Bio-materials characterization with NIR

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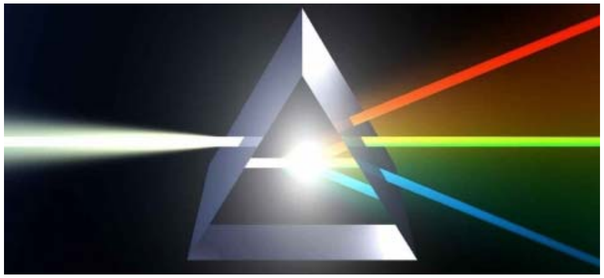
TREES AND TIMBER INSTITUTE

Outline

Tendencies in biomaterials developmnet



Why spectroscopy?

NIR in bio-materials characterization

Trends in NIR applications

Goals

- to **exploit** the potential of near infrared spectroscopy
- to **demonstrate** its capabilities for bio-based materials characterization
- to **highlight** the potential of the NIR as a tool capable of providing complementary information to other techniques
- to **present** current trends in NIR developments

Bio-materials in construction sector

- In Italy 1 on 12 buildings is made of wood and growing tendency is observed nowadays
- Bio-based materials are often used for retrofitting of existing structures, upward construction or vertical gardens
- Buildings that use bio-materials are not just sustainable, strong and durable;
  they are also beautiful

Development priorities

- **Structural components**

  (need for developed wood products - Engineered Wood Products, high strength wood, moisture resistant sills, light-weight beams/joists/studs of bio-composites, sandwich panels for exterior walls)

- **Insulation**

  (need for compactable bats of cellulose insulation, environmentally friendly fire impregnation, high-performance insulation that provides thinner walls, insulation, optimized for soundproofing)

- **Barrier Materials**

  (need for bio-based wind and vapor barrier for moisture-proof exterior walls, waterproofing for wet areas, **façade** and roofing materials **with improved durability/serviceability**

Source: Per-Erik Eriksson: Future sustainable biobased buildings

Durability and performance












Surface properties

leveling

outlook

resistance to abrassion

roughness

pattern

wetability

touch experience

resistance to dirt

brightness

facture

durability

soft feel

waviness

color

gloss

hardness

matting effect

adhesion

contamination

temperature

softiness

surface free energy

chemical activity

resistance to scratch

aseptic

water repellency

How to assess properties?

Why NIR spectroscopy?

- 👍 No need special sample preparation
- 👍 Non-destructive testing
- 👍 Relatively fast measurement
- 👍 No residues/solvents to waste
- 👍 Determination of many components simultaneously
- 👍 High degree of precision and accuracy
- 👍 Direct measurement with very low cost

- 👎 Not self standing technology
- 👎 Overlapping of spectral peaks
- 👎 Not straightforward interpretation
- 👎 Needs statistics methods for data analysis

NIR applications



chemical industry, microanalysis, pharmaceutical analysis, soil, polymers, food and beverages, surface science, fuels, textile industry, art conservation, forensics, PAT, remote sensing

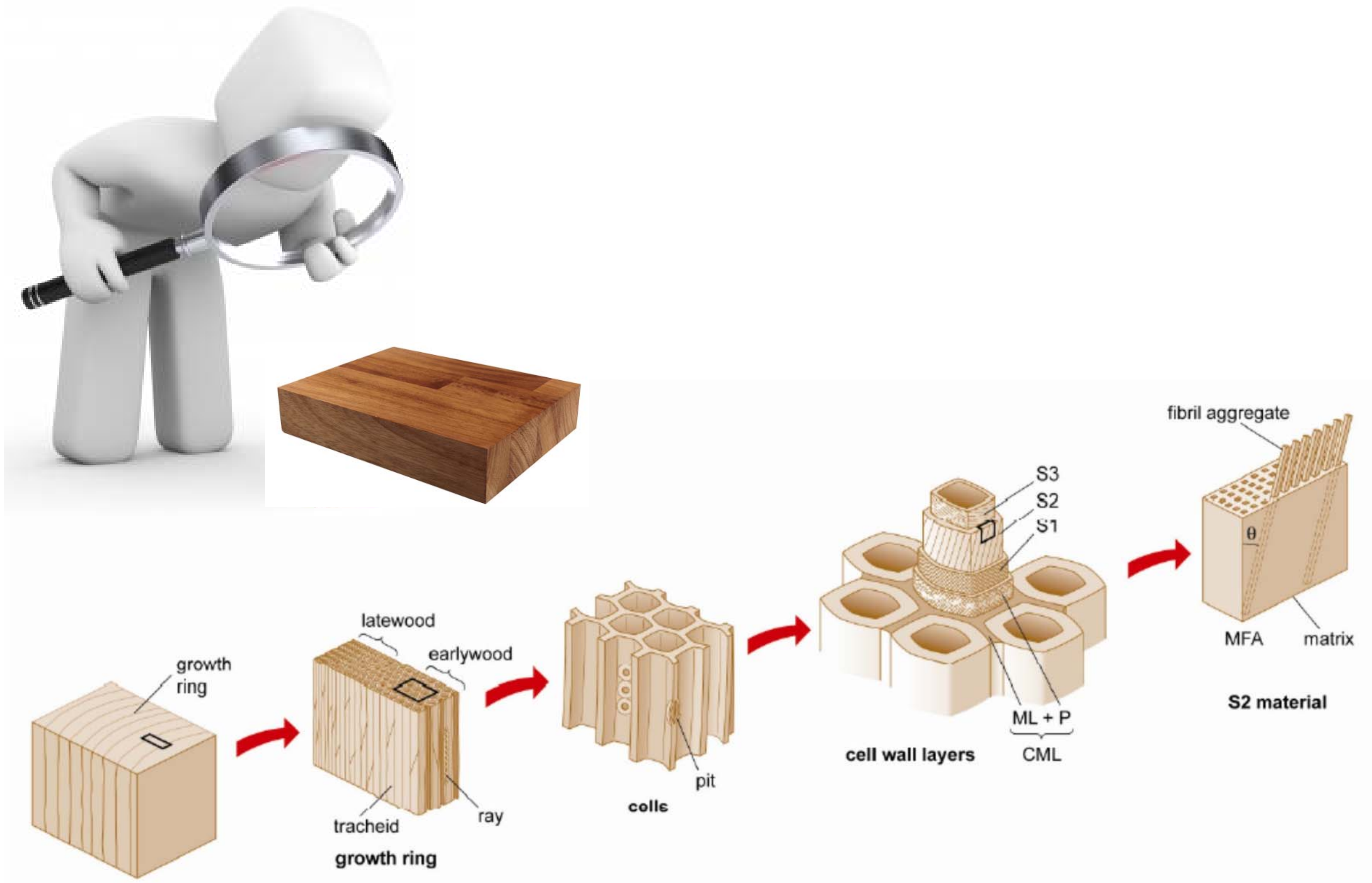
and also **wood and paper industry**





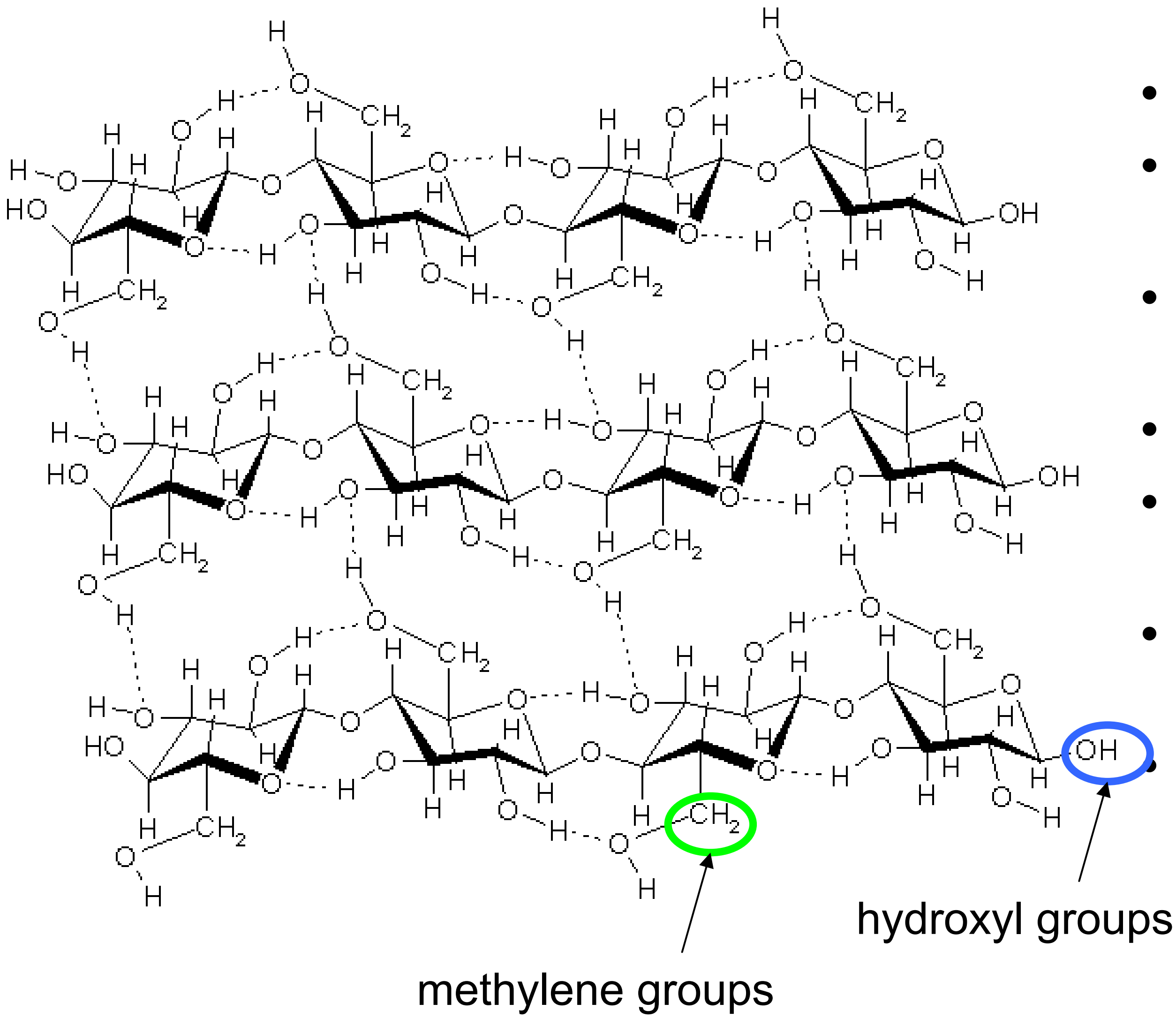



…but what can we see in wood?



http://www.ifb.ethz.ch/research/sinergia

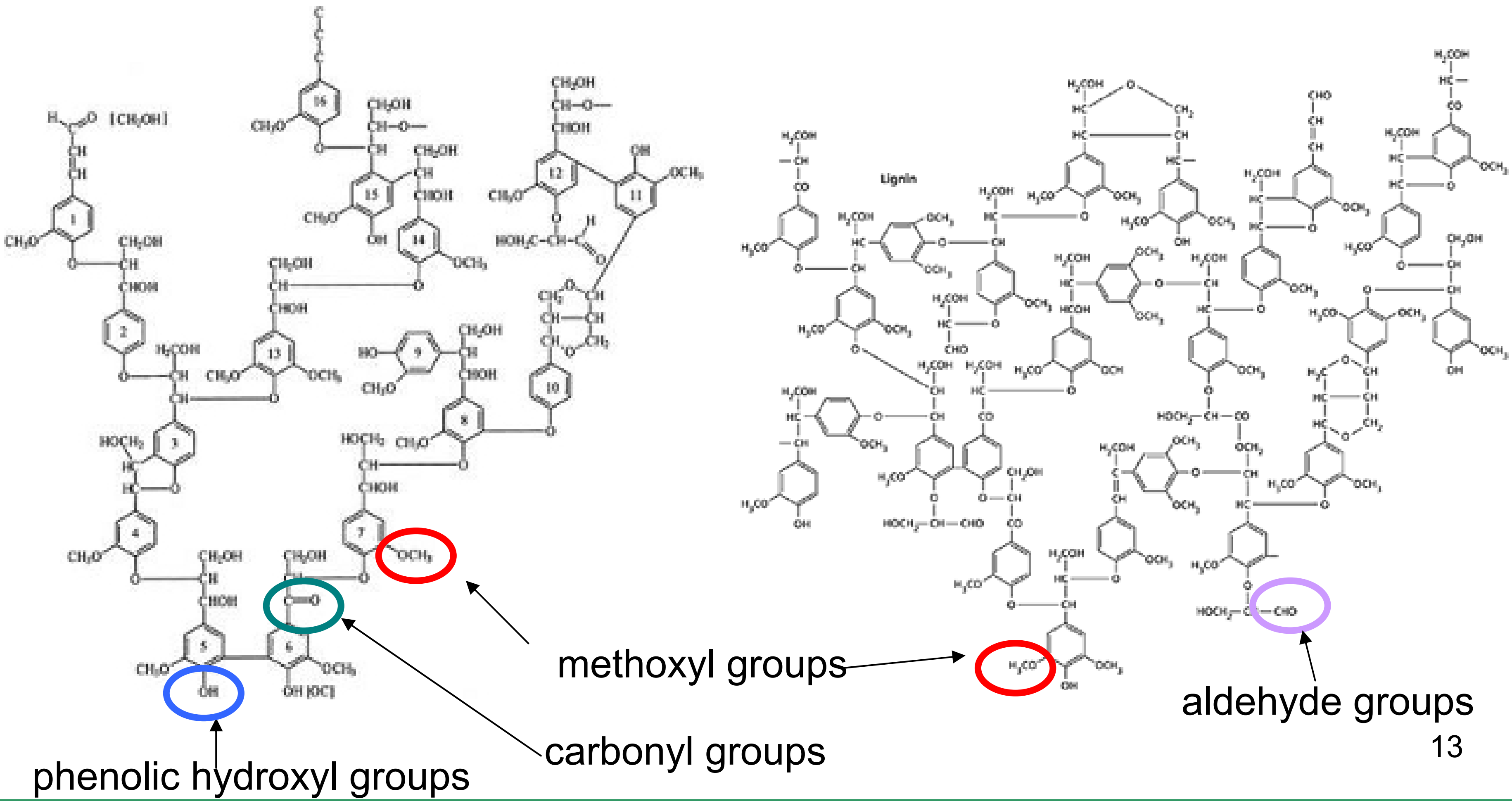
Cellulose (40-50%)



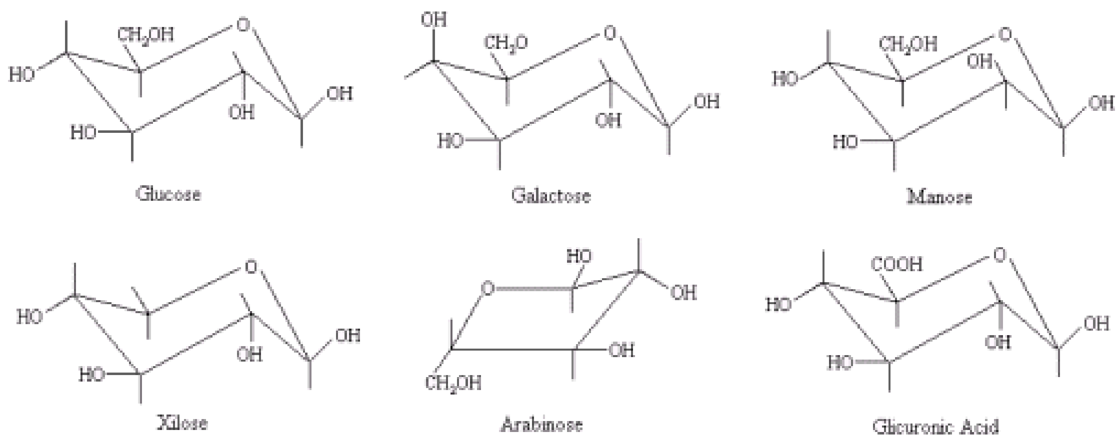
- linear polymer
- long chain (DP 5000-10000)
- B-D-Glucopyranose units
- 1,4-glycosidic bonds
- hydroxyl groups bonds
- different kind in wood:
- - amorphous,
  - semi-crystalline,
  - crystalline

Lignin (20-30%)

Softwood (guaiacyl units) Hardwood (guaiacyl + syringyl units)

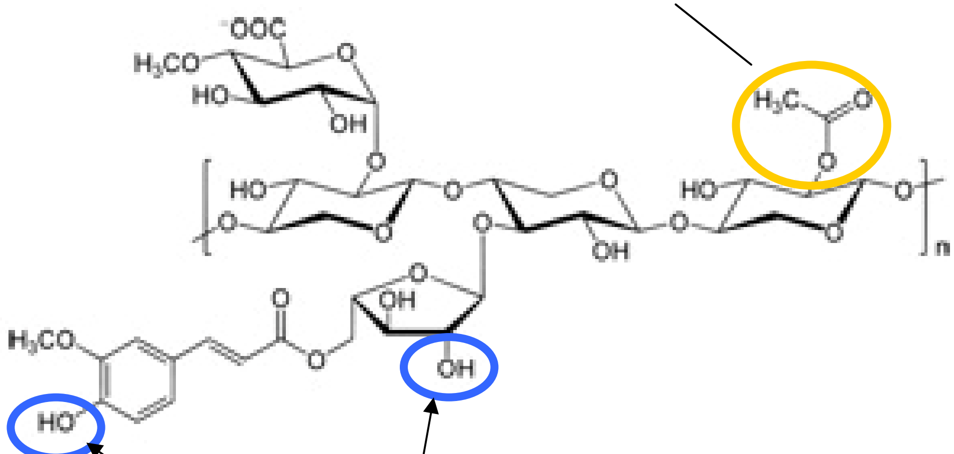


Hemicellulose (25-35%)



- hetero-polysaccharides
- short chain (DP 150-200)
- amorphous
- high reactivity
- various composition for hardwood and softwood

acetyl groups



hydroxyl groups

NIR & biomaterials characterization

- Chemical compositions
  (cellulose, lignin, extractives)
- Physical and anatomical characterization
  (density, moisture, calorific value, microfibryl angle, defects detection, sapwood/heartwood detection)
- Mechanical properties
  (compression, tension, MOE, MOR)
- Identification and monitoring others properties of wood
  (decay monitoring, weathering, waterlogging, thermal treatment, chemical modifications)
- Paper industry
  (weight, thickness, moisture, Kappa number, mechanical resistance, type of pulp/paper)

Virgin wood

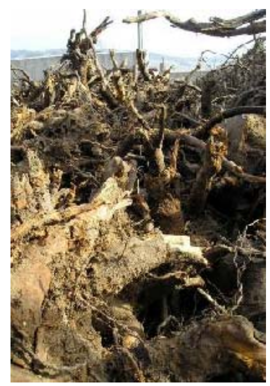




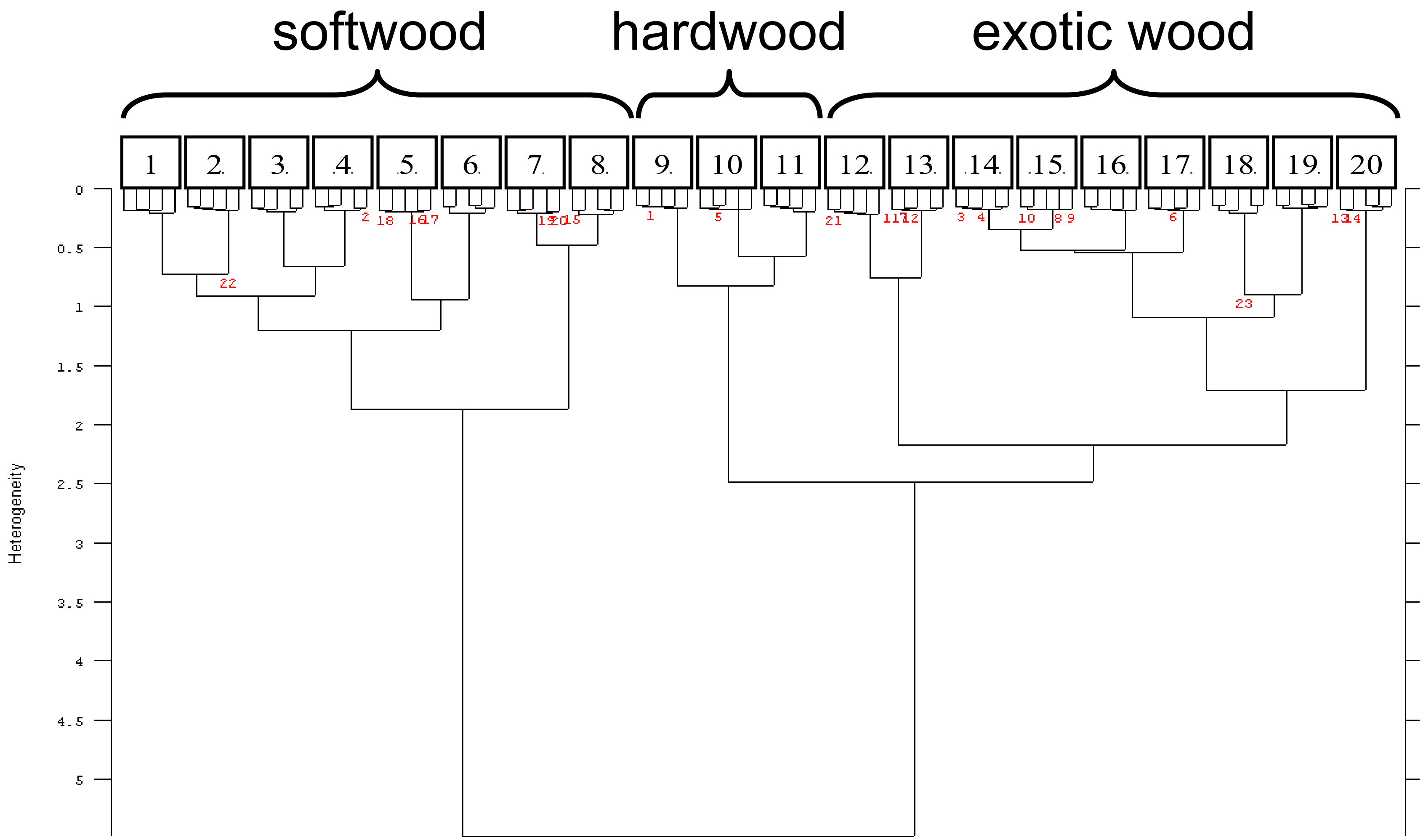
- Species recognition
- Wood provenance
- Exotic wood evaluation
- Biomass characterization
- Clones recognition





