Near-Infra-Red Spectroscopy – NIRS
(High performance tool)

M.Schwanninger & L.E. Pâques
BOKUV-Vienna / INRA-Orléans
The electromagnetic spectrum

- Gamma Rays
- X-Rays
- Ultraviolet Light
- Visible Light
- Infrared Light
- Micro Waves
- Short Waves
- Radio Waves
Spectroscopy: The study of the interactions between electromagnetic radiation (energy, light) and matter.

Vibrational Spectroscopy

Vibrational spectroscopy is a method of chemical analysis where the sample is illuminated with incident radiation in order to excite molecular vibrations. Vibrational excitation is caused by the molecule absorbing, reflecting or scattering a particular discrete amount of energy. There are two major types of vibrational spectroscopy:

Infrared (IR) and Raman.
What kind of vibrations can appear in the MIR?

Simple diatomic molecules have only one bond, which may stretch. More complex molecules have many bonds leading to infrared absorptions at characteristic wavelength that may be related to chemical groups. Stretching (valance) vibrations occur at lower wavelength than deformation vibrations. For example, the atoms in a CH$_2$ group (Carbon atom green, Hydrogen atom blue), commonly found in organic compounds can vibrate in six different ways (normal modes):

**Valence vibrations**
- Symmetrical stretching
- Antisymmetrical stretching

**Deformation vibrations**
- Scissoring
- Rocking
- Wagging
- Twisting
What is a Spectrum?

**Spectrum:** A plot or display showing the amount of interaction between radiation (light) and a sample as a function of wavelength (wavenumber) or frequency.

![Spectrum Diagram](image)
Comparison of MIR and NIR spectroscopy

How does MIR spectra look like and which information can be obtained?

FT-IR (MIR) spectra of milled pine wood and components

- Pine wood
- Holocellulose
- Cellulose
- Milled Wood Lignin
How does NIR spectra look like and which information can be obtained?

FT-NIR spectra of milled spruce and beech wood

- Beech
- Spruce

Carbohydrates mainly hemicelluloses
C-H stretching of methyl- and methylene groups
Carbohydrates mainly cellulose
OH-groups
E.g. from acetyl groups
Carbohydrates
Lignin
Water
Lignin carbohydrates
Evaluation of MIR and NIR spectra

Qualitative: differences in bands

Different species

Different components

MIR

NIR
Evaluation of MIR and NIR spectra

How does NIR spectra look like and which information can be obtained?

e.g. orientation of bondings in cellulose

Figure. (left side) Polarised FT-NIR absorbance spectra (baseline corrected) of radial spruce wood sections (black) and wood sections degraded by *P. placenta* - 16% mass loss (grey). A: 7300 – 3800 cm\(^{-1}\), B: 7200 – 5350 cm\(^{-1}\). Thin lines: spectra recorded in 0\(^\circ\) polarisation; thick lines: spectra recorded in 90\(^\circ\) polarisation. (right side) Cellulose structure
Evaluation of MIR and NIR spectra

Qualitative: changes of band heights and band heights ratios

Different numbers of acetyl groups due to chemical modification

Acetylation with acetic acid anhydride

Principal Component Analysis (PCA)

Differentiation between strains of fungi grown on wood up to 14 days

2nd derivatives of NIR spectra of fungi-treated spruce wood

Loading plots

Scores plots

Traceability of wood by NIR

Trees of Norway spruce from 75 locations in 14 European countries

2163 samples (trees) measured
x 5 spectra/sample
= 10815 spectra

Traceability of wood by NIR

PCA of Norway spruce wood of different European provenances

Heartwood extractives

- widely determine **wood colour**, and
- play a **major role in decay resistance against fungi**
  (especially terpenoids, stilbenes, lignans and polyphenols)
- are usually determined directly through **wet-lab chemistry methods**
  (extraction with different solvents, gravimetric determination of the residuum)

---

**Applications to lignocellulosics**

**Determination of heartwood extractives contents in *Larix* sp.**

**Heartwood extractives**

Applications to lignocellulosics

Determination of the natural durability of *Larix* sp.

