NIR in Forestry: From leaves to soil

José Rodrigues
ULisboa/ISA/CEF former IICT
1 – Basic introduction to NIR spectroscopy:
   Historic development
   Why NIR
   What is NIR
   NIR spectral Information

2 – NIR in the Forestry:
   From leaves to soil
Historical development

1800 – Discovery of (near) infrared Herschel

1881 – First NIR spectra recorded Abney & Festing

19** – Assignment of functional groups
  Coblenz 1905; Ellis 1929

1945 - Karl Norris, USDA. Basis for NIR applications NIR-MLR

1960 - 30 NIR references (moisture, protein and fat content)

1983 - NIR-PLS Martens & Jensen
  NIR sleeper among spectroscopy Wetzel

1989 – Earlier applications in forestry

1993 - Journal of Near Infrared Spectroscopy

1998 - From sleeping technique to the morning star Davies
The electromagnetic spectrum

\[ \nu = c \lambda \]

\( \nu \) wavenumber (cm\(^{-1}\))

\( \nu \) frequency (Hz)

\( \lambda \) wavelength (nm)
What is (vibrational) Spectroscopy?

**Spectroscopy:** The study of the interactions between electromagnetic radiation (energy, light) and matter.
What is (Vibrational) Spectroscopy?

**Spectroscopy**: Interactions between electromagnetic radiation (energy, light) and matter.

Change the vibration of matter
What kind of vibrations can appear in the MIR?

- Stretching (valence) vibrations (lower wavelength)
- Deformation vibrations (higher wavelength)

Valence vibrations
- Symmetrical stretching
- Antisymmetrical stretching

Deformation vibrations
- Scissoring
- Rocking
- Wagging
- Twisting
Influence of bond strength

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

1) The higher the force constant \( k \), i.e. the bond strength, the higher the wavenumbers (at which a band appears):

- \( \sim 2250 \text{ cm}^{-1} \) (C≡N)
- \( \sim 1650 \text{ cm}^{-1} \) (C = N)
- \( \sim 1050 \text{ cm}^{-1} \) (C – N)
**Influence of mass**

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

Reduced mass \[ \mu = \frac{m_1 \ast m_2}{m_1 + m_2} \]

2) The larger the vibrating atomic mass, the lower the vibrational frequency (in wavenumbers; at which a band appears)

\[ ^1\text{H} - \text{O} \quad \mu = 0.9 \]

\[ ^2\text{H} - \text{O} \quad \mu = 1.8 \]

\[ \nu = \sim 3300 \text{ cm}^{-1} \]

\[ \nu = \sim 2700 \text{ cm}^{-1} \]
IR spectra of water

Transmission

Wavenumber cm\(^{-1}\)
NIR spectra

- NIR spectra are the result of:
  - **overtones** of the fundamental vibrations
    and
  - **combination of bands** of the fundamental vibrations (FTIR):
Overtone bands

1\textsuperscript{st} overtone $2 \times 3500 \approx 7000$ cm$^{-1}$
2\textsuperscript{nd} overtone $3 \times 3500 \approx 10500$ cm$^{-1}$
3\textsuperscript{rd} overtone $4 \ldots$
Combination bands

3500 + 1640 = 5140 cm\(^{-1}\)

~5,200 cm\(^{-1}\)

~3,500 cm\(^{-1}\)

~1,640 cm\(^{-1}\)
NIR spectra are the result of **overtones** and **combination** of the bands:

C-H, N-H, O-H and S-H

H – heteroatom
NIR spectra information

- Besides chemical information, NIR spectra also contain physical information.
NIR physical information

- Particle size
- Compactness
- Density
- Temperature
- Viscosity
- Turbidity

![Graph showing wavenumber vs. Log(1/R) for compressed and non-compressed samples. The graph indicates peaks at different wavenumbers for coarse and fine particles.](image-url)
Spectral characteristics:

- NIR absorption bands are typically 10–100 times weaker than the corresponding fundamental mid-IR absorption band
- NIR absorption bands are very broad (bandwidths of 50–100 nm) and highly overlapped
- Chemical and physical information in same spectra
The weak absorption is in fact the strength of NIR allows direct analysis of strongly absorbing, highly light-scattering matrices such as slurries, suspensions, pastes, and powders

Virtually all biological systems can be analyzed by NIR since all have at least one C-H, N-H or O-H bonds,