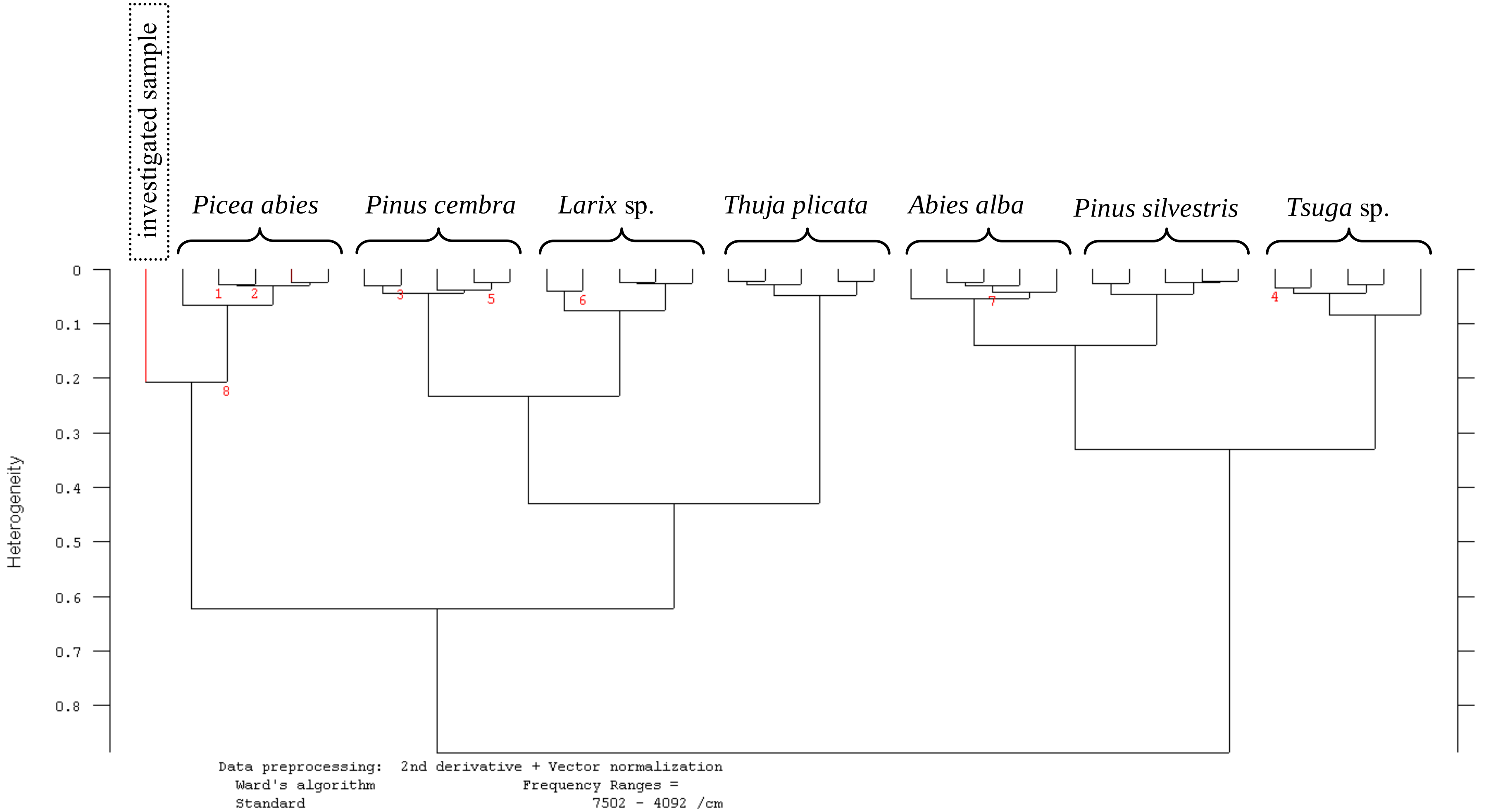


Recognition of wood species



01- Picea abies, 02-Abies alba, 03-Pinus cembra, 04-Larix decidua, 05-Pinus sylvestris, 06-Pinus ponderosa, 07-Tsuga, 08- Thuja sp., 09-Quercus robur, 10-Robinia pseudoacacia, 11-Castanea sativa, 12-Iroko, 13-Afrormosia, 14-Okumè, 15-Sipo, 16-Meranti, 17-Wengè, 18-Azobè, 19-Ipè, 20-Itauba, 21-Pau Rosado, 22-Teck, 23-Bangkirai

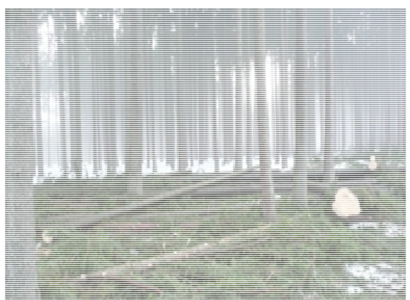
Use of CA for species classification



Wood provenance & NIRS

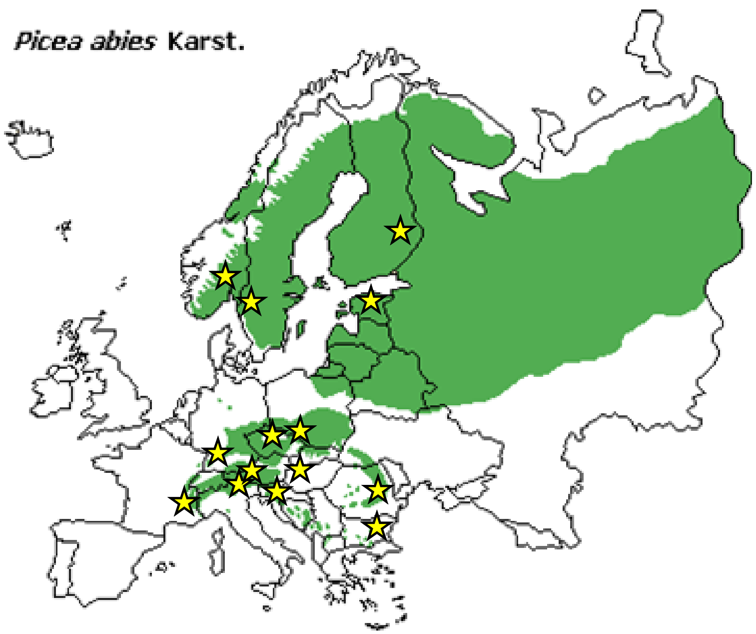
2163 trees of Norway spruce
from 75 location
in 14 European countries

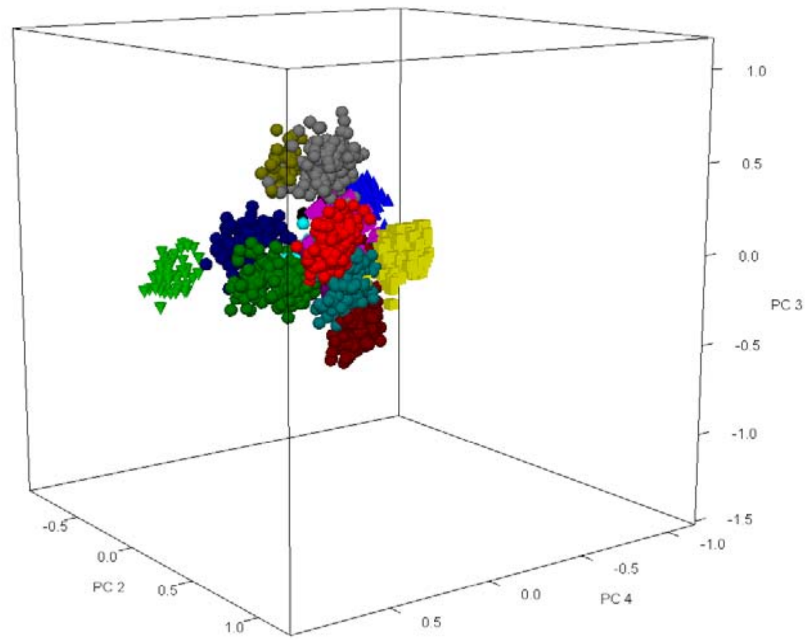
2163 samples measured
x 5 spectra/sample
= **10815 spectra**

Differentation of origin

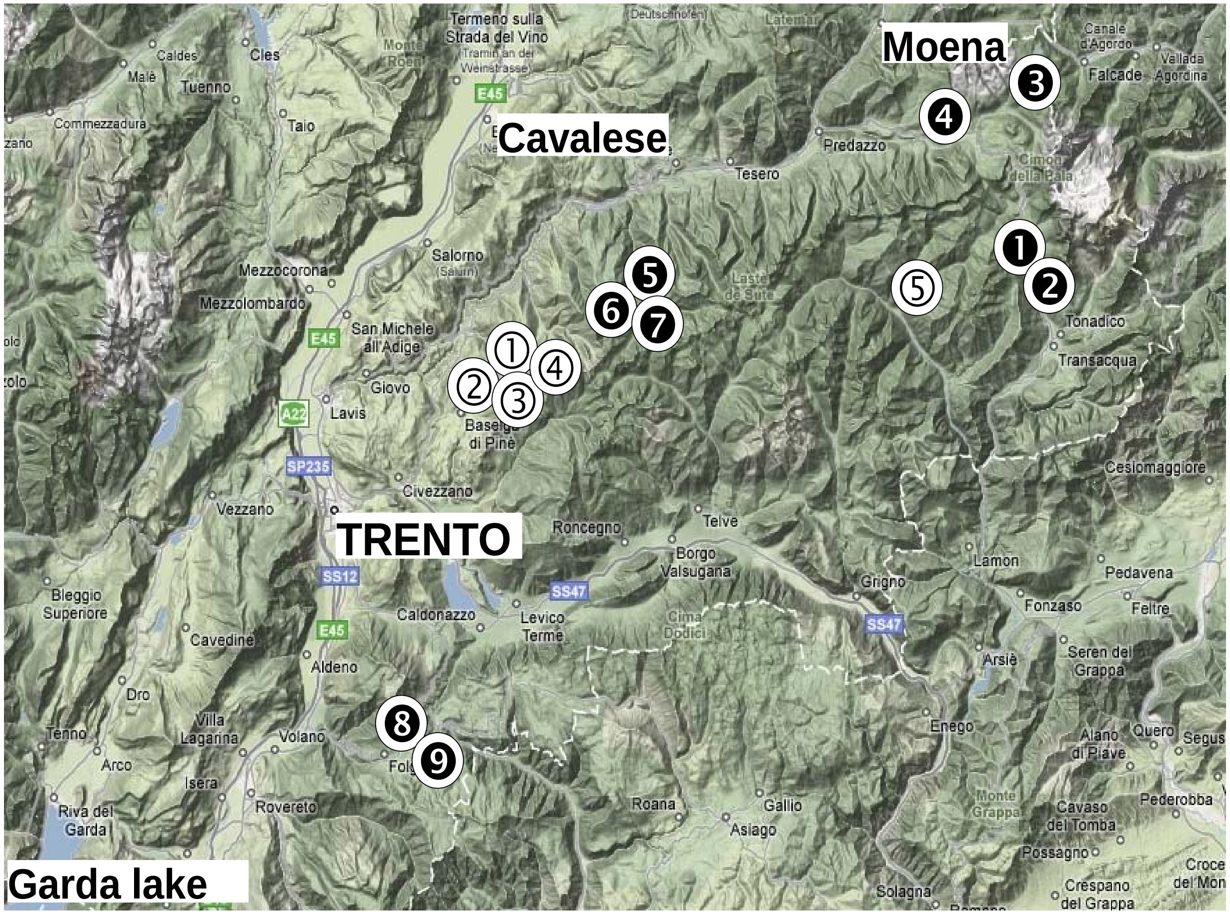
samples form 14 countries (75 locations); totally **10815 spectra** was analyzed and evaluated



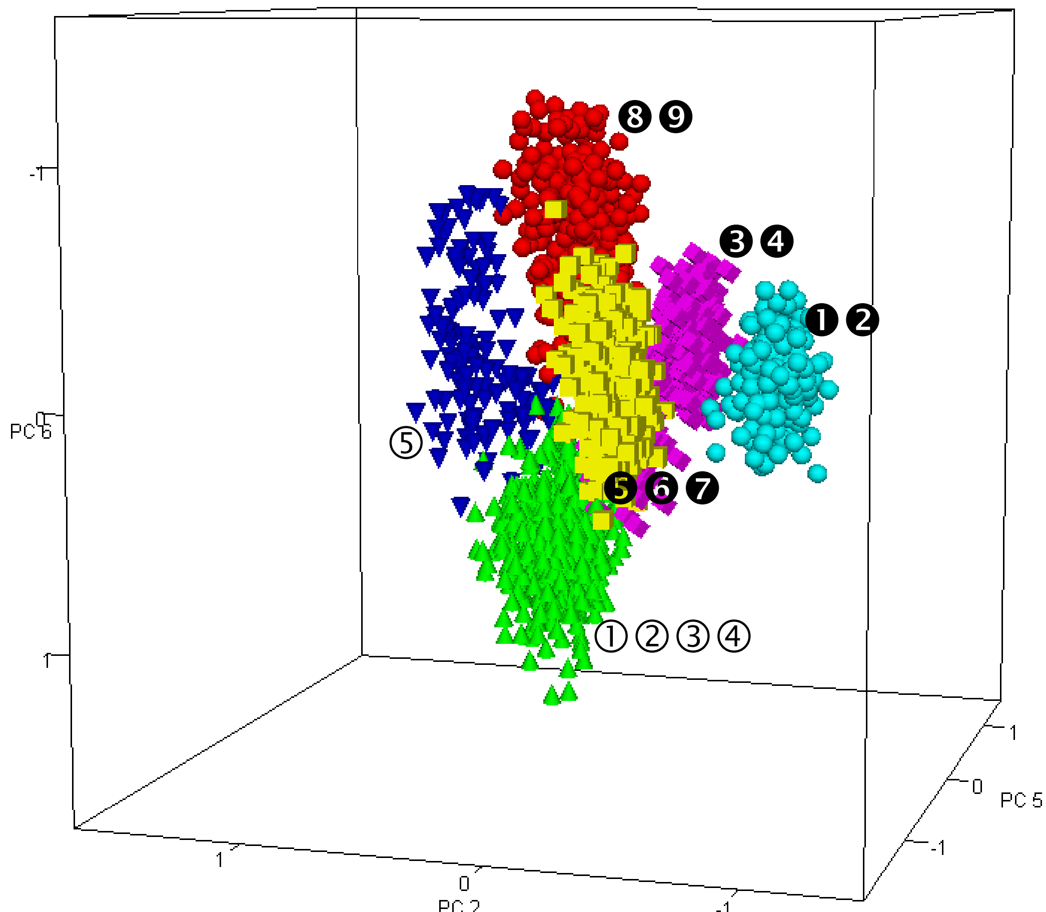


● Austria ▲ Bulgaria ▼ Czech Republic ■ Croatia ■ Estonia ● Finland ● France
● Germany ● Hungary ● Italy ● Norway ● Poland ● Romania ● Sweden

Italy


Moena
Cavalese
TRENTO
Garda lake
Predazzo
Tesero
Salorno
Mezzocorona
Mezzolombardo
San Michele all'Adige
Giovo
Lavis
Baselga di Pinè
Civezzano
Vezzano
Roncegno
Telve
Borgo Valsugana
Caldonazzo
Levico Terme
Aldeno
Cavedine
Bleggio Superiore
Dro
Villa Lagarina
Volano
Tenno
Arco
Isera
Rovereto
Riva del Garda
Roana
Gallio
Asiago
Grigno
Lamon
Fonzaso
Feltre
Pedavena
Arsiè
Seren del Grappa
Enego
Alano di Piave
Quero
Cavaso del Tomba
Pederobba
Possagno
Crespano del Grappa
Solagna
Tonadico
Transacqua
Cesiomaggiore
Falcade
Canale d'Agordo
Vallada Agordina
Cles
Caldes
Malè
Tuenno
Taio
Commezzadura
Termeno sulla Strada del Vino

Principal Component Analysis

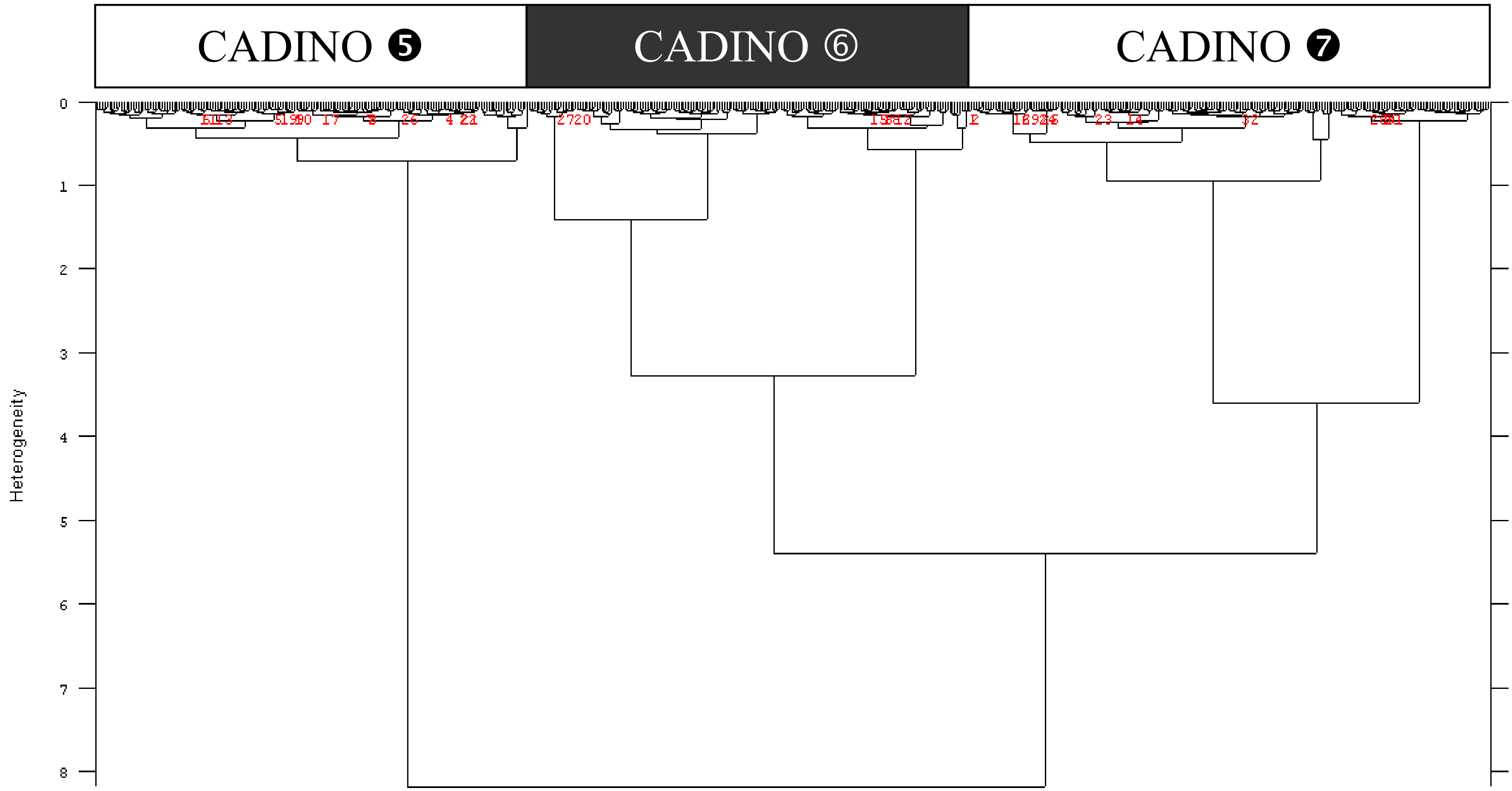


- ❶ Strada Alta Valcigolera
- ❷ Strada Orti Forestali,
- ❸ Juribello
- ❹ Paneveggio
- ❺ Cadino 06
- ❻ Cadino 43
- ❼ Cadino 49
- ❽ Folgaria 04
- ❾ Folgaria 22
- ① Monte Sover 7
- ② Monte Sover 11
- ③ Monte Sover 14
- ④ Monte Sover 69
- ⑤ Caoria Valsorda

PCA of spectra of wooden samples coming from six different locations (14 sites) in Trentino region

Note: second derivative, vector normalization, method: factorization (5 factors) region: 9590-5250cm^{-1}, 5100-4160cm^{-1}

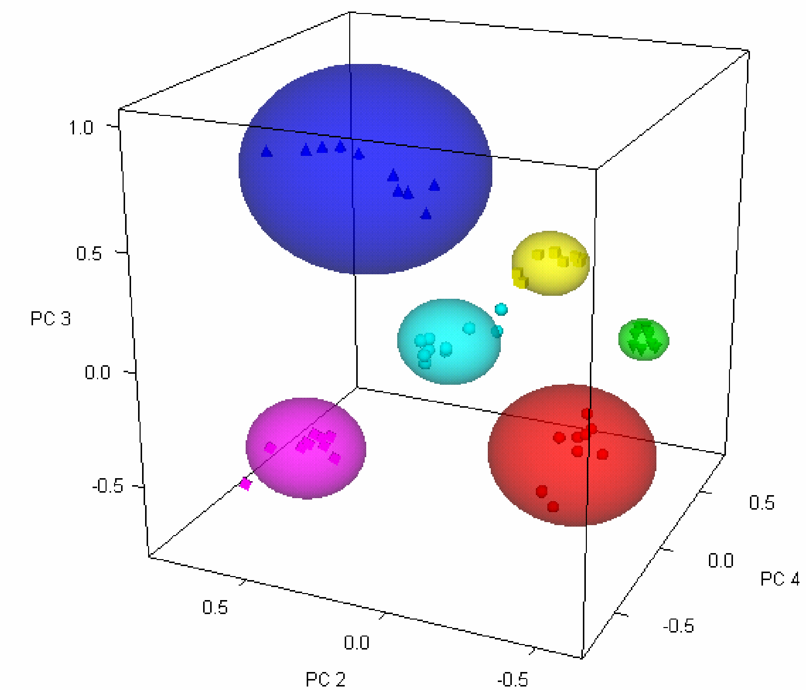
Cluster Analysis



CA – wooden samples from 3 different districts of Cadino valley ❺⑥❼

Note: second derivative, vector normalization, Ward's algorithm, region: 7089-5072cm^{-1}

