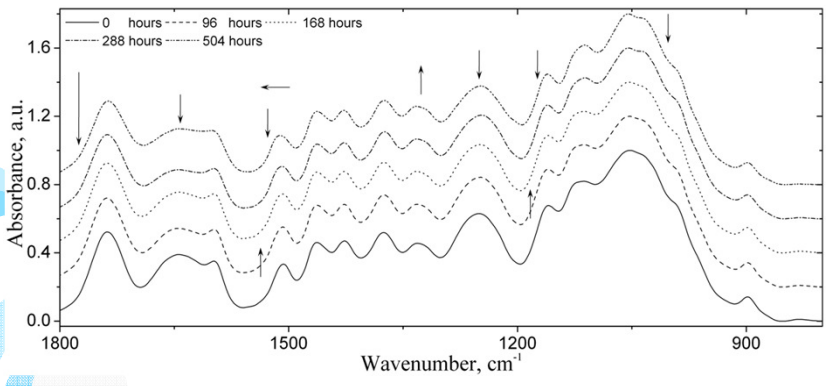
PCA identifies variability and does not differentiate between within group and between group variations.

NIR - thermal treated lime wood



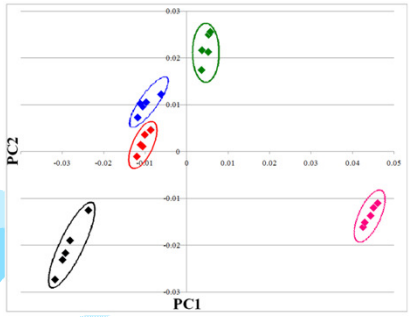
T = 140 °C
RH = 10%
t = 0, 4, 7, 12, 21 days