Larch wood after 16 weeks growth of the fungi: *Coniophora puteana* and *Gloeophyllum trabeum*

*Coniophora puteana*  
*Gloeophyllum trabeum*  
*Gloeophyllum trabeum*

After removal of the mycel and drying and weighing

*Gloeophyllum trabeum*  
*Gloeophyllum trabeum* treated larch wood
Applications to lignocellulosics

Determination of the natural durability of *Larix* sp.

Three brown rot fungi for the wood decay tests: *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta* (data not shown)

Test specimens from heartwood
50 mm x 25 mm x 15 mm

Collection of three NIR spectra per specimen from the radial surface (12% moisture content)

100 boards with five samples per fungus and board = 500 samples per fungus

Inoculation with a fungi

After 16 weeks

Mass loss  NIR spectra

**PLS-R Model**
Applications to lignocellulosics

Determination of the lignin content of *Picea abies*

1. **wood disk** → **milling** → **drying** → **wood meal** → **extraction** → **extractives-free wood meal**

2. **Klason lignin** and **acid soluble lignin** results = **total lignin content**

3. **NIR fibre optic**

4. **lignin determination**

5. **PLS-R model**

6. **NIR**
Lignin distribution in larch wood

Johner, N. (Bruker), Schwanninger, M., Gierlinger, N. (BOKU) 2002
NIR imaging

NIR imaging of a larch wood strip and a Scots pine disk

Wallbäcks L. and Lundqvist S.-O. (INNVENTIA) 2013
Applications to lignocellulosics

Further applications: determination (prediction) of

- **Kappa number**
  

- **H/G ratio**
  

- **Biotechnology – Biopulping / Fungi treatment / Biodegradation**

  
  
  
  
  
Applications to lignocellulosics

Further applications: determination (prediction) of

- **Chemical / thermal modification / photodegradation**

- **Wood components (lignin, extractives, ....)**
Applications to lignocellulosics

Further applications: determination (prediction) of

Wood components (lignin, extractives, ....)


Cellulose


Pulp yield

Applications to lignocellulosics

Further applications: determination (prediction) of

- **Special**

- **Composts / Waste material**

- **Reviews on the use of NIR for wood, pulp, and paper**
Infrared spectroscopy in T4F

NIR spectroscopy as a tool for indirect assessment of wood properties

a) Development or improvement of calibration models to predict wood properties and new adaptive traits based on acquired infrared spectra
   i. Feasibility of NIRS to predict hydraulic conductivity and vulnerability to cavitation
   ii. Lignin composition determined by analytical pyrolysis to be used for NIRS calibrations
   iii. Prediction of extractives content (e.g. phenolics) with NIRS in relation to natural durability/ heartwood colour
   iv. Prediction of mass loss of larch wood with existing NIR PLS-R models
   v. Verification of the predicted mass losses by additional decay tests
   vi. Comparison of DSC-TGA results with wet-chemical analysis results with results from NIR imaging
Infrared spectroscopy in T4F

NIR spectroscopy as a tool for indirect assessment of wood properties

b) Calibration transfer
   i. Standardization of NIRS calibration methods for important wood properties
   ii. Inter-laboratory tests on representative samples from several species for different traits
   iii. Development of calibration transfer protocols

c) Transfer to research infrastructure
   i. Results on new methodologies and techniques for medium to high throughput phenotyping will be disseminated towards researchers and end-users, organisation of training workshops and presentations at meetings
Thank you very much for your attention

BOKU Vienna: Gierlinger, N., Luss, S., Rosner, S., Schwanninger, M.
CIRAD Montpellier: Chaix, G.
CIS-Madeira Spain: Touza, M.
IICT Lisbon; Rodrigues, J.
INNVENTIA Stockholm: Lundqvist, S.-O., Wallbäcks, L.
INRA-Orléans: Charpentier, J.P., Pâques, L., Segura, V
IVALSA Trento: Sandak, A., Sandak, J.