Identification of agricultural residues



Helianthus tuberosus

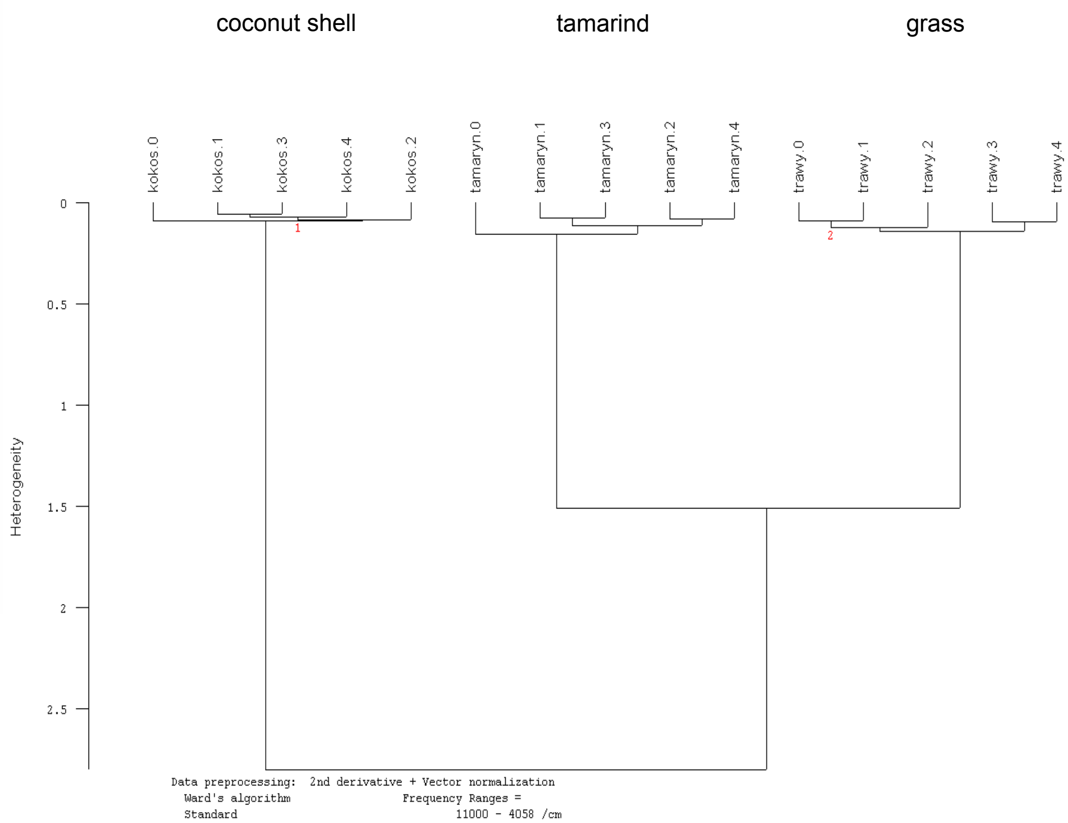
Sida hermaphrodite

Miscanthus sinensis

Salix viminalis

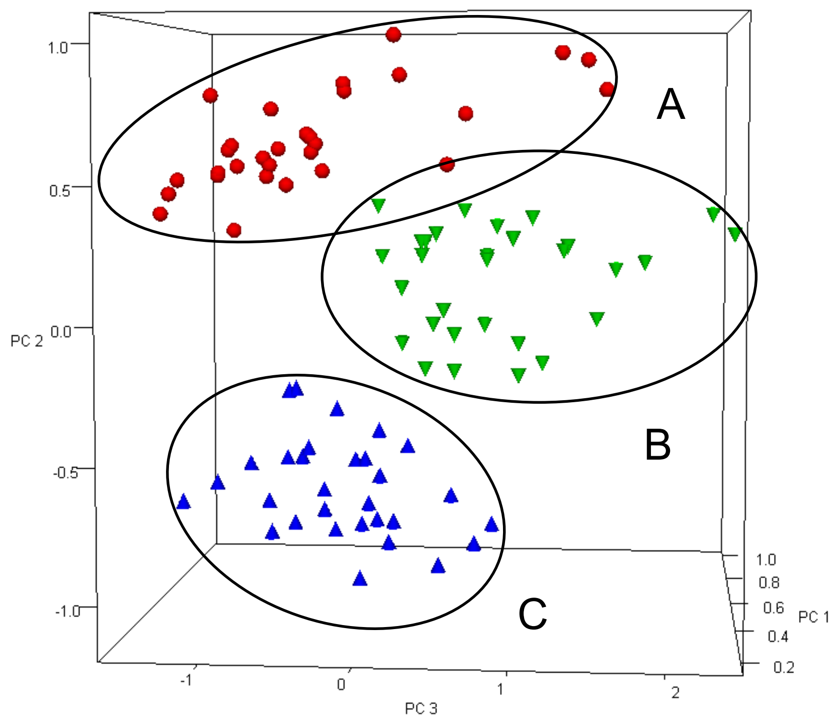
Miscanthus giganteus

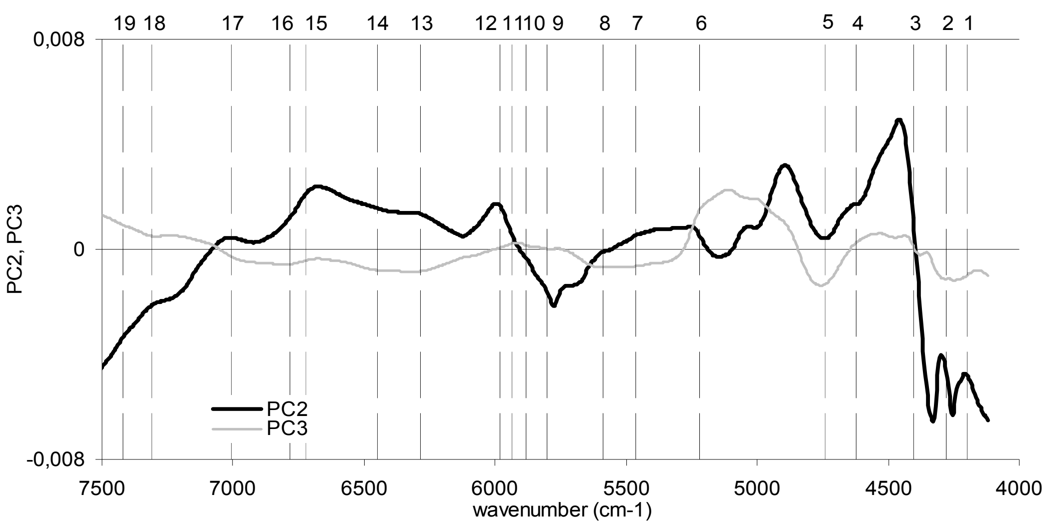
Reynoutria sachalinensis



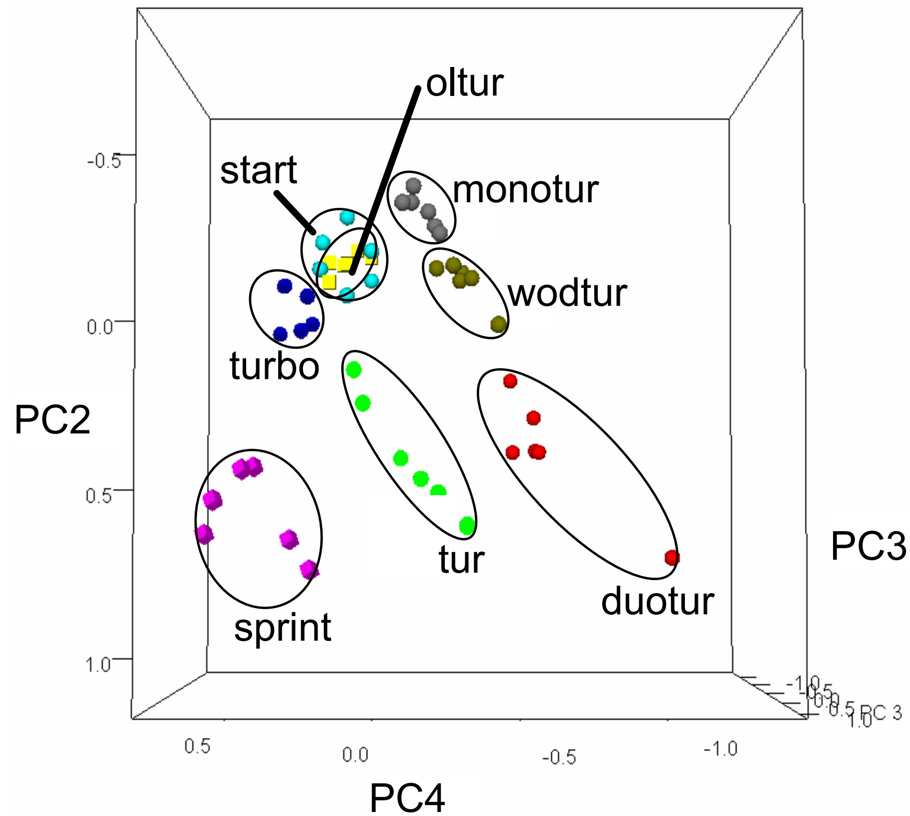
Particleboards characterization

Raw resources: Eastern redcedar (*Juniperus virginiana* L.)
Single- and three-layers panels
manufactured from raw material using 9% urea formaldehyde, combination of 15% modified corn starch and 2% urea formaldehyde adhesive



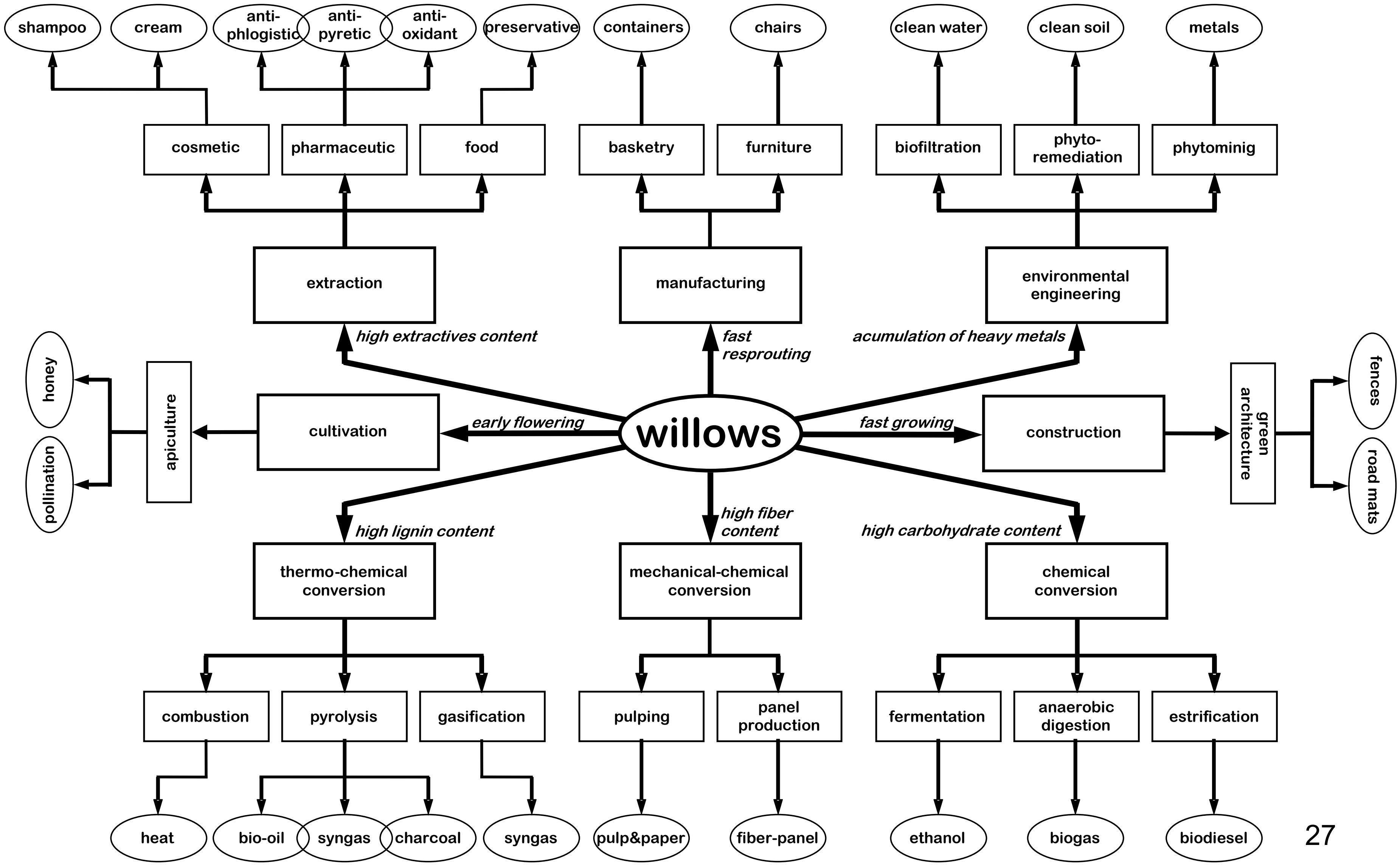


Selection of biomass
for optimal bio-conversion process

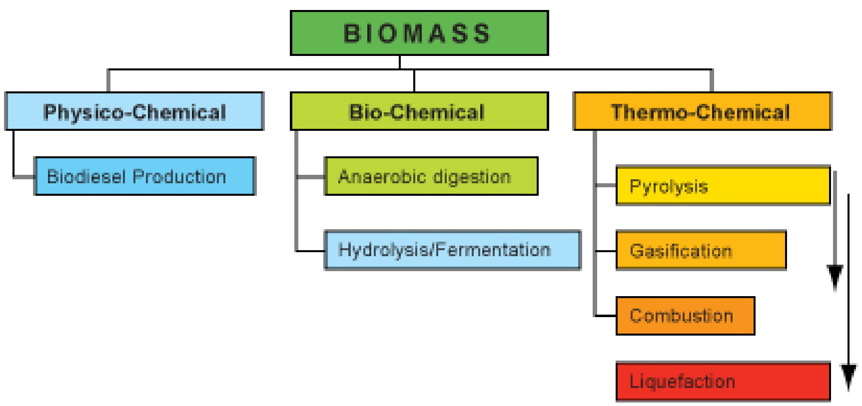


PCA of willow clones. Note: pre-processing: 2nd derivative + vector normalization, 17 smoothing points, region: 6869-5847 cm^{-1}, method: factorization, 3 factors

Willows utilization



Suggested conversion path



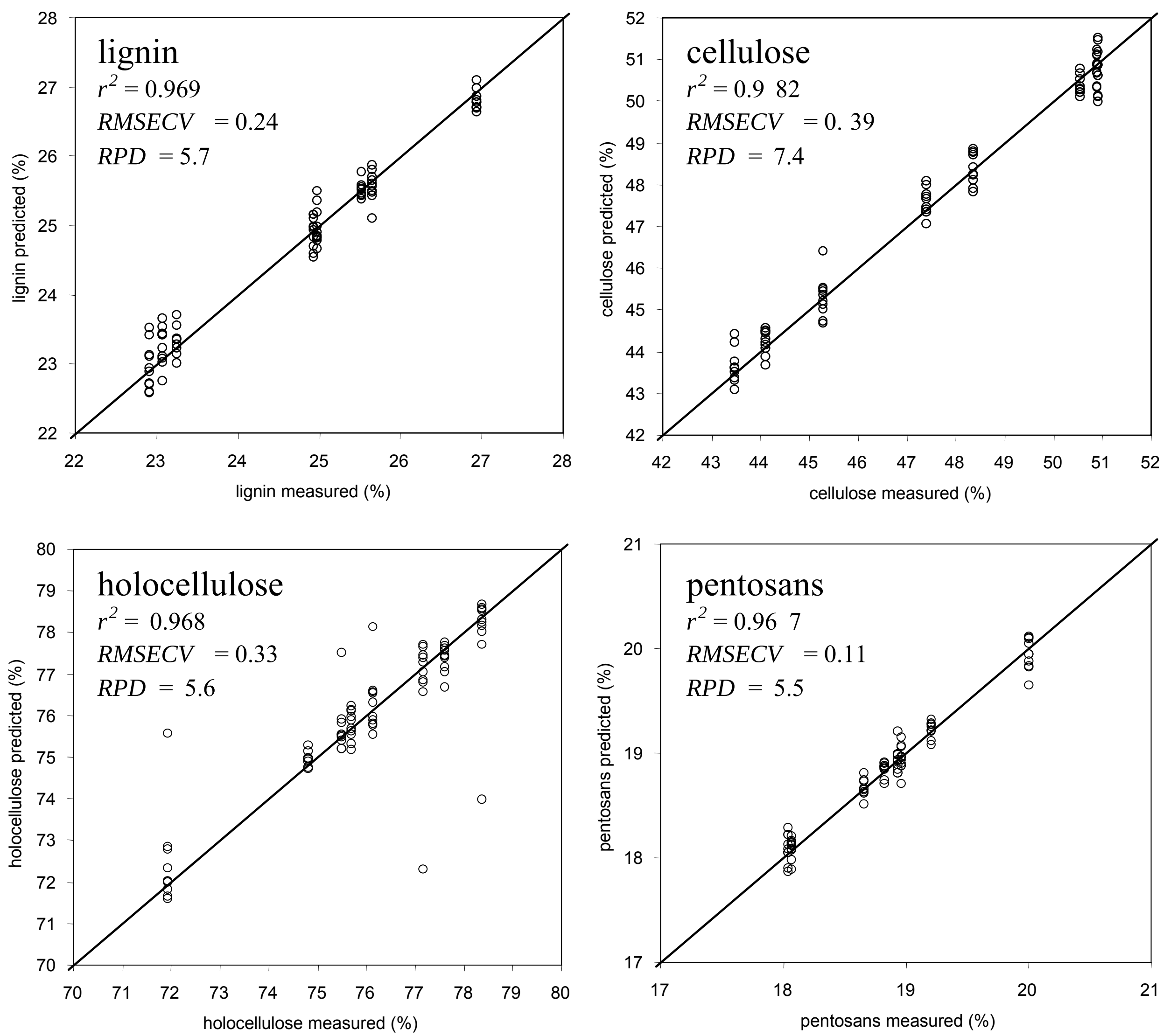
http://www.seco.cpa.state.tx.us/publications/renewenergy/biomassenergy.php

	thermo-chemical	mechano-chemical	chemical	pharmaceutical	phytoremediation		
#1	✓ 0.93	✗ 0.07	✗ 0.13	✓ 0.96	✗ 0.19	✗ -0.10	✗ 0.00
#2	✓ 0.98	✗ 0.04	✗ -0.01	✓ 0.98	✗ 0.44	✗ -0.03	✗ 0.02
#3	✓ 0.97	✗ 0.13	✗ 0.01	✓ 1.02	✗ 0.57	✓ 0.88	✓ 0.33
#4	✓ 1.05	✗ -0.07	✓ 1.04	✓ 0.99	✗ 0.61	✓ 0.99	✗ 0.20
#5	✓ 0.89	✗ 0.13	✗ 0.19	✓ 0.80	✗ 0.57	✗ -0.06	✓ 0.19
#6	✗ 0.05	✗ -0.05	✗ -0.13	✓ 1.14	✓ 0.68	✗ 0.15	✗ 0.42
#7	✗ -0.08	✓ 0.78	✗ 0.02	✗ 0.03	✗ 0.33	✗ -0.07	✗ 0.50
#8	✗ 0.09	✓ 1.10	✗ -0.07	✗ -0.11	✗ 0.06	✗ 0.00	✗ -0.03
#9	✗ -0.05	✓ 0.90	✗ -0.06	✗ 0.02	✗ 0.28	✗ 0.15	✗ 0.30
#10	✗ -0.03	✗ 0.04	✗ 0.07	✗ 0.03	✗ 0.09	✗ 0.14	✗ -0.11
#11	✗ -0.02	✗ -0.05	✓ 1.01	✗ -0.06	✓ 1.19	✓ 0.84	✗ 0.31
#12	✗ -0.04	✗ -0.07	✓ 1.05	✗ -0.04	✓ 1.32	✗ -0.15	✗ 0.22
#13	✗ -0.02	✗ -0.04	✓ 0.93	✗ 0.08	✓ 1.22	✗ 0.32	✗ 0.35
#14	✗ -0.04	✗ -0.04	✓ 0.92	✗ 0.10	✓ 1.00	✓ 0.86	✓ 0.66
#15	✓ 1.11	✓ 0.95	✓ 0.84	✗ 0.00	✓ 1.04	✗ 0.09	✗ 0.11
#16	✗ 0.16	✓ 1.12	✗ -0.02	✗ 0.06	✓ 1.31	✓ 1.12	✓ 0.60
#17	✗ 0.06	✗ 0.06	✓ 1.07	✗ 0.01	✓ 1.10	✗ -0.14	✗ -0.05
Discrimination rule	high HHV	high content of: cellulose	hemicelluose	extractives	high accumulation of: Zn	Pb	Cu
Threshold rule	HHV_{exp}>20.0	X_c>38%	X_{he}>34%	X_e>11%	X_{Zn}>55ppb	X_{Pb}>8ppb	X_{Cu}>8ppb
Average prediction error	0.06	0.08	0.07	0.06	0.29	0.11	0.29

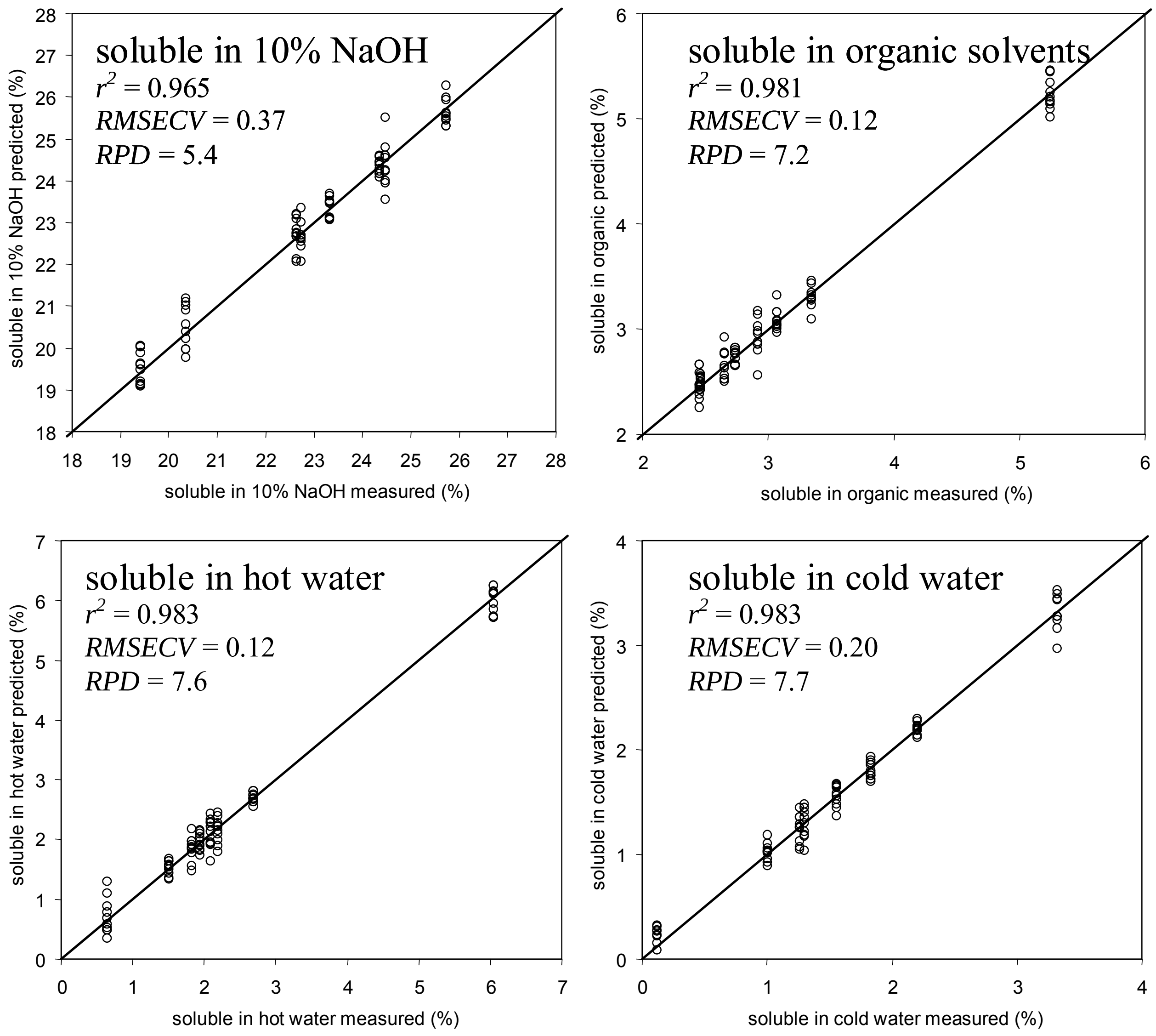
Chemical analysis

- cellulose (by Browning)
- holocellulose (by Browning)
- lignin (T 222 om-06 TAPPI)
- pentosans (T 223 cm-01 TAPPI)
- hot water extractives (T 207 cm-08 TAPPI)
- cold water extractives (T 207 cm-08 TAPPI)
- 1% NaOH extractives (T 212 om-07 TAPPI)
- organic solvent extractives (T 204 cm-07 TAPPI)