MIR - thermal treated lime wood

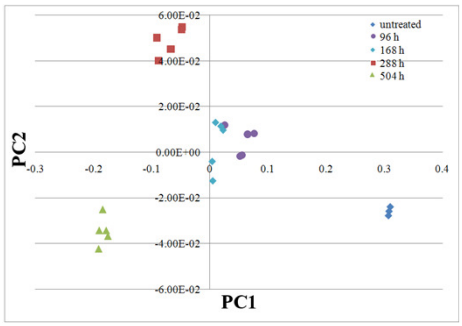


T = 140 °C
RH = 10%

PCA



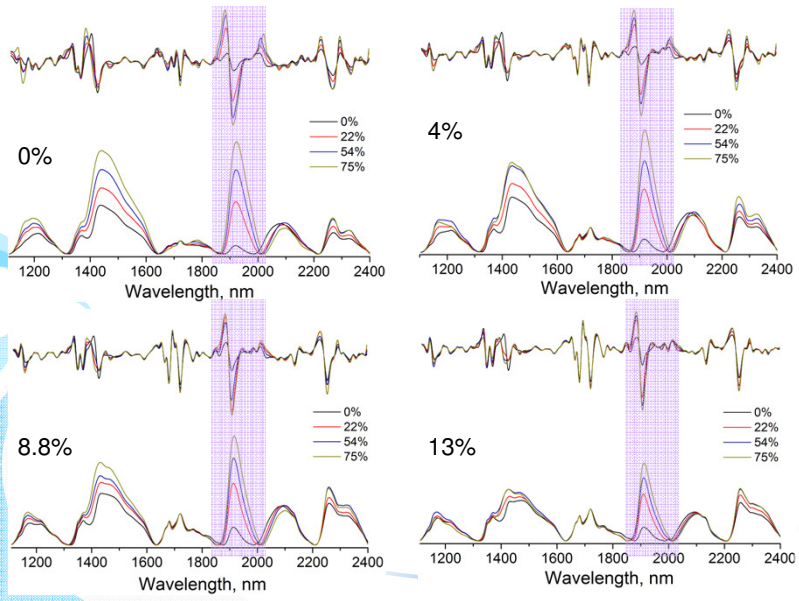
NIR



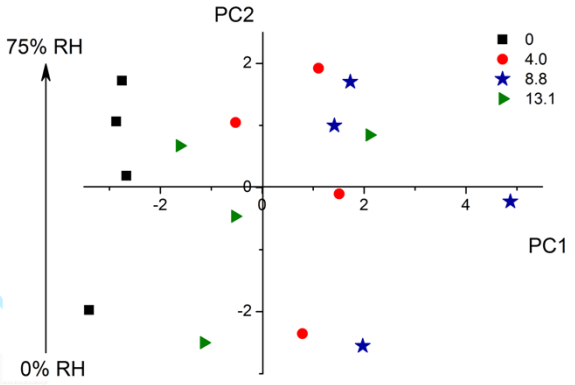
MIR

PC1 - considered as the time axis
PC2 - considered as the axis representing the structural modification of wood components

NIR - acetylated birch wood



PCA



PC1 - considered as the axis representing the chemical modification (WPG)
PC2 - considered as the moisture content axis

PLS

Can provide physical and chemical information about wood in a laboratory / industrial environment.

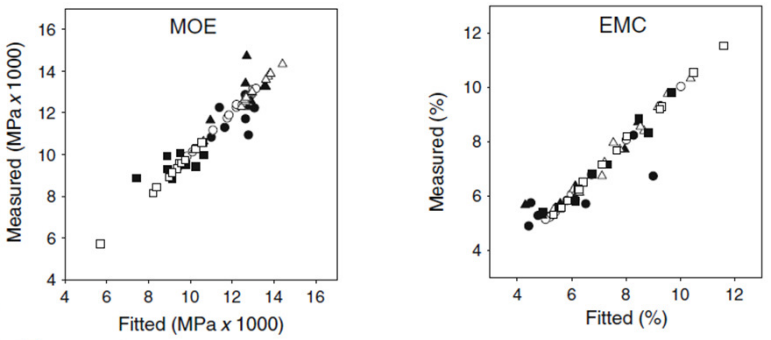
PLS is often compared to PCA in terms of its ability to classify data or to discriminate between different groups

It is best for prediction, and as a routine analysis for quality control

PLS requires the data of interest to be split into two data sets, a calibration set and a validation set.

PLS is known to overfit data, quality assessment (permutation test) of the obtained PLS result

PLS



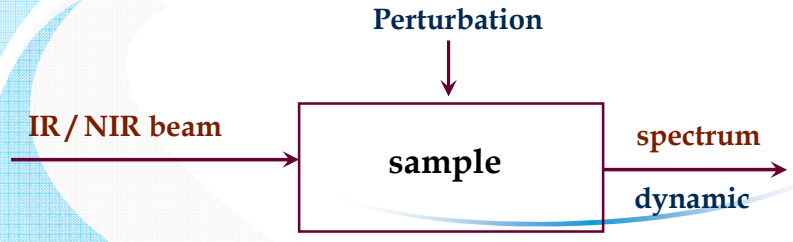
Calibration plots for MOE and EMC for thermally modified beech (circle), pine (triangles) and spruce (squares) woods.
Open symbols, calibration set; filled symbols, prediction set.

M.M. González-Peña, M.D.C. Hale, Wood Sci Technol (2011) 45:83–102

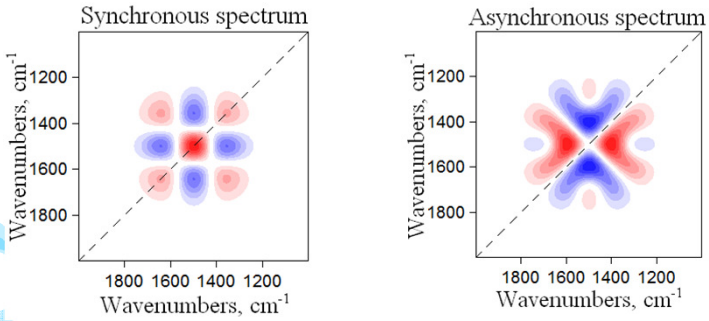
2D-COS

2D-COS attempts to transform spectra into useful qualitative information that describes a chemical system