.......in virtually any state!
2- NIR in the Forestry: From leaves to soil
NIR in the soil

- **Soil texture**
  - Clay (< 0.002 mm)
  - Silt (0.002-0.05 mm)
  - Sand (>0.05 m)

- **Organic matter**
- **Moisture**
- **Total C**
- **Total N**

- **Not fertility**
- **Not slipping but not progressing**
NIR in the leaves

Wavenumber cm⁻¹

Absorbance Units

Nitrogen content predicted (g/kg)

Nitrogen Kjeldahl [%]

Absorbance Units

Nitrogen Kjeldahl [g/kg]

Wavenumber cm⁻¹

Designing Trees for the Future
- Besides nitrogen it would be possible at least for phosphorous and potassium
- NIR has the potential for real time monitoring
- NIR has the potential to be a nutrition management tool
- Implementation is not hampered by technique rather by economics
The koala is a highly specialized folivore, feeding almost exclusively on Eucalyptus foliage, but showing strong selectivity among individual trees, both between and within tree species.
E propinqua
E nicholii
E robusta
E regnans
NIR spectra of *Eucalyptus globulus* leaves resistant (blue) and susceptible (red) to *Leptocybes invasa*.
Earlier forestry applications

- 24 years later...
- Wright, J.A, Birkett MD and Gambino MJT. Prediction of pulp yield and cellulose content from wood samples using near infrared reflectance spectroscopy. *Tappi Journal* 73, 8, 164-166 (1990)
Applications to lignocellulosics

Determination of the lignin content of *Picea abies*

The predicted versus the true lignin contents covering a total lignin content range from 25.05% to 29.71%.

Using all spectra: 2 PCs, $R^2 = 92.6\%$, RMSEE = 0.244\%, RMSECV = 0.248\%, with a RPD of 3.7 and a bias of 0.00038

Average spectra: 2 PCs, $R^2 = 92.9\%$, RMSEE = 0.242\%, RMSECV = 0.244\%, RPD = 3.7 and a bias of 0.00032
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
NIR-based PLS-R X-ray density model

- 168 NIR spectra - cross-validation (85 spectra) and a test set (83 spectra).

\[ r^2 = 0.983 \]
\[ \text{RMSECV} 19.6 \text{ kg/m}^3 \]
\[ \text{RPD} 7.6 \]
- 10 outliers removed

\[ r^2 = 0.98 \]
\[ \text{RMSEP} 22.7 \text{ kg/m}^3 \]
\[ \text{RPD} 7.2 \]
- 31 outliers removed

NIR-predicted versus measured density of the calibration / cross-validation set.

NIR-predicted versus measured density of the test set.
X-ray microdensity profile of the Larch wood sample between 120 and 160 mm. Black line represents the X-ray microdensity. Pink line the predicted the filled green squares are the cross-validation results, the filled orange circles are the test-set validation results, the filled red circles are outliers or spectra which led to large deviations in density.
Applications to lignocellulosics

Further applications: determination (prediction) of

- Wood chemical composition:
  - Lignin content
  - Lignin composition H/G, S/G
  - Cellulose content
  - Extractives content
  - Extractives composition

- Physical properties:
  - Density
  - MOE, MOR, etc

- Biotechnology – Biopulping / Fungi treatment / Biodegradation

Take a look poster 19

Take a look poster 4
Applications to lignocellulosics

Further applications: determination (prediction) of

- Pulp yield
- Biotechnology – Biopulping / Fungi treatment / Biodegradation
- Composts / Waste material
- Chemical / thermal modification / photodegradation

Reviews

Thank you very much for your attention
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)

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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)

Inoculation with a fungi

After 16 weeks

Determination of the natural durability of *Larix* sp.

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

PLS-R Model

Mass loss NIR spectra

Inoculation with a fungi

NIR

weighing

Wood decay tests
Applications to lignocellulosics

Determination of the lignin content of *Picea abies*

A structural model of softwood lignin proposed by Sakakibara

Applications to lignocellulosics

Determination of the lignin content of *Picea abies*

- wood disk
- milling
- drying
- wood meal
- extraction
- extractives -free wood meal
- lignin determination
- Klason lignin and acid soluble lignin results = total lignin content
- NIR fibre optic
- NIR
- PLS-R model
Quantitative: Linear regression (univariate)

Determination of the lignin content from MIR spectra and the 2nd derivatives of NIR spectra of spruce wood

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**
  
  