NIR PLS calibration models #1
of willows chemical composition (pilot study)



NIR PLS calibration models #2
of willows chemical composition (pilot study)



Wood modifications & NIRS

- Thermal treatment
- Decay
- ISPM-15
- Densification
- Mechanical testing
- Wood after wood machining
- Coatings
- Weathering
- Service life prediction
- …

Wood thermal treatment

Termovuoto: open system:
(volatile products of the process are continuously removed from the kiln by means of a vacuum pump)

The treatment time: **3 hours**
Pressure: **0.2 bar**
treatment temperatures of **160, 180, 200 and 220ºC**.

	fir		spruce		larch	
parameter	ML	EMC	ML	EMC	ML	EMC
range (cm^{-1})	7502-6098 5450-4246	6102-4246	10996-10098 9303-8501 5018-4435	8505-4435	9403-5446	9403-7498 6102-5446
pre-processing	1der +MSC	1 der + VN	VN	1 der + VN	1 der + VN	1 der +MSC
r^2	98.67	97.58	98.48	98.83	97.88	97.69
RMSECV	0.26	0.25	0.25	0.17	0.39	0.19
RPD	8.66	6.42	8.11	9.42	6.87	6.58
rank	3	3	3	4	4	5

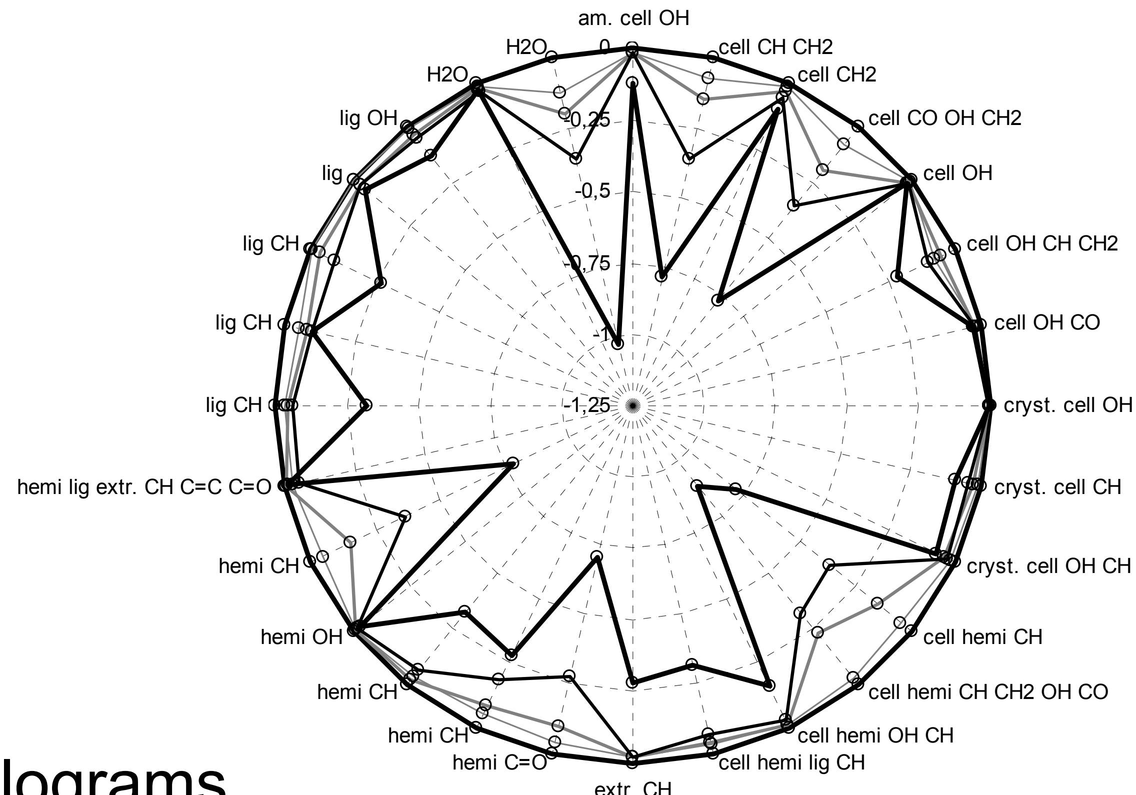
+ 5 hardwoods…

195 samples measured x 5 spectra/sample = **975 spectra**

New spectra presentation

Wild cherry
(*Prunus avium*)

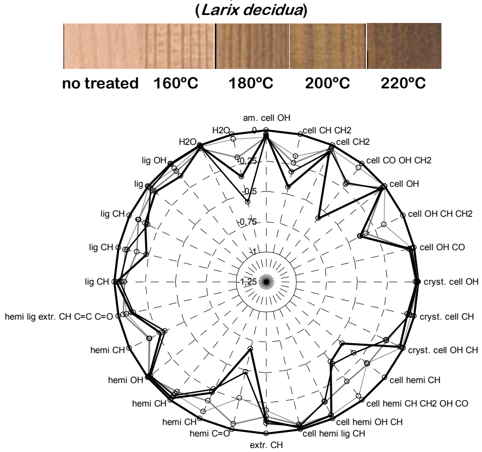
no treated 160°C 180°C 200°C 220°C



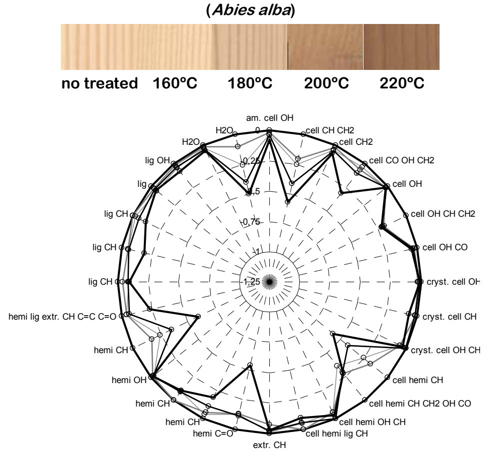
xylograms

Xylograms; different species

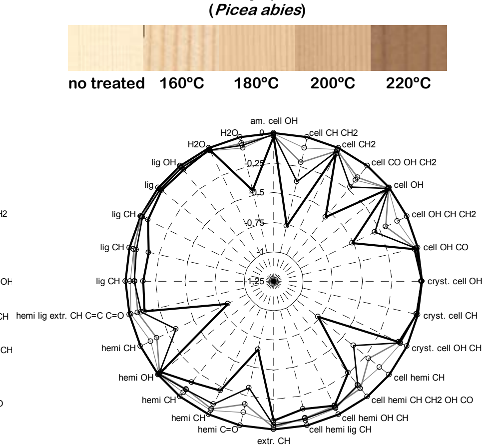
European larch
(*Larix decidua*)



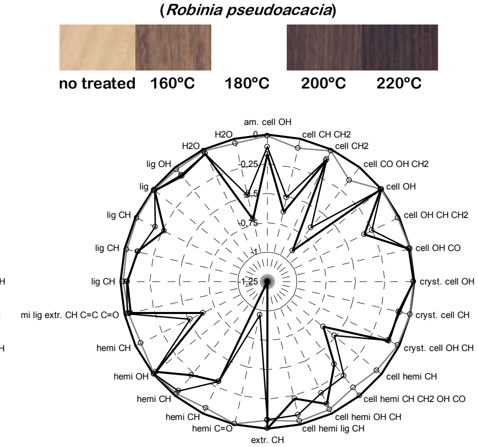
Silver fir
(*Abies alba*)



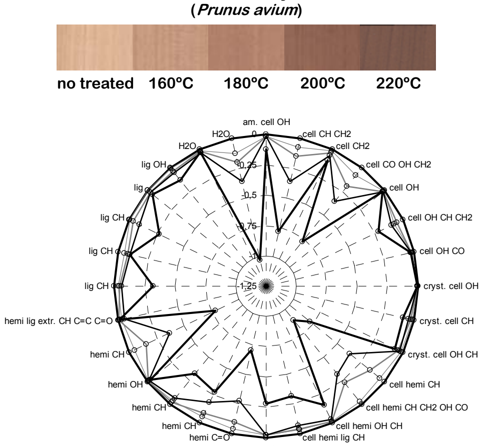
Norway spruce
(*Picea abies*)



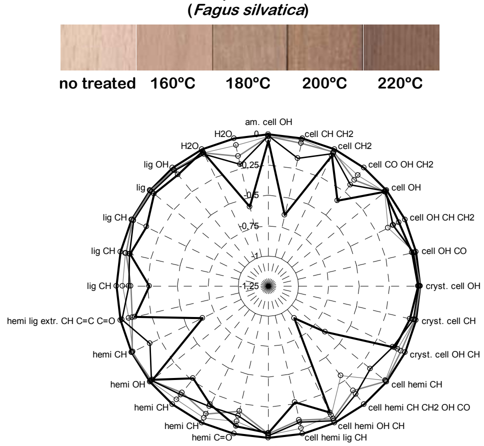
Black locust
(*Robinia pseudoacacia*)



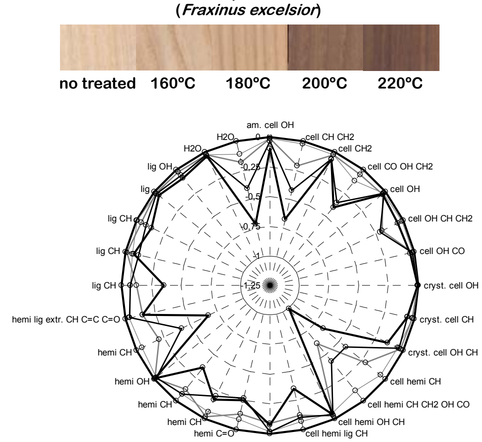
Wild cherry
(*Prunus avium*)



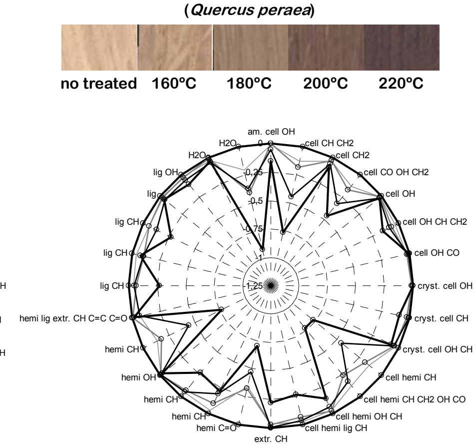
European beech
(*Fagus silvatica*)



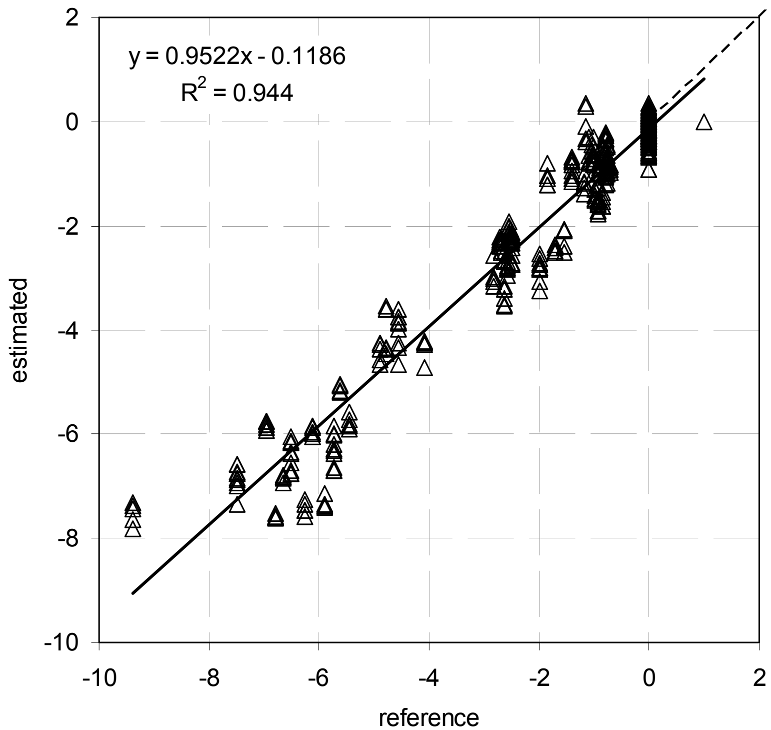
European ash
(*Fraxinus excelsior*)



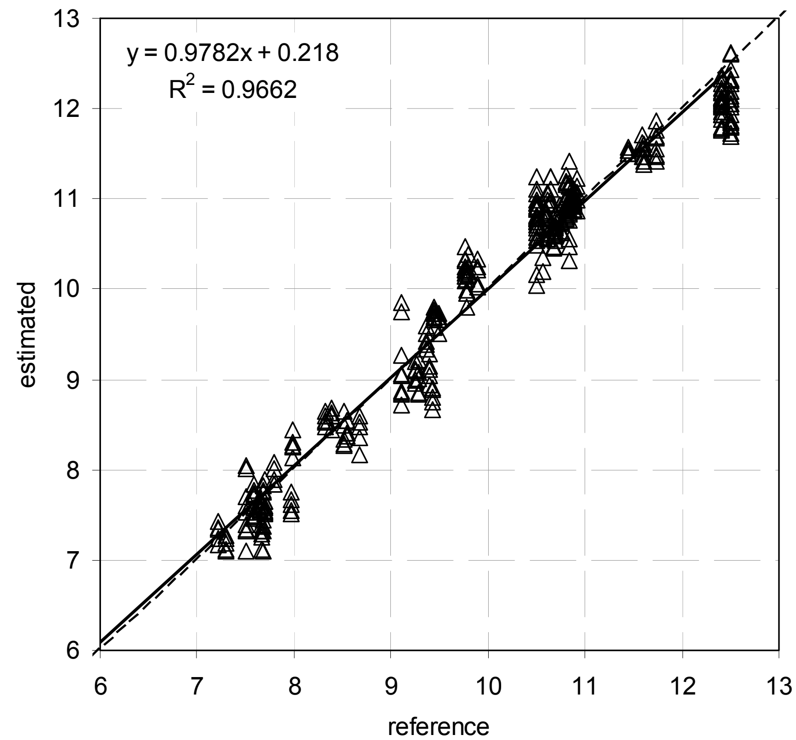
Sessile oak
(*Quercus peraea*)



PLS models for TM softwoods

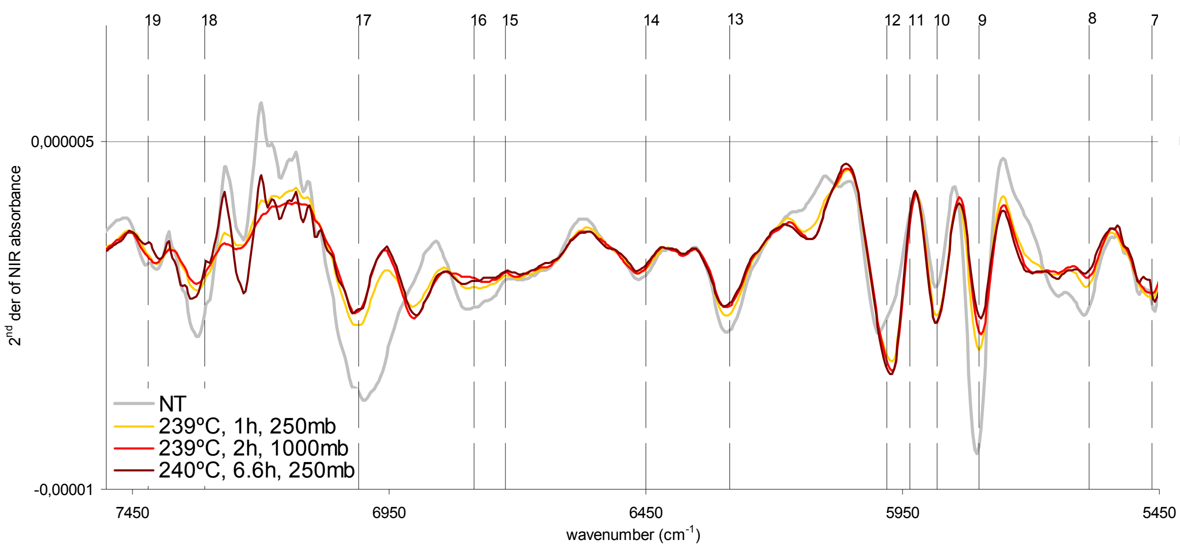


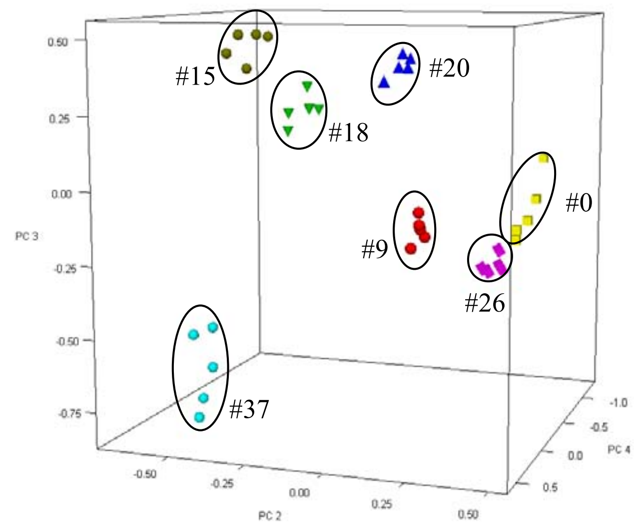
Mass loss



Equilibrium Moisture Content

TM of poplar veneers





#0	NT
#26	155ºC, 1h, 250mb
#9	174ºC, 22h, 250mb
#20	210ºC, 1h, 250mb
#18	239ºC, 1h, 250mb
#15	239ºC, 2h, 1000mb
#37	240ºC, 6.6h, 250mb

Wood sterilization

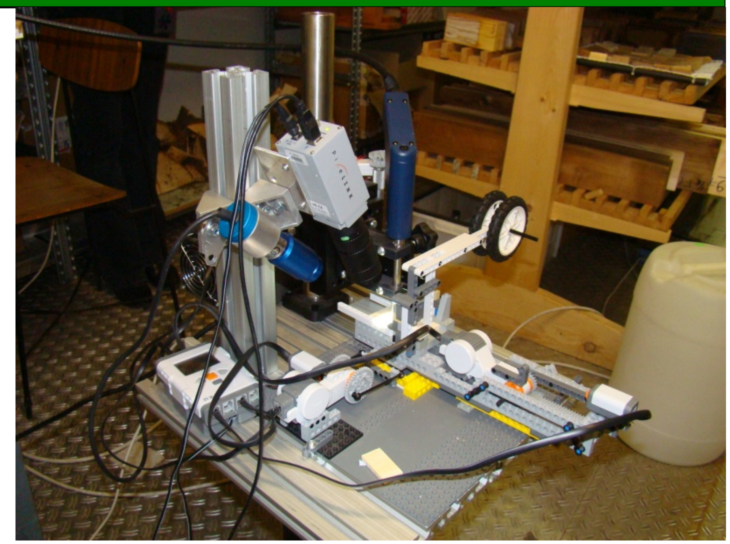
How to detect if the wood was appropriately thermally treated?