Requires some form of perturbation: time, concentration, temperature, pressure or other chemical or physical variable



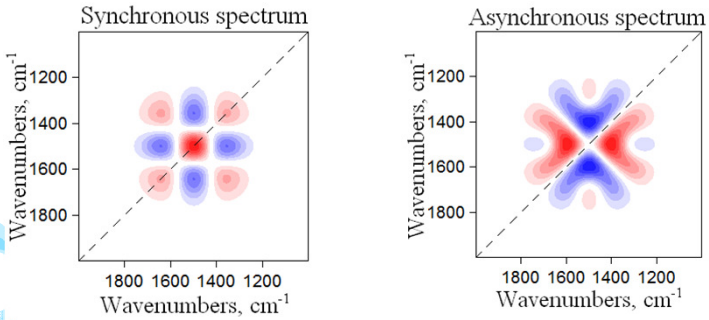
2D-COS



The **synchronous spectrum** shows which bands modify during the applied perturbation

The **asynchronous spectrum** allows to determine events in time, non-linear behaviours, to detect the field effects experienced by different functional groups of the same compound/molecule

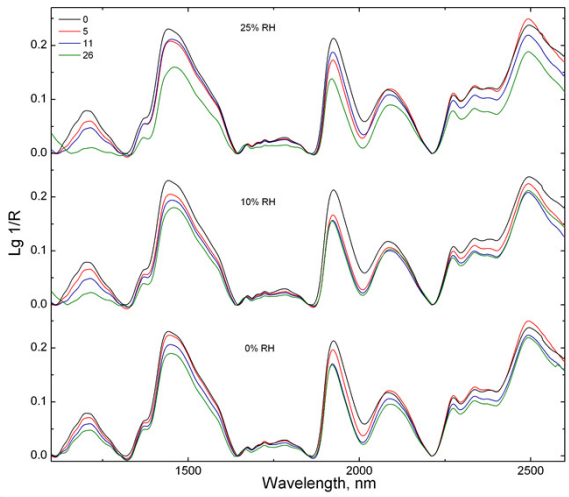
2D-COS



Limitations - primarily apply to the **asynchronous spectrum**, specially problems created by baseline variations, drift, artifacts and noise, baseline correction is sometimes required to generate meaningful spectra