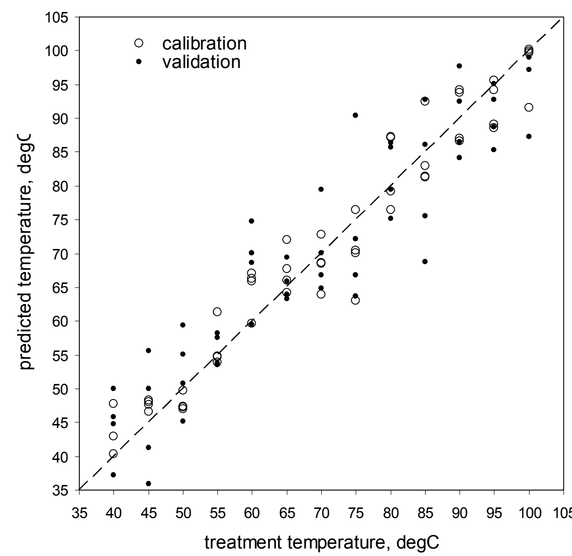
- standard **ISPM Nº15;**
  - Temperature: 56°C in the core of wood
  - Treatment time: 30minutes

ISPM-15

Low temperature thermal treatment of wood

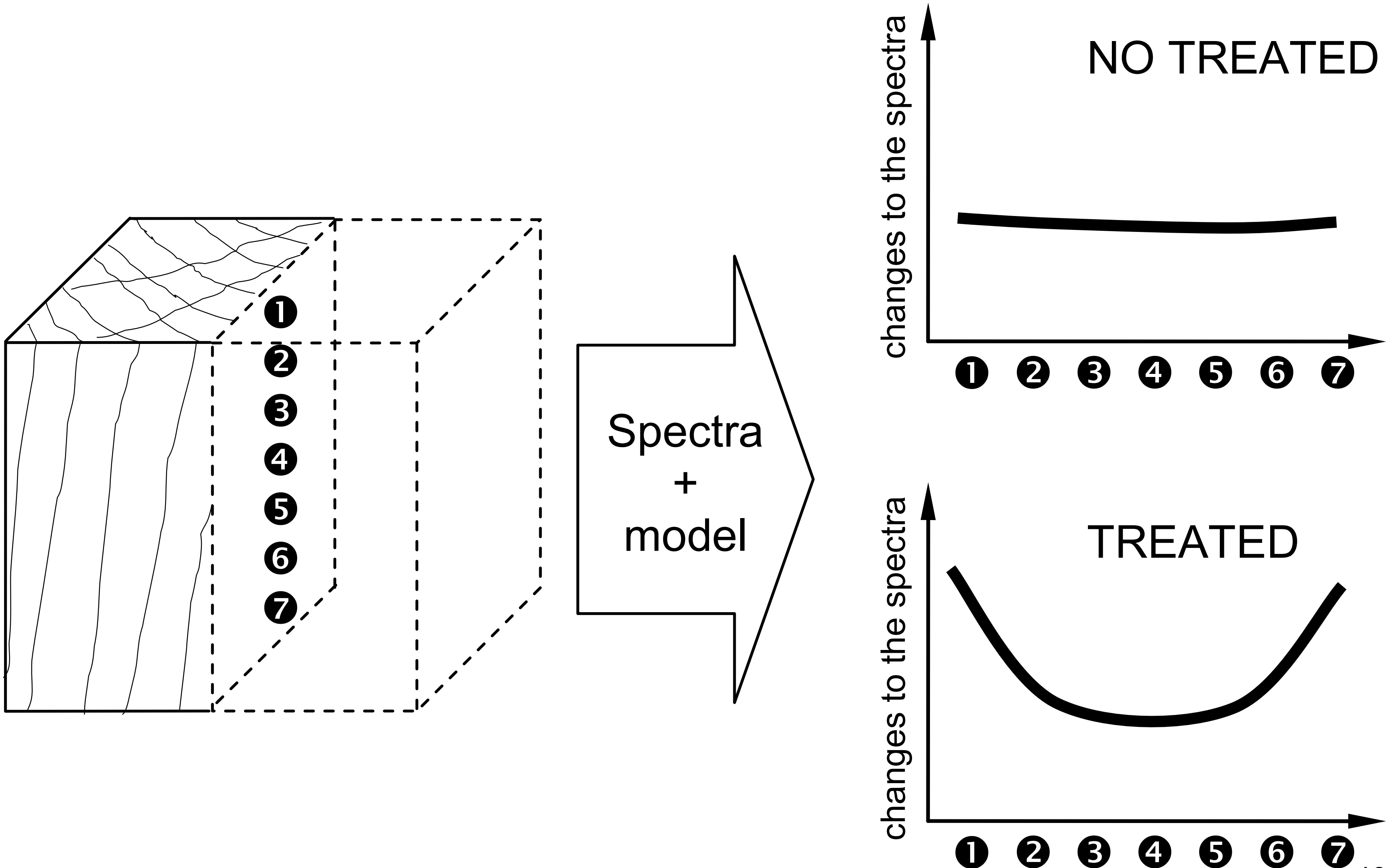
- to investigate an effect of the temperature on wood samples of different wood species:
    - Spruce (softwood with resin)
    - Fir (softwood without resin)
    - Poplar (hardwood)
- different treatment times:
    - 0.5 hours (30 minutes)
    - 1 hour
    - 3 hours
    - 6 hours
- different treatment temperatures:
    - 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100°C
- three samples for repetition/statistics
- five-times spectra measurements for analysis of weathering effect:
    - Conditioned after treatment
    - Measured after 1month
    - Measured after 3 months
    - Measured after 6 mounts
    - Measured after 12 mounts



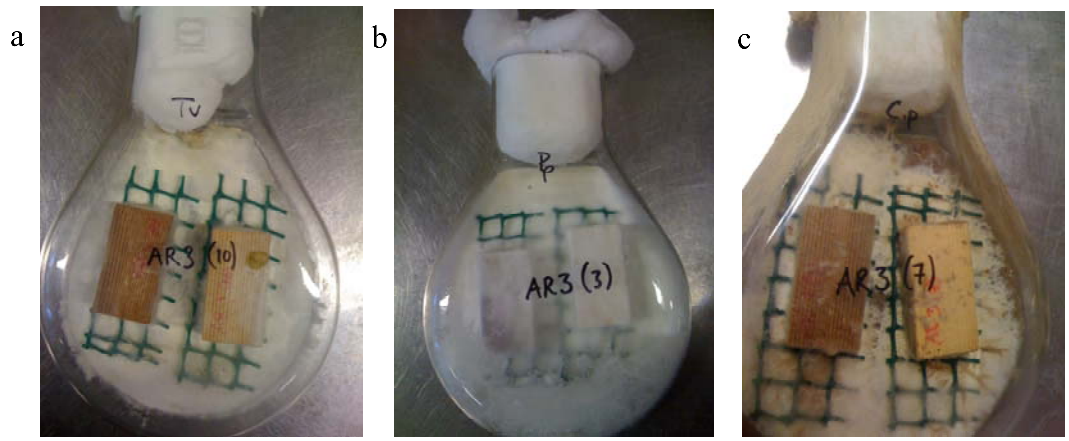


468 samples measured x 5 spectra/sample x 5 repetition/sample = **9360 spectra**

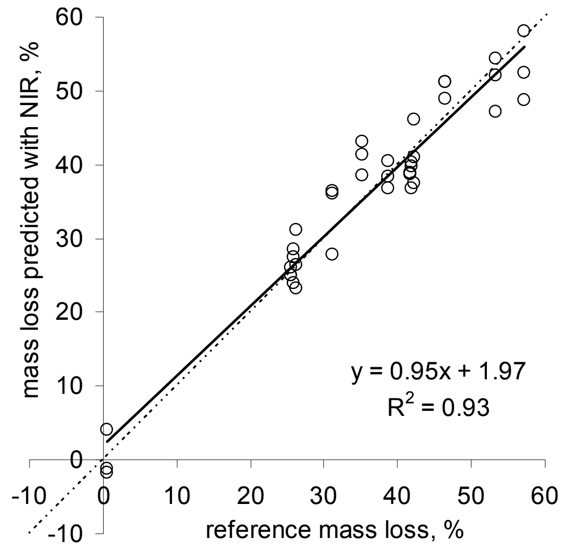
NIR-based method for verification of the ISPM-15 treatment*

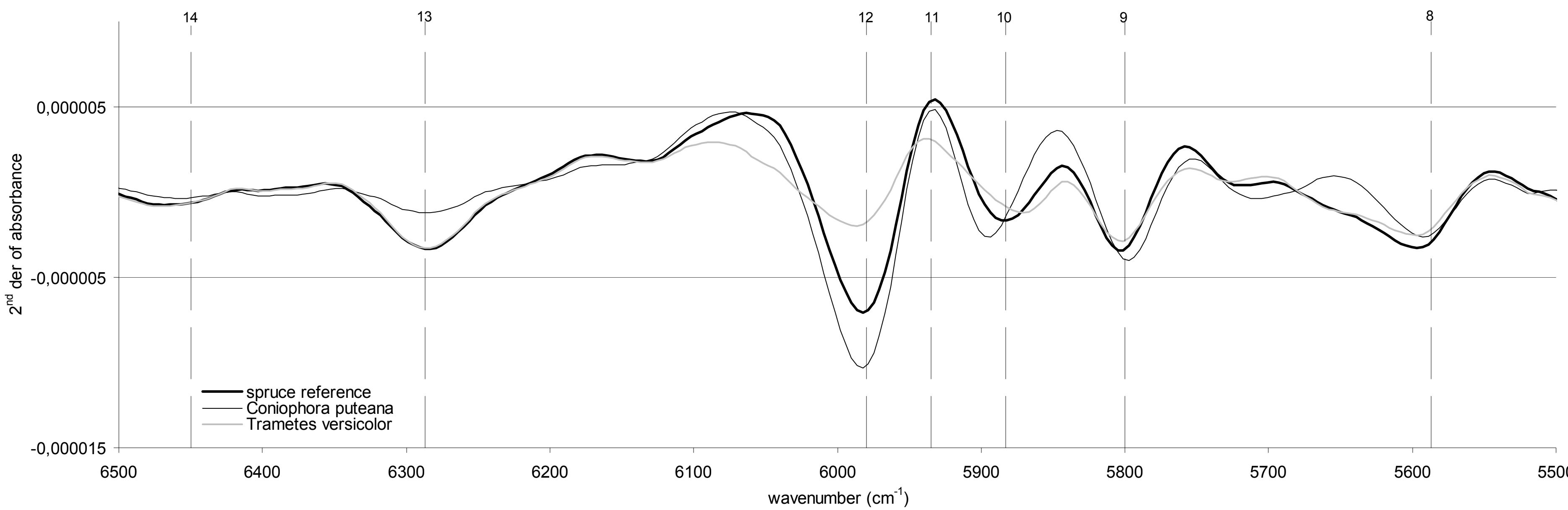


Wood decay

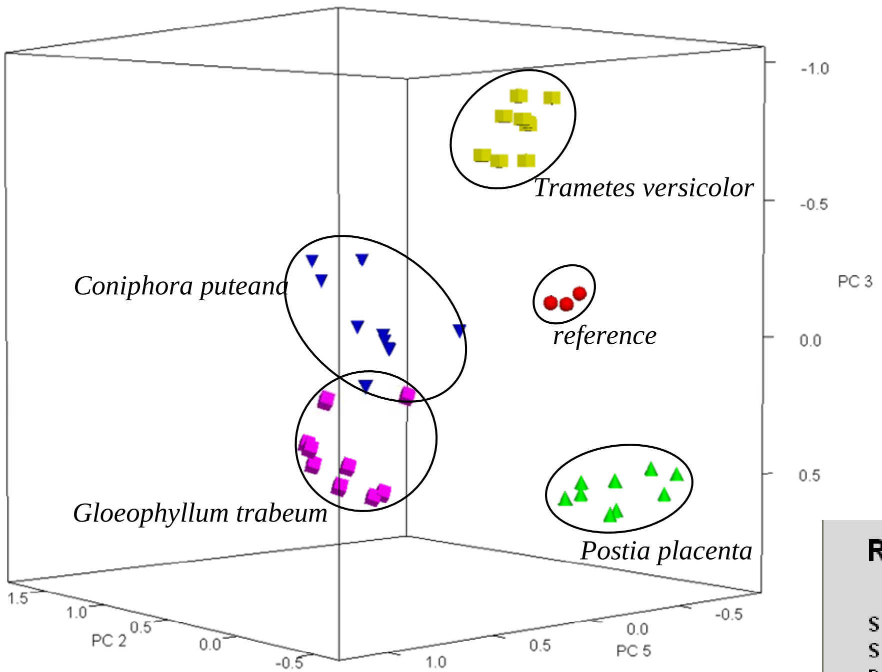


Trametes versicolor *Postia placenta* *Coniophora puteana*





Decay type identification



Result of IDENT evaluation:

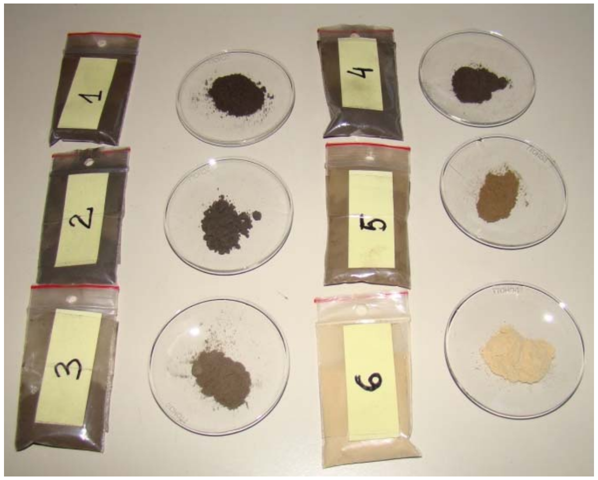
Sample name: wood | Av. of 3
Sample: D:\TENNO\Av.right degraded inside.0
Date and time (measurement): 2011/06/06 12:21:35 (GMT+2)
Method file: D:\Nasco wood\analysis\all fungi general classification.faa

Hit no.	Sample name	Hit qual.	Threshold	Group
1	prova1	0.21635	0.02779	reference
2	prova1	0.51081	0.95521	brown rot
3	prova1	0.90321	0.14314	white rot

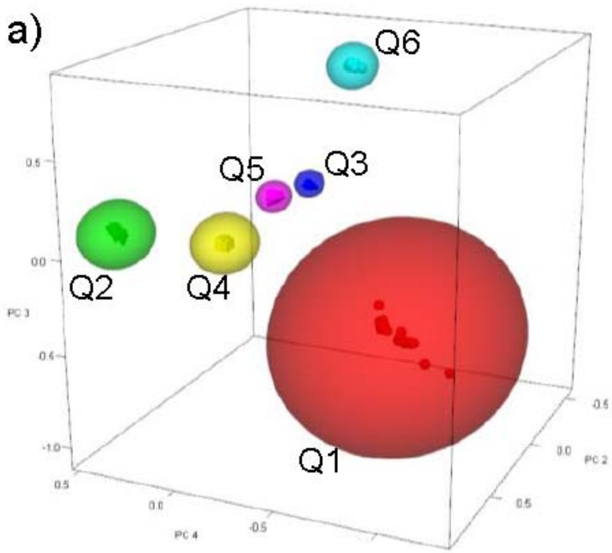
IDENTIFIED AS brown rot

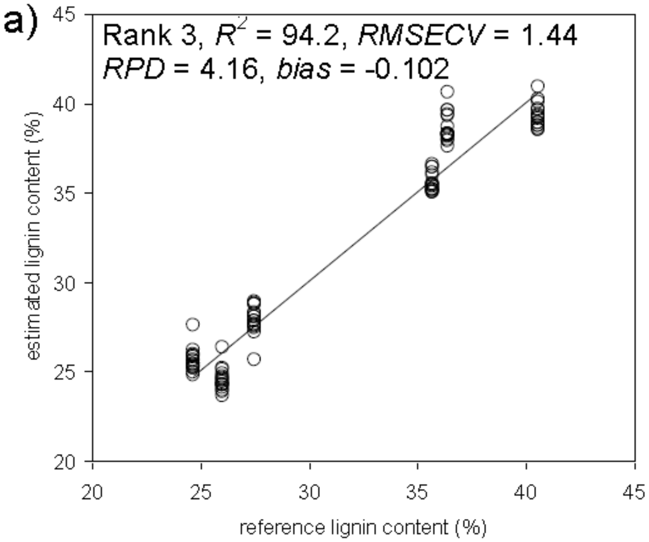
✓ **OK**

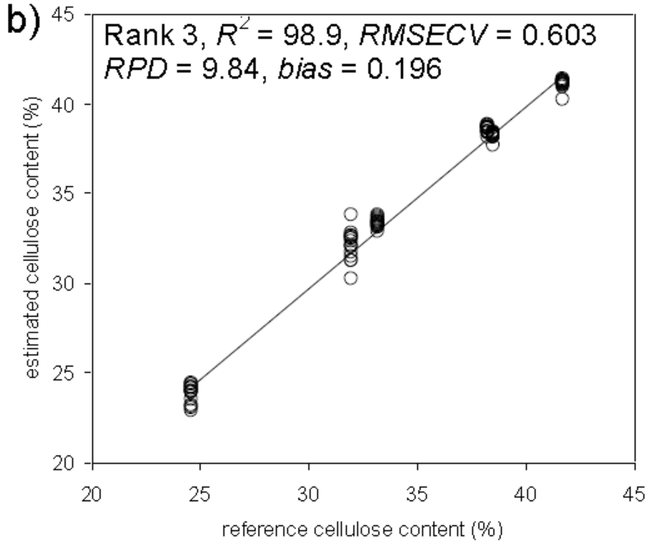
Archaeological wood



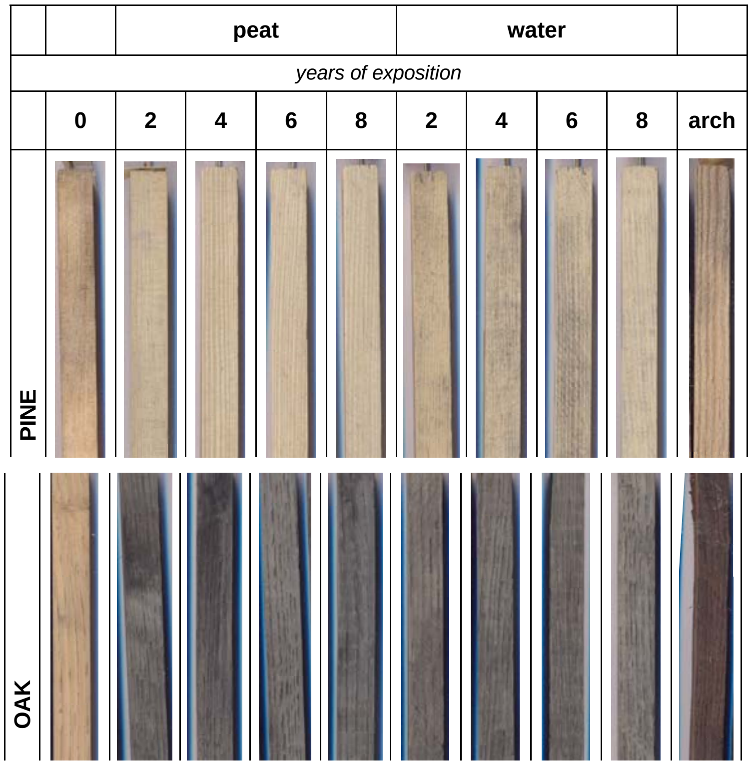
700-2700 years old







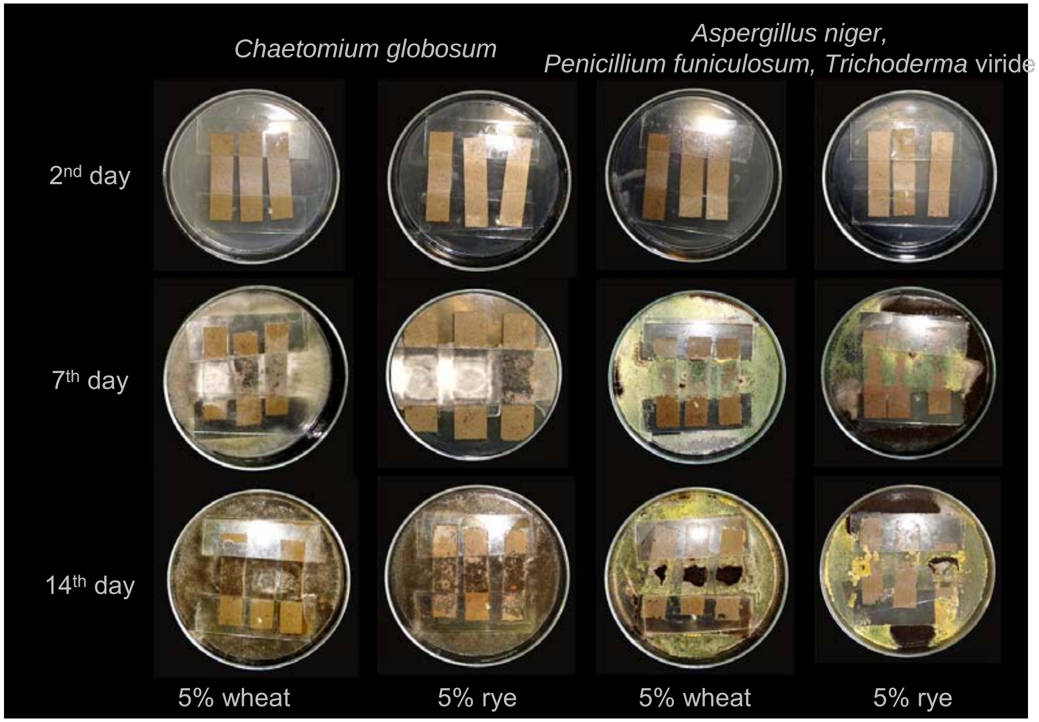
Short term waterlogging



360 samples measured x 3 spectra/sample = **1080 spectra**

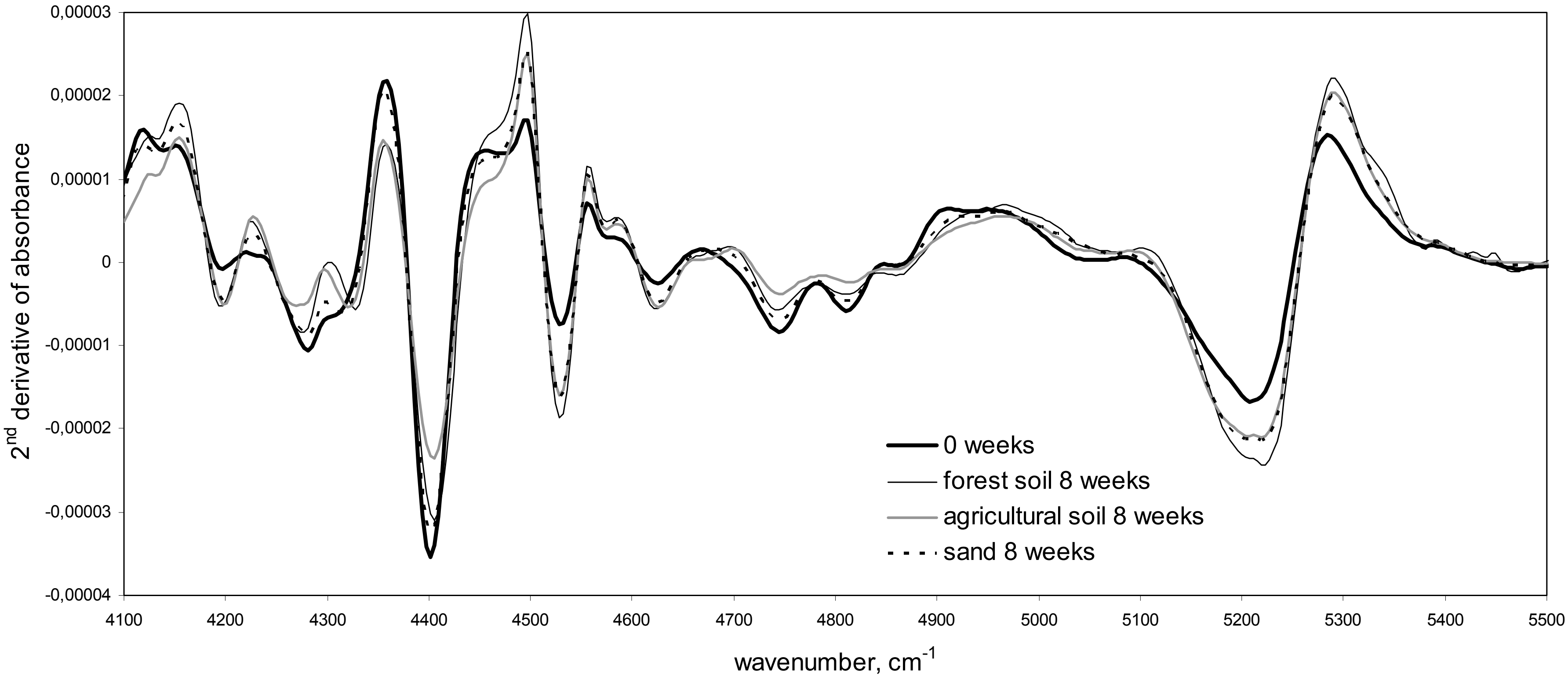
nr	band assessment: wave number (cm^{-1})	wood component	functional group	pine: peat	pine: water	oak: peat	oak: water
1	4195	lignin	not assigned	○	○	×	◦
2	4268	cellulose	CH, CH_2	○	○	○	○
3	4401	cellulose, hemicelluloses	CH, CH_2, OH, CO	○	○	◯	○
4	4546	lignin	CH, C=O	×	×	◦	•
5	4608	cellulose, hemicelluloses	not assigned	×	×	◦	×
6	4686	hemicelluloses, lignin, extractives	CH, C=C, C=O	×	×	●	●
7	4739	cellulose	OH	○	○	○	○
8	4808	cellulose semi-crystalline and crystalline	OH, CH	○	◯	○	○
9	5051	water	OH	×	×	○	○
10	5198	water	OH center of the range	○	○	○	○
11	5245	hemicelluloses	C=O	◯	◯	◯	◯
12	5495	cellulose	OH, CO	×	×	◦	◦
13	5593	cellulose semi-crystalline and crystalline	CH	◦	○	×	◦
14	5666	not assigned	CH, CH_2	●	●	◦	○
15	5692	not assigned	CH_2	●	●	×	×
16	5800	hemicelluloses (furanose / pyranose)	CH	○	○	◯	◯
17	5865	hemicelluloses	CH	○	○	◦	○
18	5935	lignin	CH	◦	○	○	◦
19	5980	lignin	CH	◯	◯	○	○
20	6126	cellulose	OH	◦	○	×	×
21	6286	cellulose crystalline	OH	◦	◦	◦	◦
22	6334	cellulose	OH	×	×	×	×
23	6472	cellulose crystalline	OH	◦	◦	×	×
24	6715	cellulose semi-crystalline	OH	◦	◦	◦	◦
25	7003	amorphous cellulose, water	OH	◦	◦	◦	◦
26	7092	lignin, extractives	OH	◯	◯	◯	○

Paper & NIR



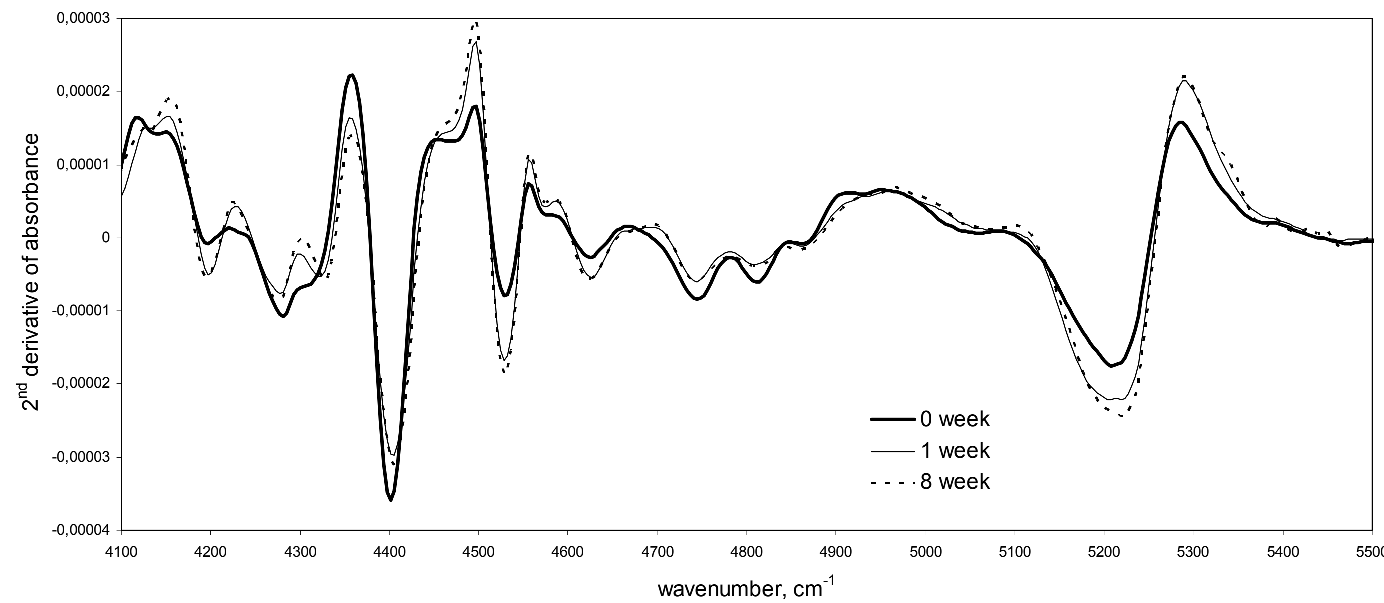
3240 samples measured
x 3 spectra/sample =
9720 spectra

Effect of soil type



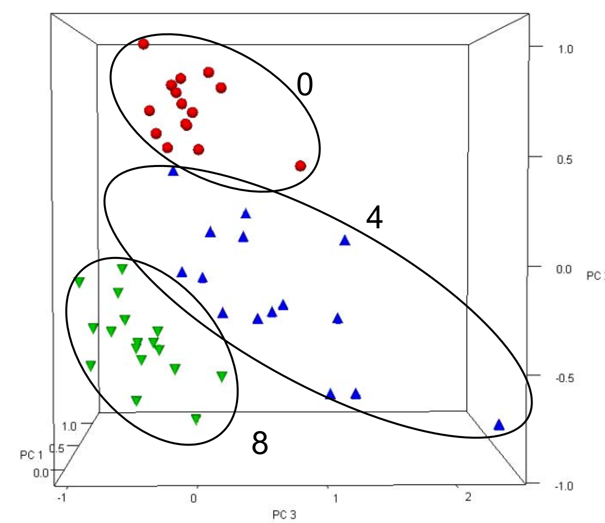
biodegradation of the recycled paper with addition of 5% wheat bran

Effect of time



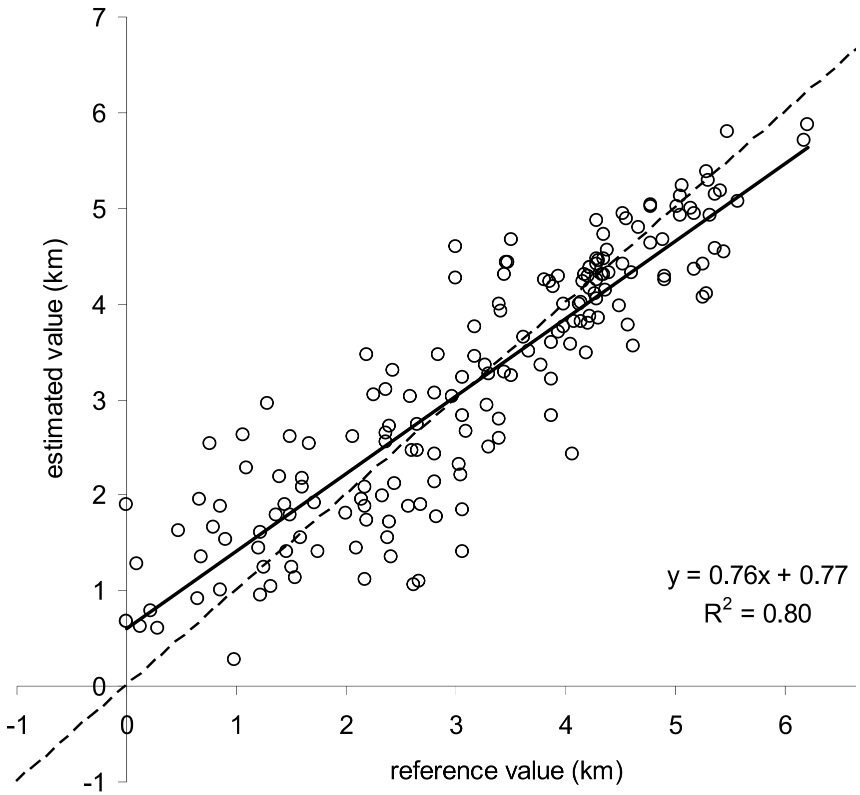
biodegradation of the recycled paper with addition of 5% wheat bran in the forest soil

PCA analysis of NIR spectra of paper before degradation tests and decomposed in forest soil for 4 and 8 weeks.
Note: spectral range: 11000-4150cm^{-1}, pre-processing: 2nd derivative + VN

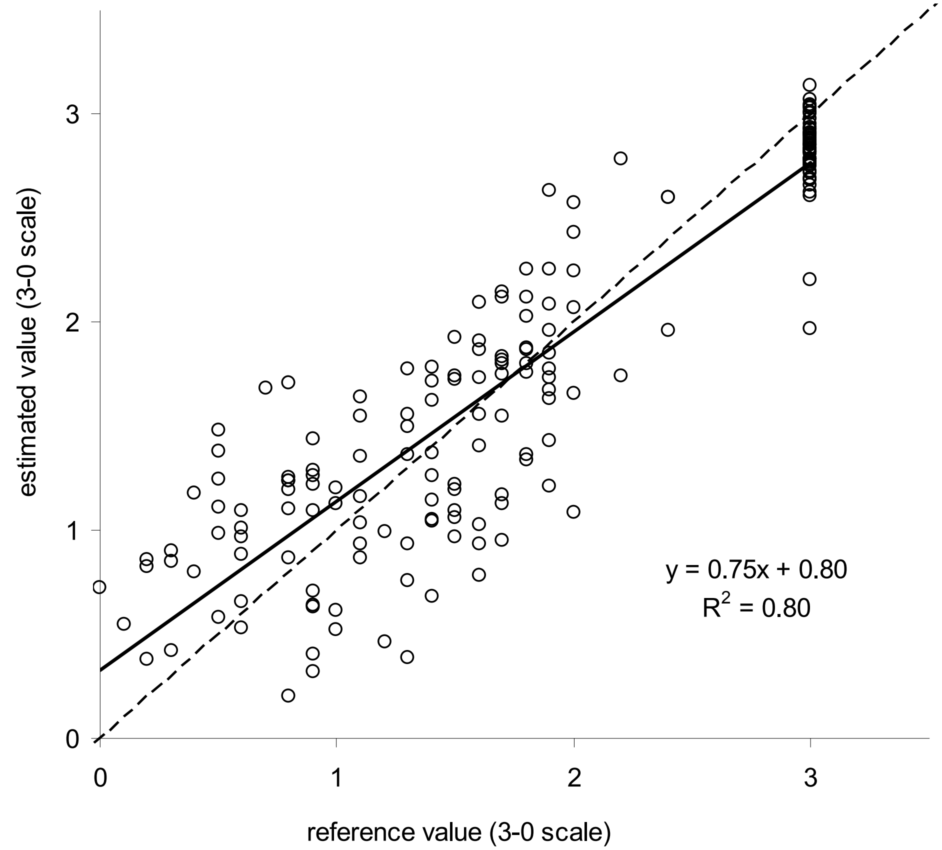


PLS models for paper samples

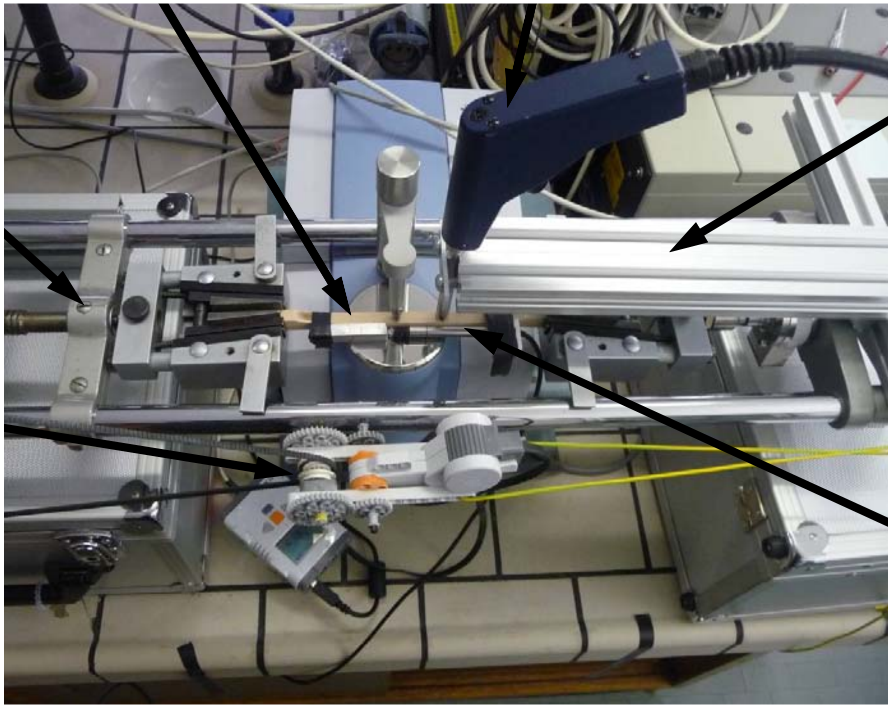
breaking length

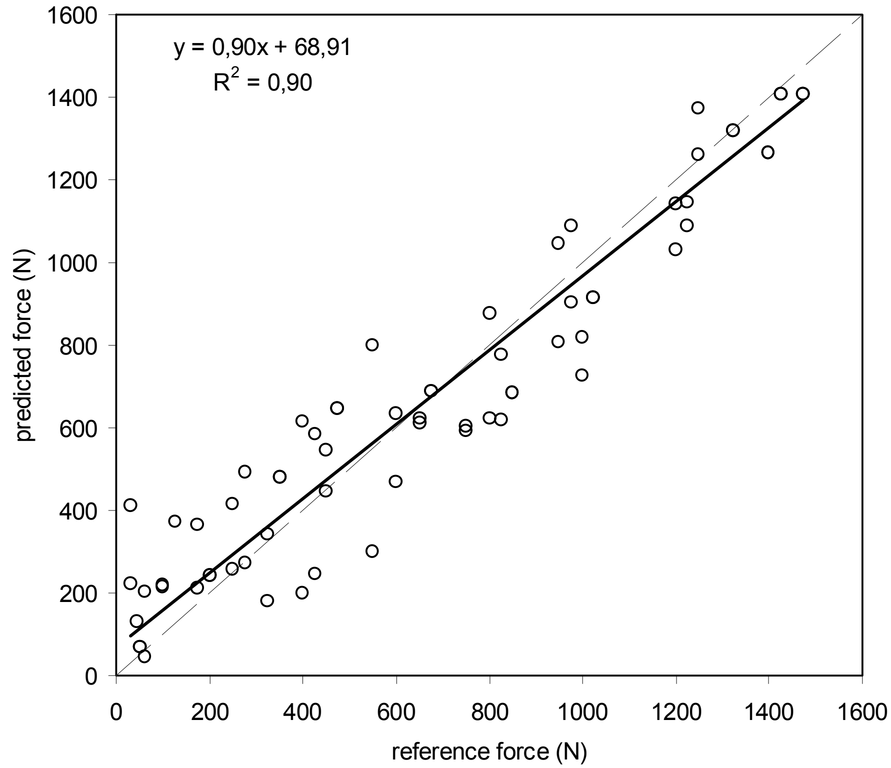


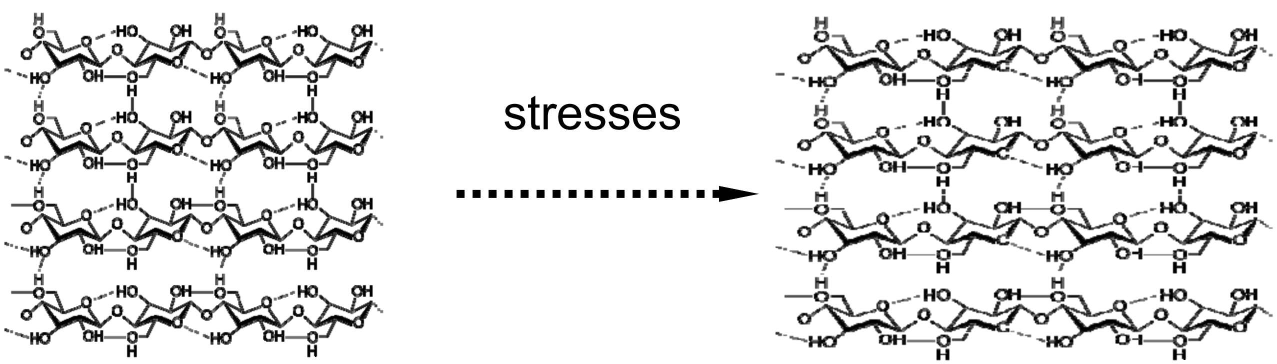
growth degree



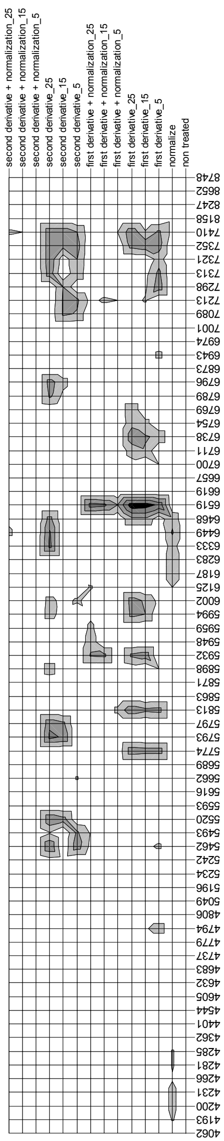
Estimation of mechanical stress



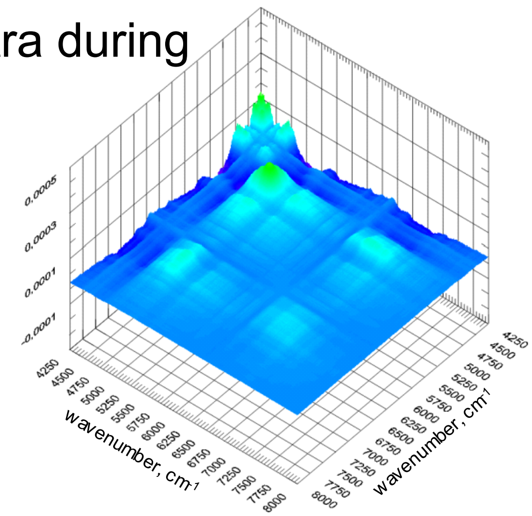


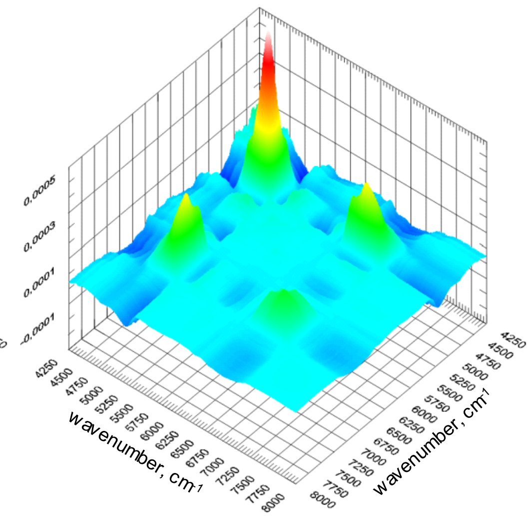


why does it work?