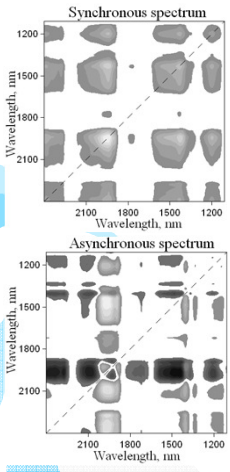
NIR - thermal treated spruce wood

T = 150 °C
RH = 0, 10, 25%
t = 0, 5, 11, 26 days

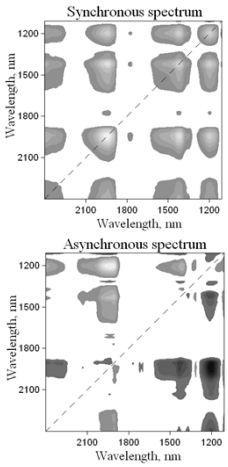


2D-COS

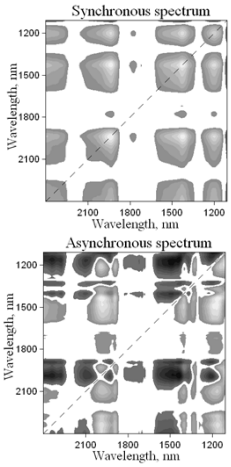
T =150 °C, RH = 0%



T =150 °C, RH = 10%

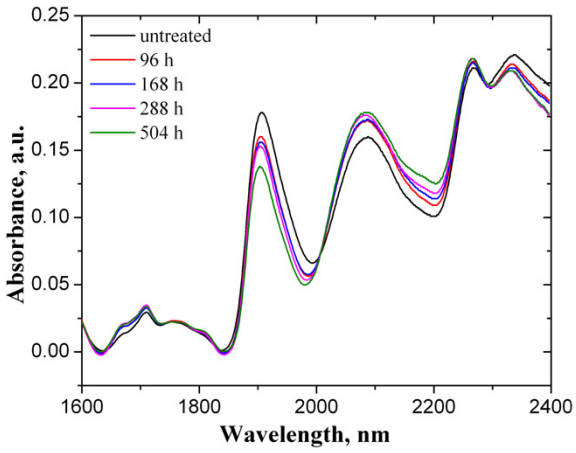


T =150 °C, RH = 25%



O-H water and extractives and lignin → CH_3 hemicelluloses and lignin → O-H and C-H from cellulose → CH all components

NIR - thermal treated lime wood



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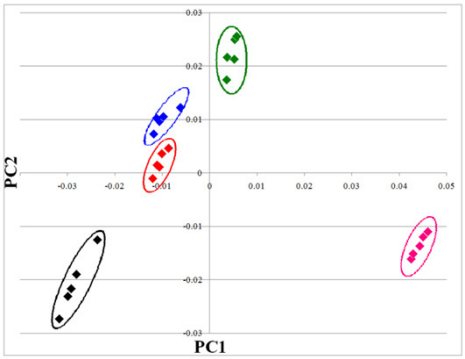
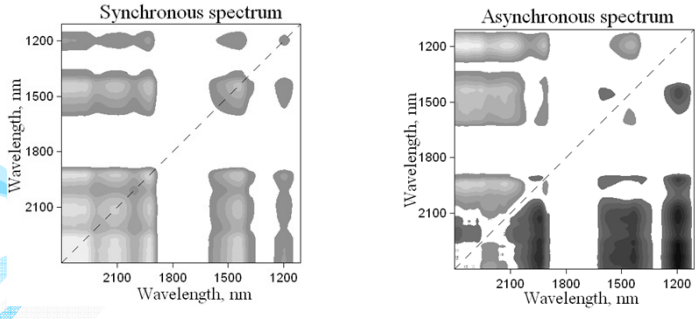
PCA



2D-COS

Set 1 (between 0 and 9 weeks)

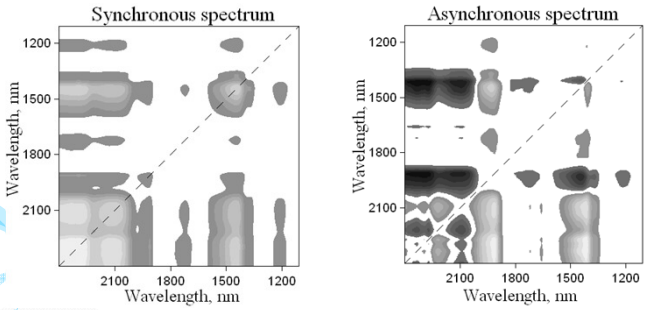


1930, 2313 nm → 1449 nm →2117, 2267 nm →1197 nm

O-H, C-H of CH_3 from acetyl (H) → O-H from extractives → O-H from cell → CH_3 groups from lignin

2D-COS

Set 2 (between 10 and 19 weeks)



2218, 1932, 1411 nm → 1449 nm → 2337, 2274 nm → 2092 nm → 1725,1211 nm

O-H water and extractives and lignin, CH_3 lignin → OH extractives → C-H hemicelluloses → O-H and C-H from cellulose → CH all components

Conclusions

- in the characterization of the spectral features whenever these contain robust information about chemical bonds, and sometimes compositional information is not directly available from their results
- online calibration models for products processing are required
- monitoring processes in real time
- determining useful structural parameters
- advantages / limitations

Thank you for your attention!