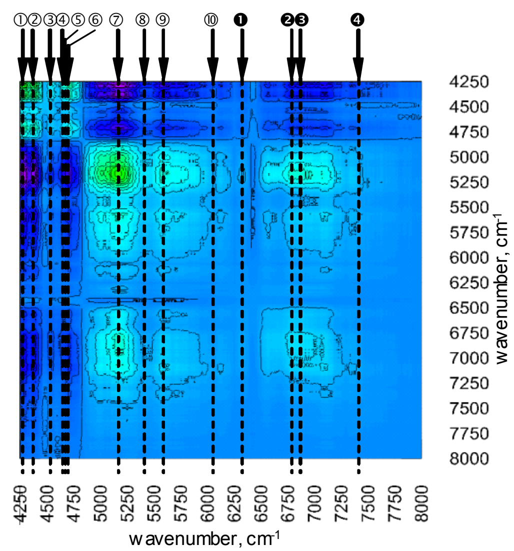
2D synchronous spectra during wood tension

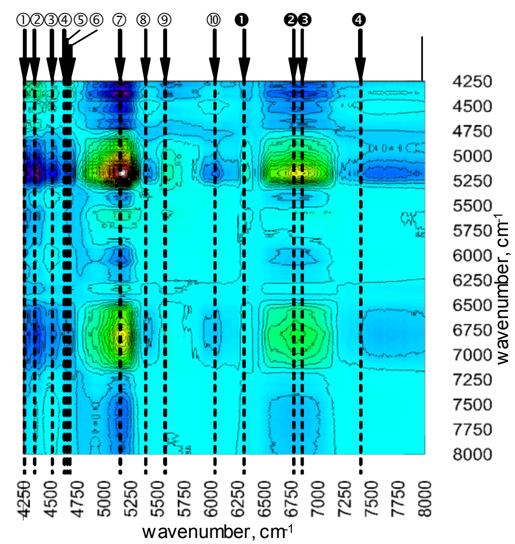




in the elastic field

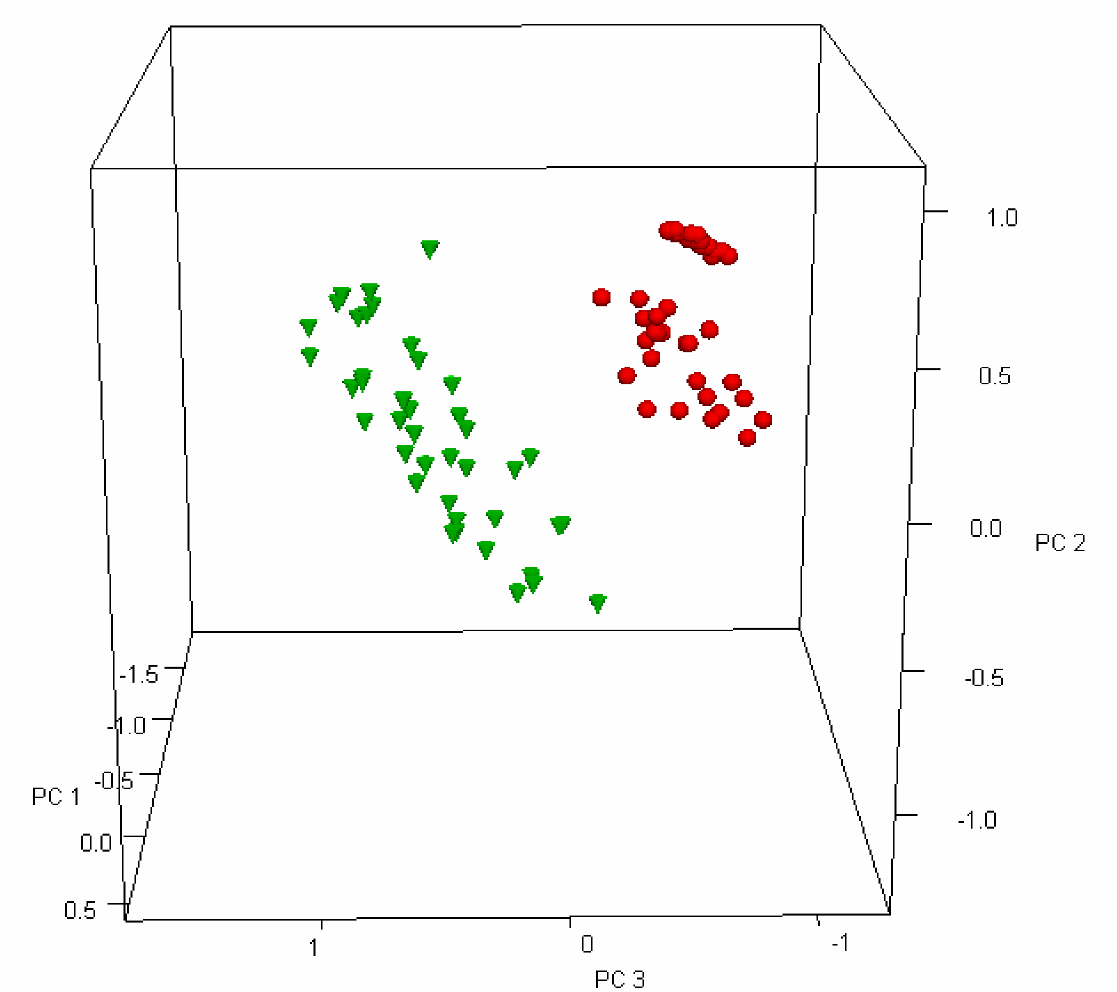
in the plastic field





Determination coefficients (r^2) between NIR spectra amplitude and tension stresses in a relation to the spectra preprocessing method

Identity test – coating recognition



Water solvent based products: #13, #26, #41

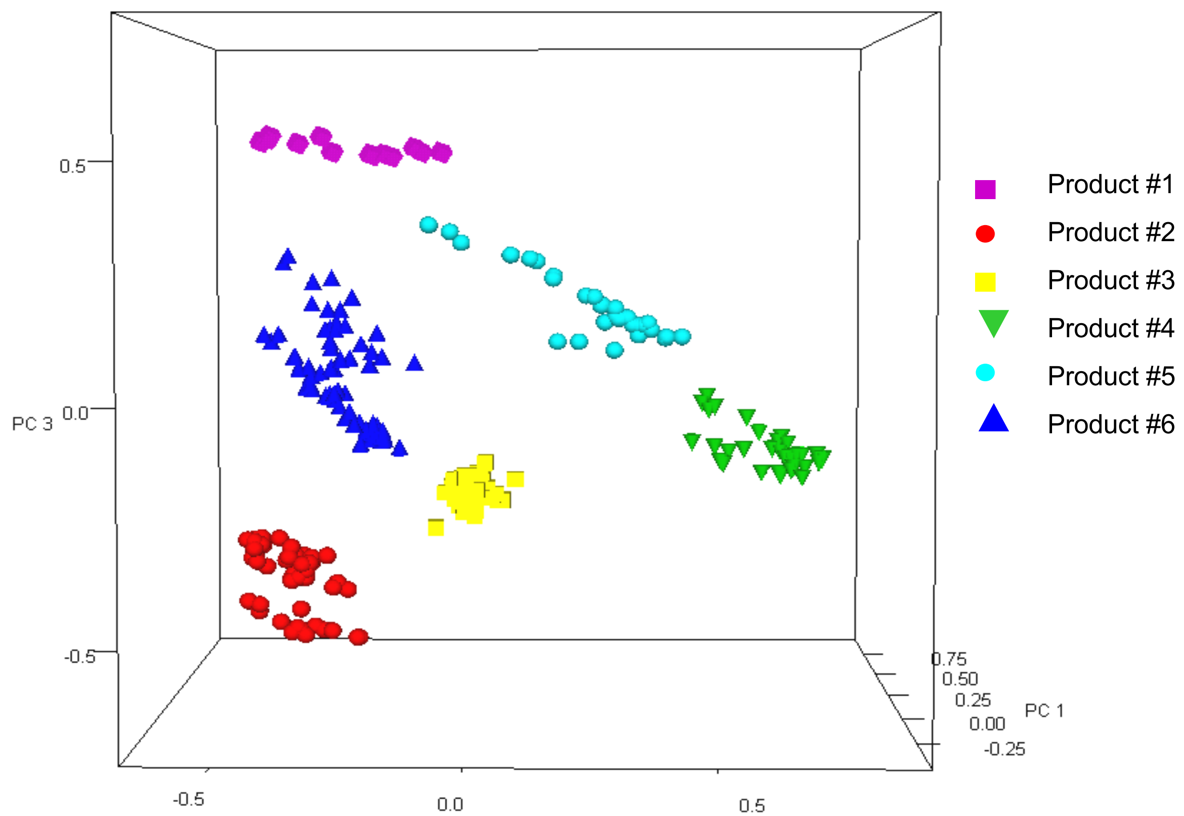
Organic solvent based products: #11, #12, #42

Preprocessing: 2 derivative + vector normalization, 9 smoothing points

Method: factorization

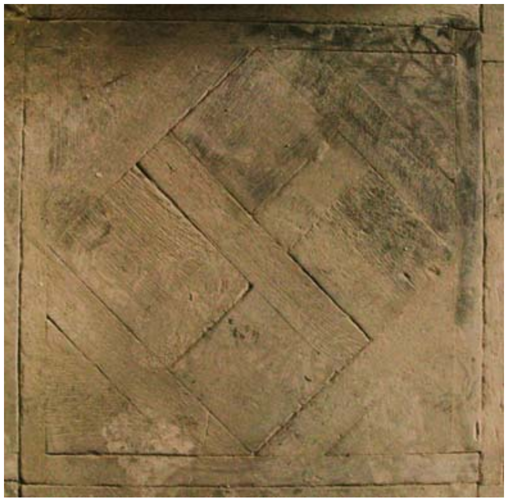
Regions (cm^{-1}): 4135-4350, 5365-5520, 5800-6000, 6290-6480, 7000-7200

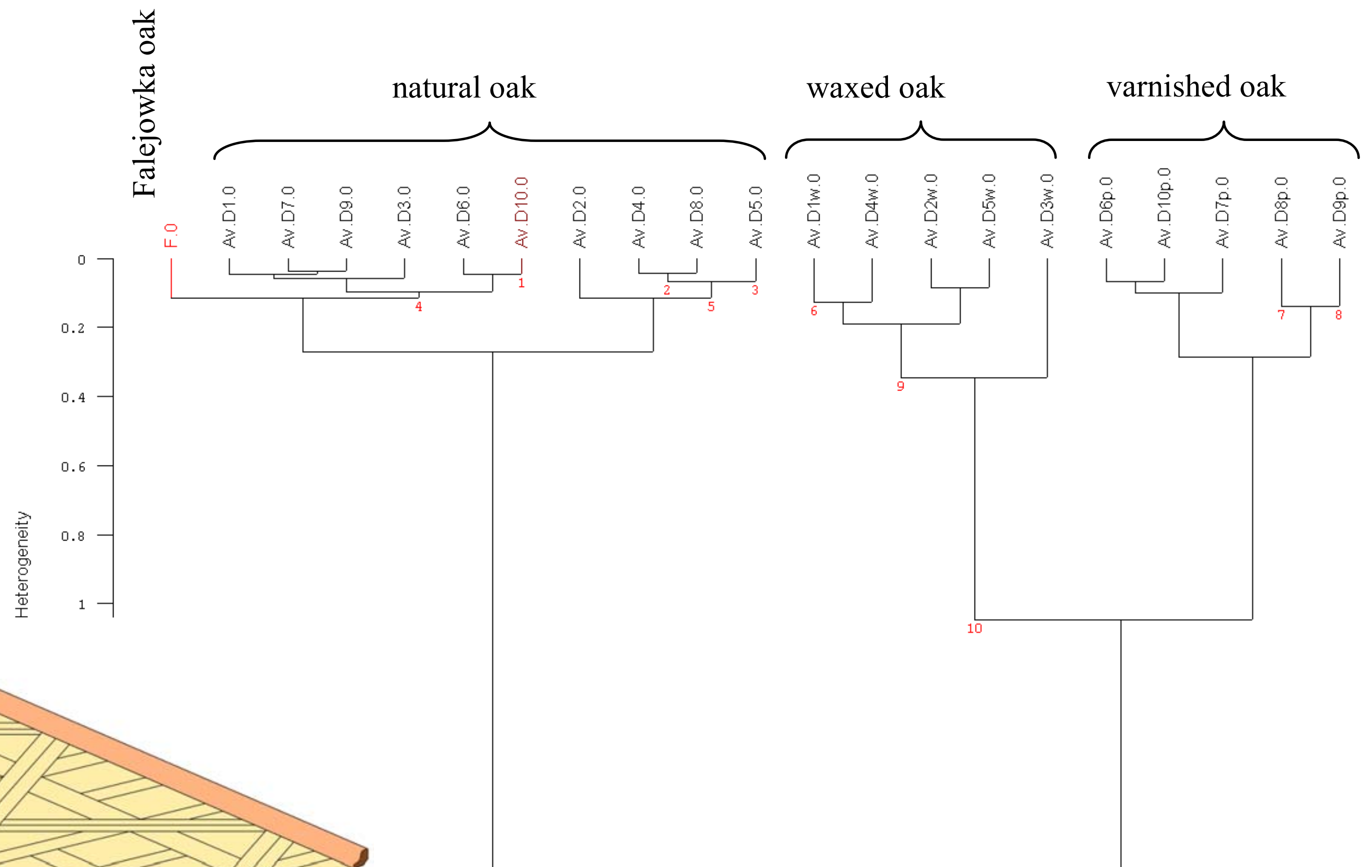
Identification of coatings

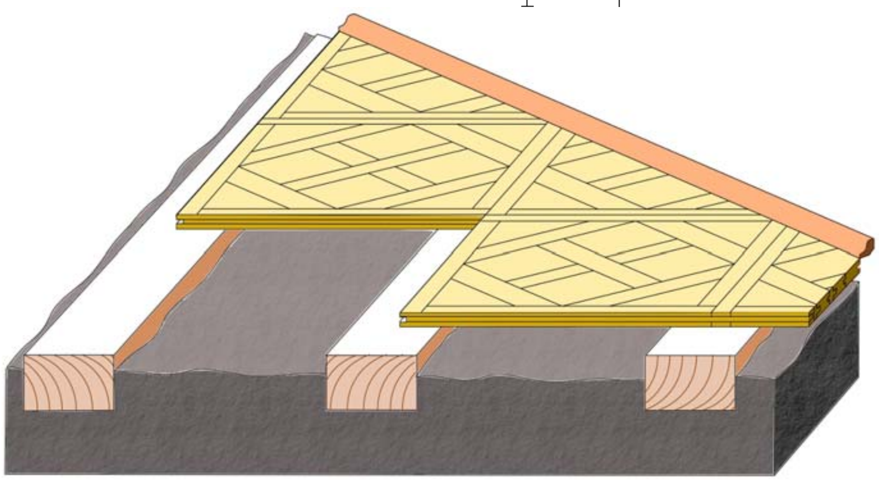


band: 4200-10000cm^{-1}, 2 derivative, 5 smoothing points, vector normalization, 2 factors

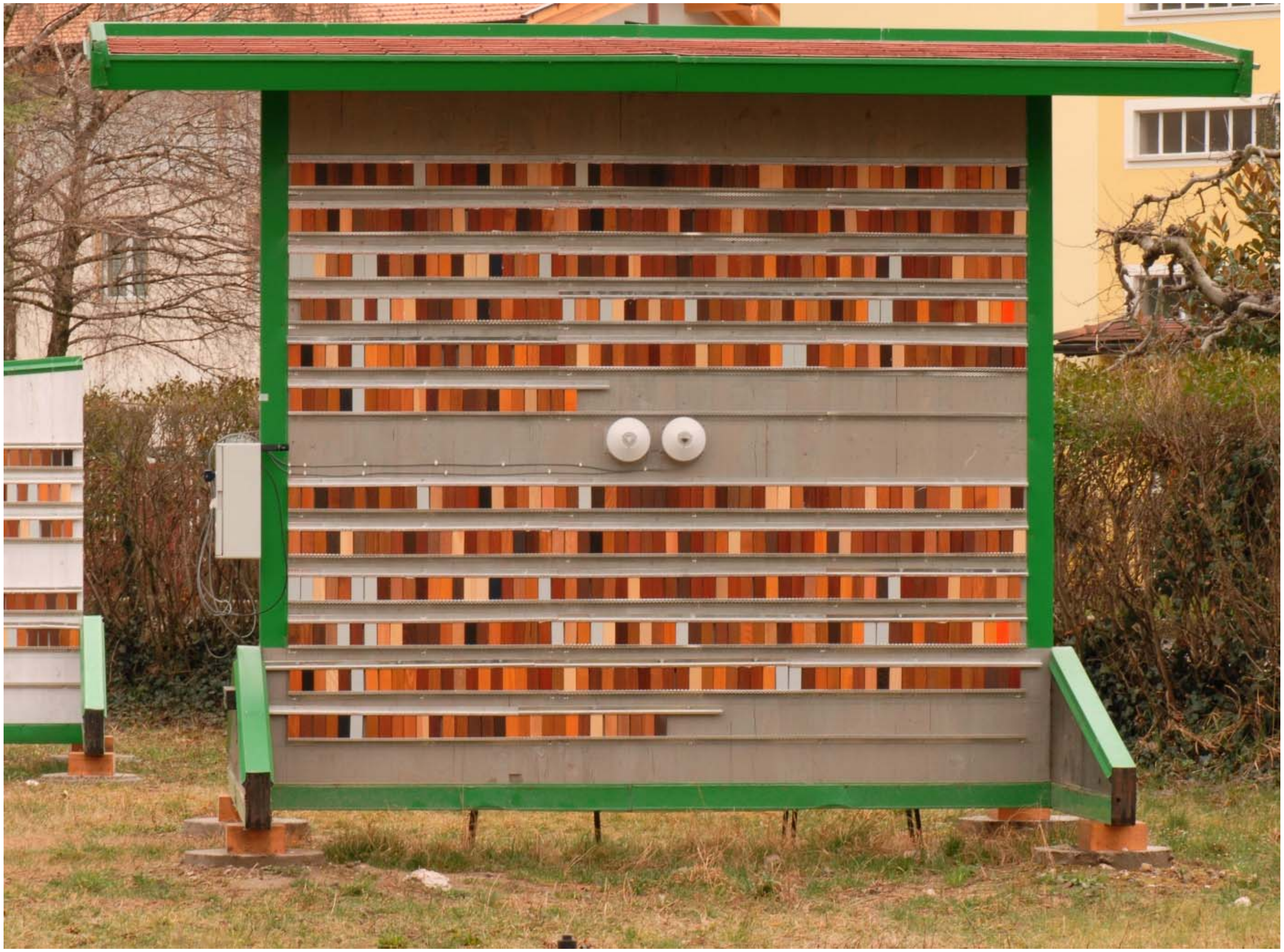
Antique wooden floors





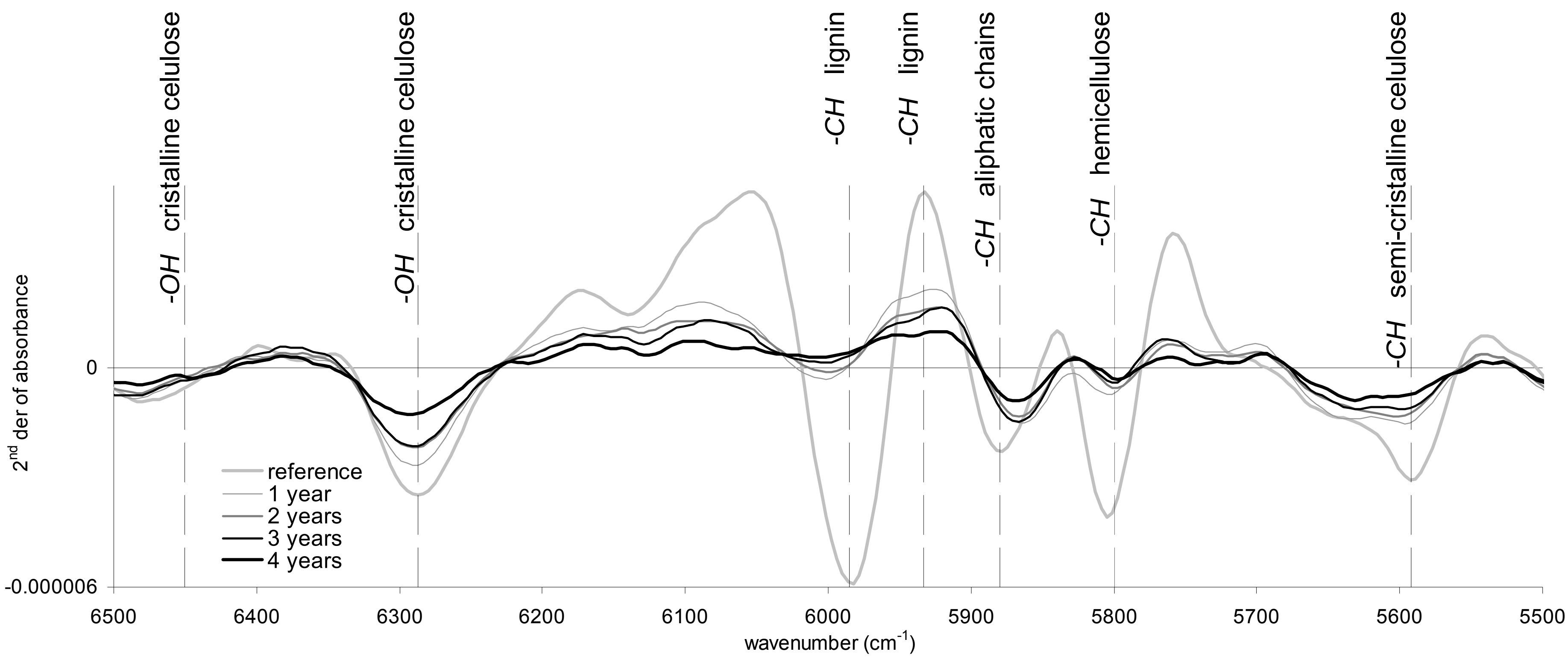


Monitoring of weathering

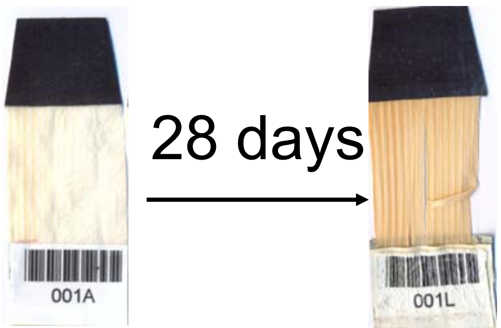


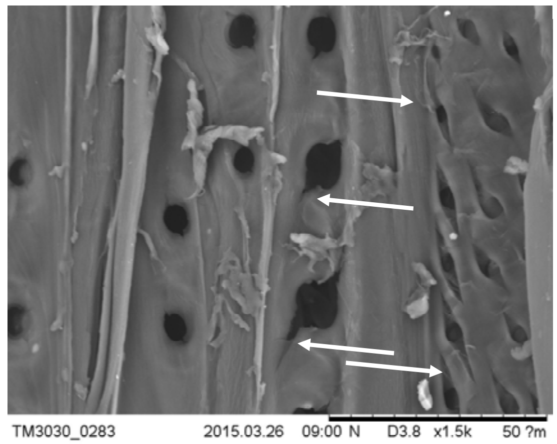
8 softwood, 3 hardwood, 12 exotic, 3 thermo modified wood
21 various water/organic based products with synthetic/natural/acrylic/alkyd resins/oils

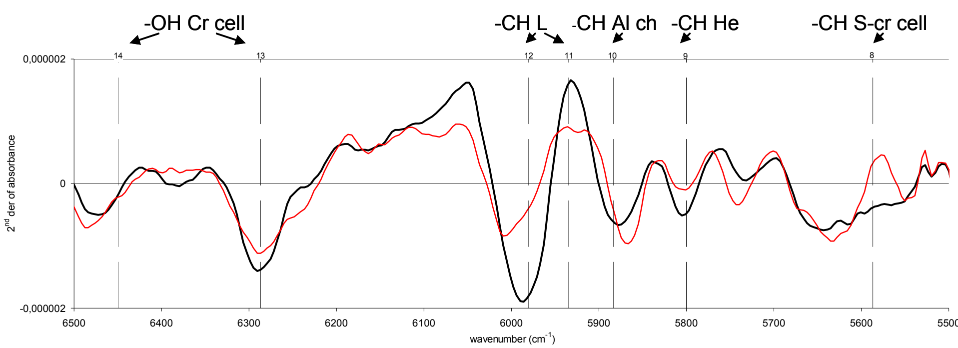
Monitoring wood weathering

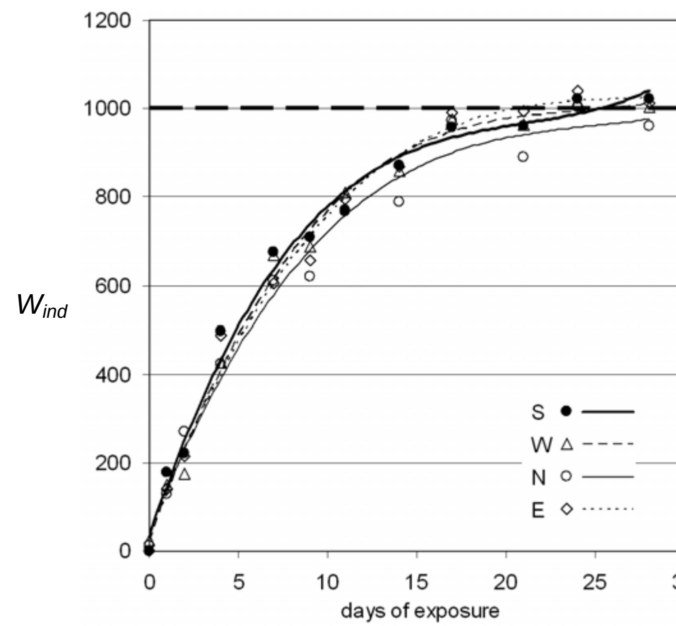


Short term weathering of wood

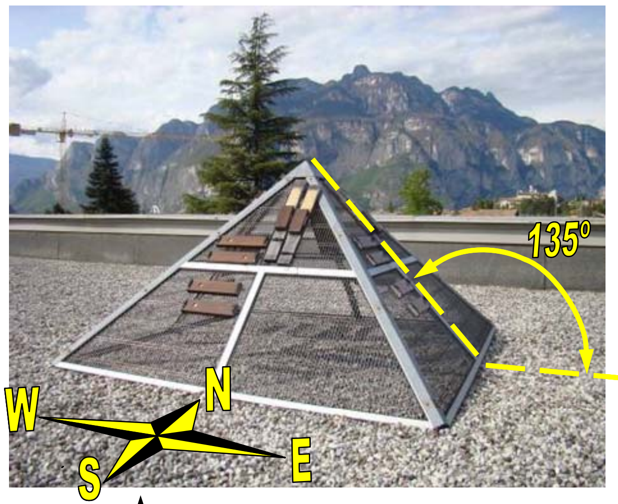


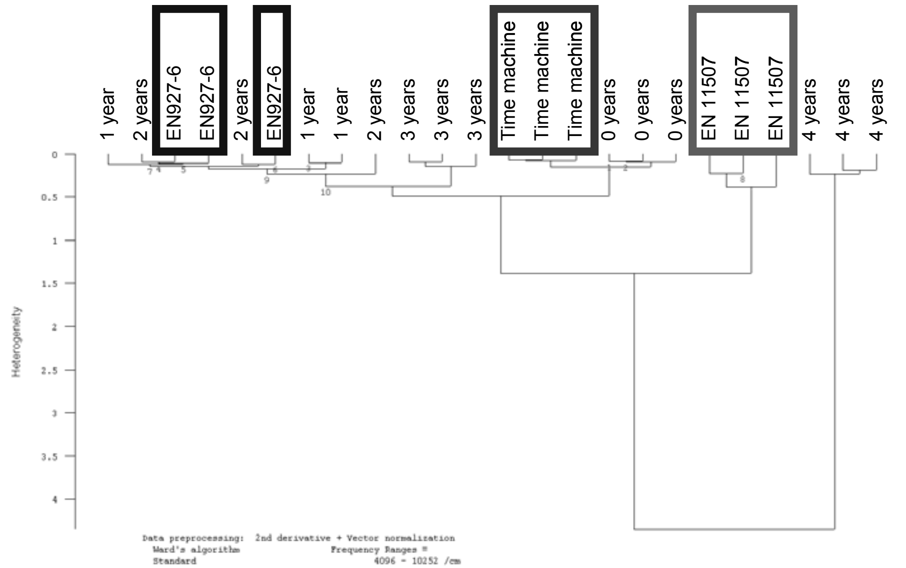


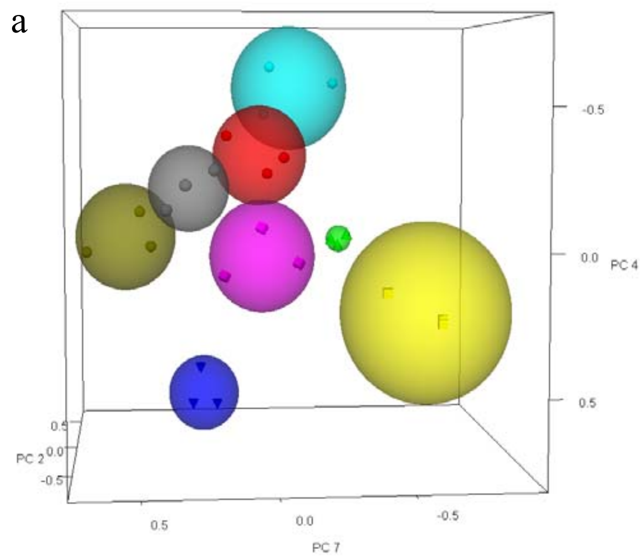




Service life prediction





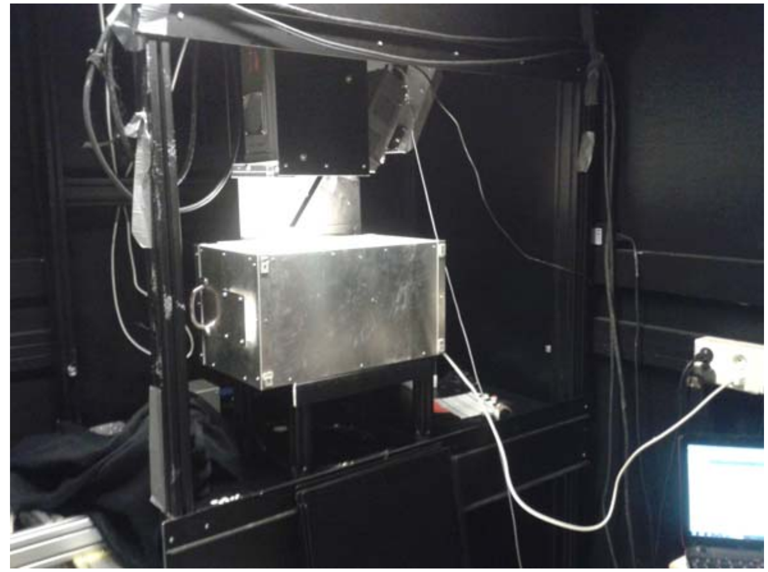


PCA of NIR spectra of non coated samples exposed to South (4 years of natural weathering);

- Reggio Emilia
- Roma
- Loninghens
- Macerata
- Udine
- Trento
- Lecce
- standard

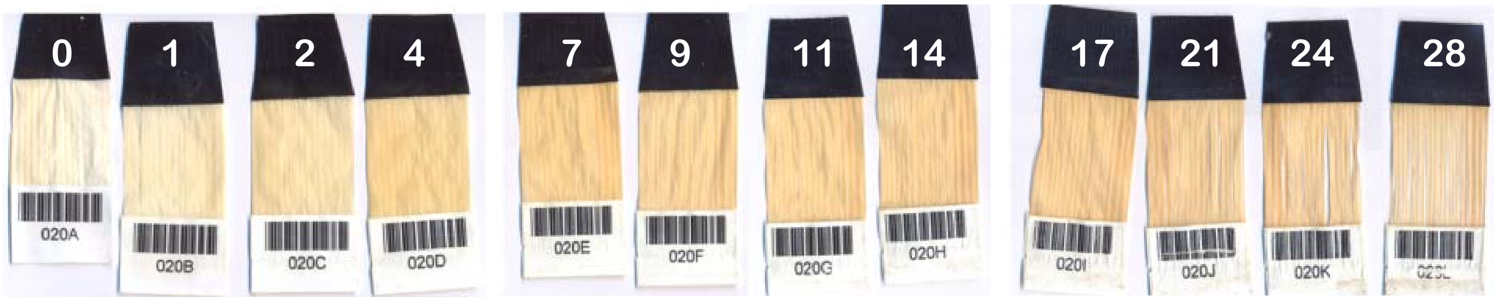
Research directions

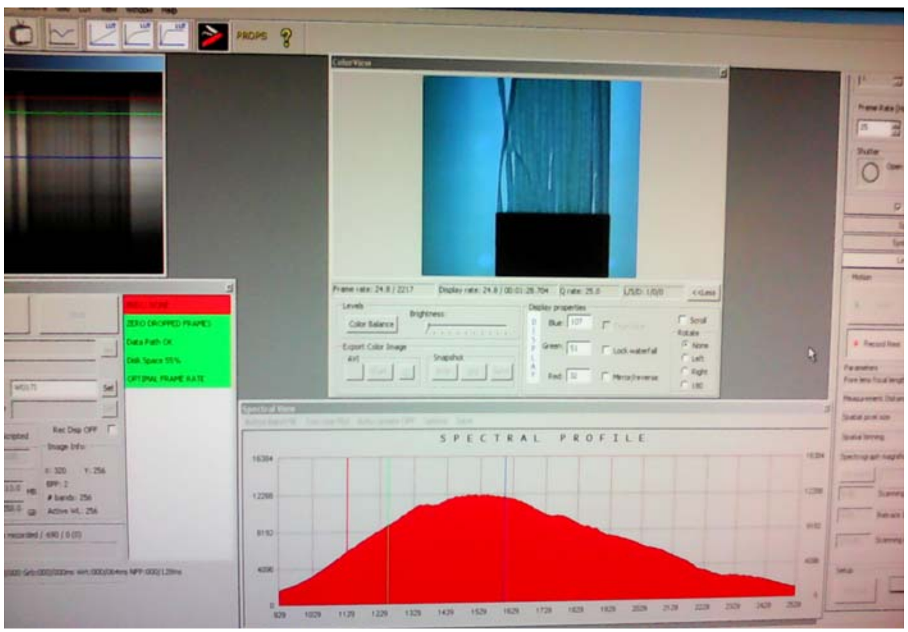
spatial measurement
Hyperspectral Imaging



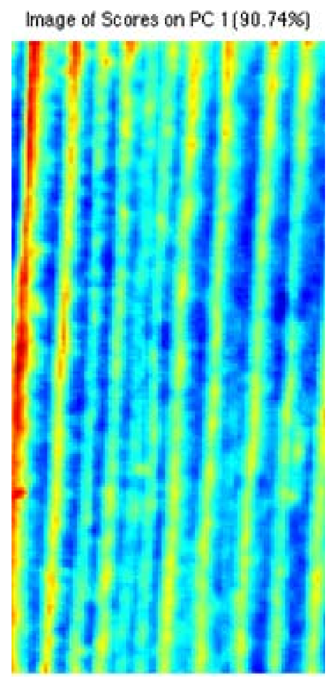
in field measurement
portable equipment

Weathered wood

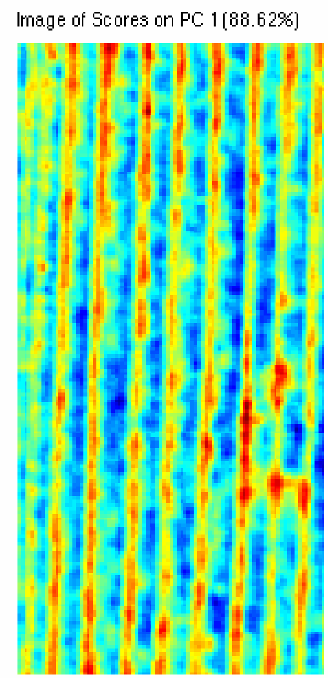




a)

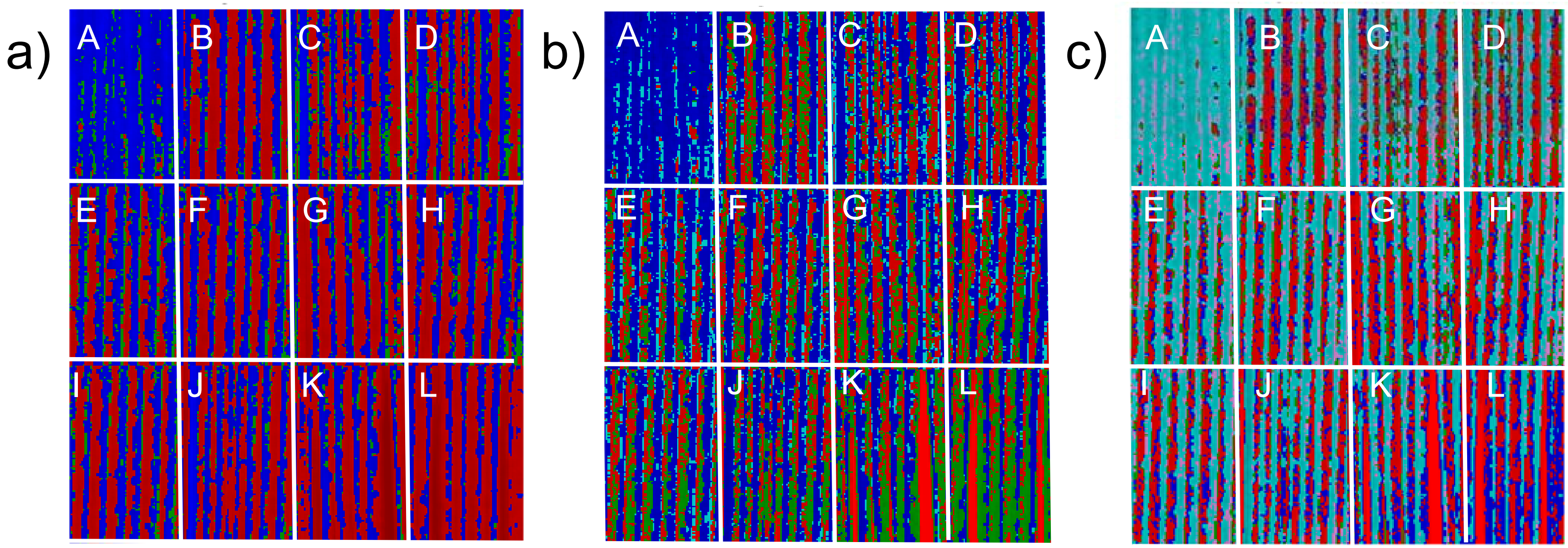


b)



PCA analysis performed on not weathered (a) and sample after 28 days of weathering (b)

K-means classification

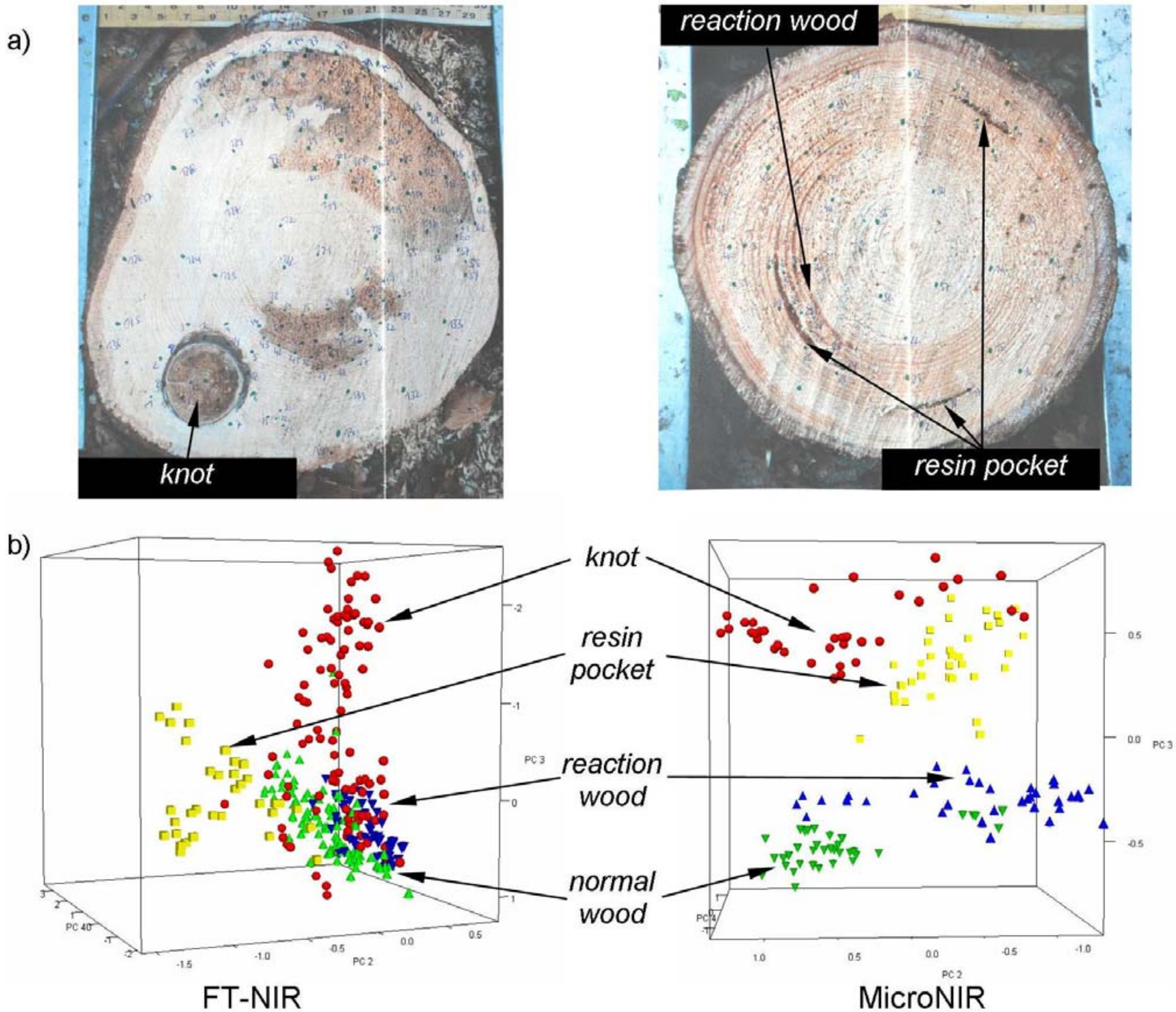


K-means clustering on the mosaic of weathered wood after pre-selecting 3 (a), 4 (b) and 5 classes (c)

NIR for log/biomass quality index in mountain forest

wood measurement at various harvesting moments

Wood defects detection

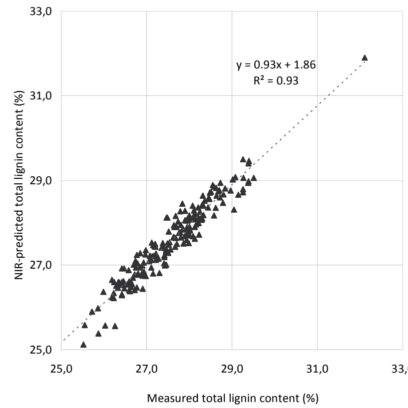


range 12500-5900cm^{-1}
2nd derivative + VN

Calibration transfer

measurement of samples with equipment #1

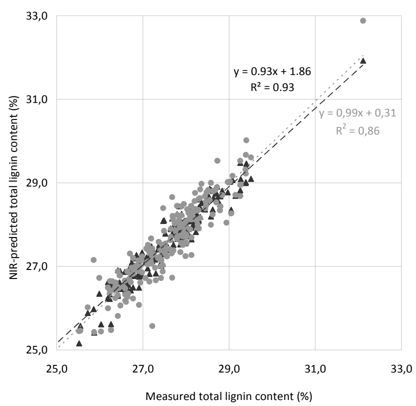
model #1 development



selection of calibration samples by Kennard Stone algorithm

measurement of selected samples with equipment #2

calculation of transfer matrix



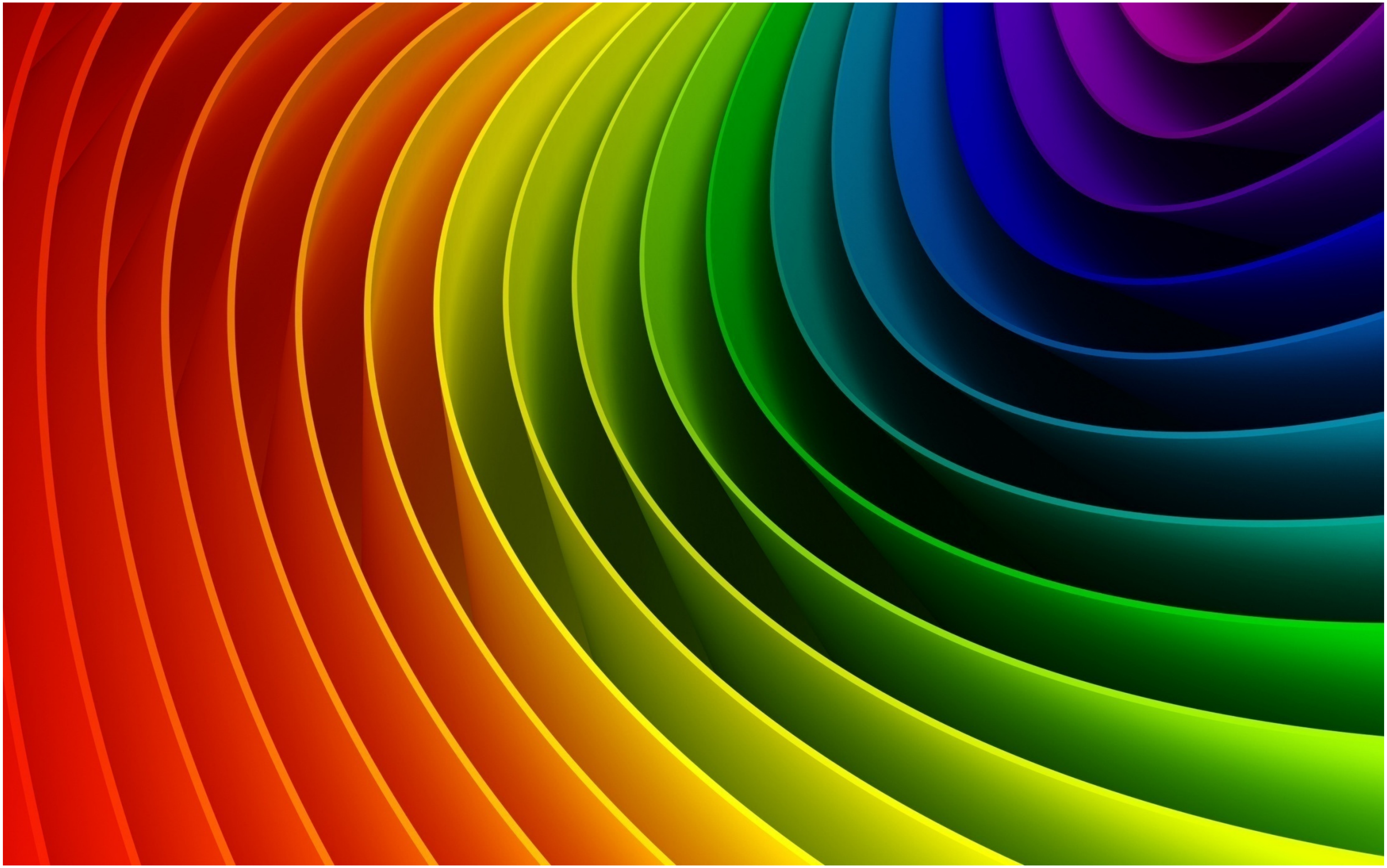
equipment #2 model development based on samples measured with instrument #1

Conclussions

NIR technique has been successfully used for:

- species and provenance recognition
- estimation chemical composition, physical and mechanical properties
- monitoring chemical changes in wood during thermal modification, weathering, waterlogging and decay
- recognition and classification of coatings
- characterization of archeological wood and cultural heritage objects
- service life prediction of wooden elements and structures
- paper characterization
- in-field applications

Current developments in the fields of optics and electronics open new application for NIR. Its non-destructive character and simple measurements allows assisting experts in the estimation of material properties in a fast and repeatable way



Thank you very much