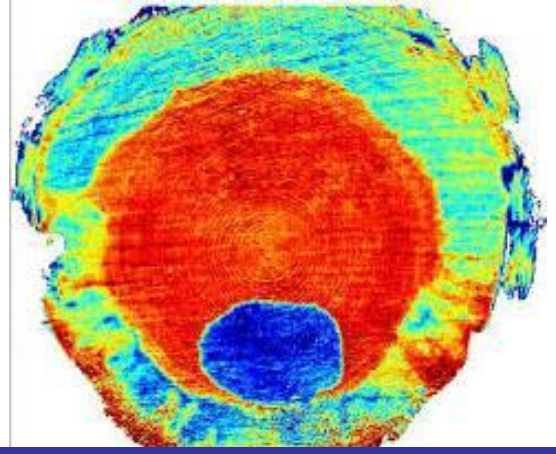


Characterization of biomaterials – surface and bulk

Jakub & Anna Sandak

COST Action FP1407 Training School:
Service life of modified wood - Understanding Test Methodologies

outline

- few definitions
- aesthetics of wood surface
- sensors for :
  - color
  - color maps
  - gloss
  - roughness
  - topography maps
  - wettability
- characterization of bulk
- inter-relations
- concussions

why to study this?

- importance of the surface (quality, performance)
- relationships between surface properties and:
  - manufacturing process conditions (tool wear, machine, coating technology)
  - functional properties of wood/bio products
  - performance of the biomaterials during service life
  - …
- several unsolved problems (technical/scientific) related to wood surface
- an interest of the industry and scientific community to develop suitable methodologies dedicated to assessment of biomaterials surfaces

Evaluation of the surface properties in general has got two main reasons:

- to predict a **prospect surface performance**
- to **monitor** the manufacturing **process**

but, the surface of wood is as much more related to the **esthetics than by functional reasons** what influences environmental impact and LCA

The objective of this presentation it to survey various aspects related to the wood **surface/bulk characterization**, with a special interest in development of **dedicated sensors**

wood & surface are…

wood:

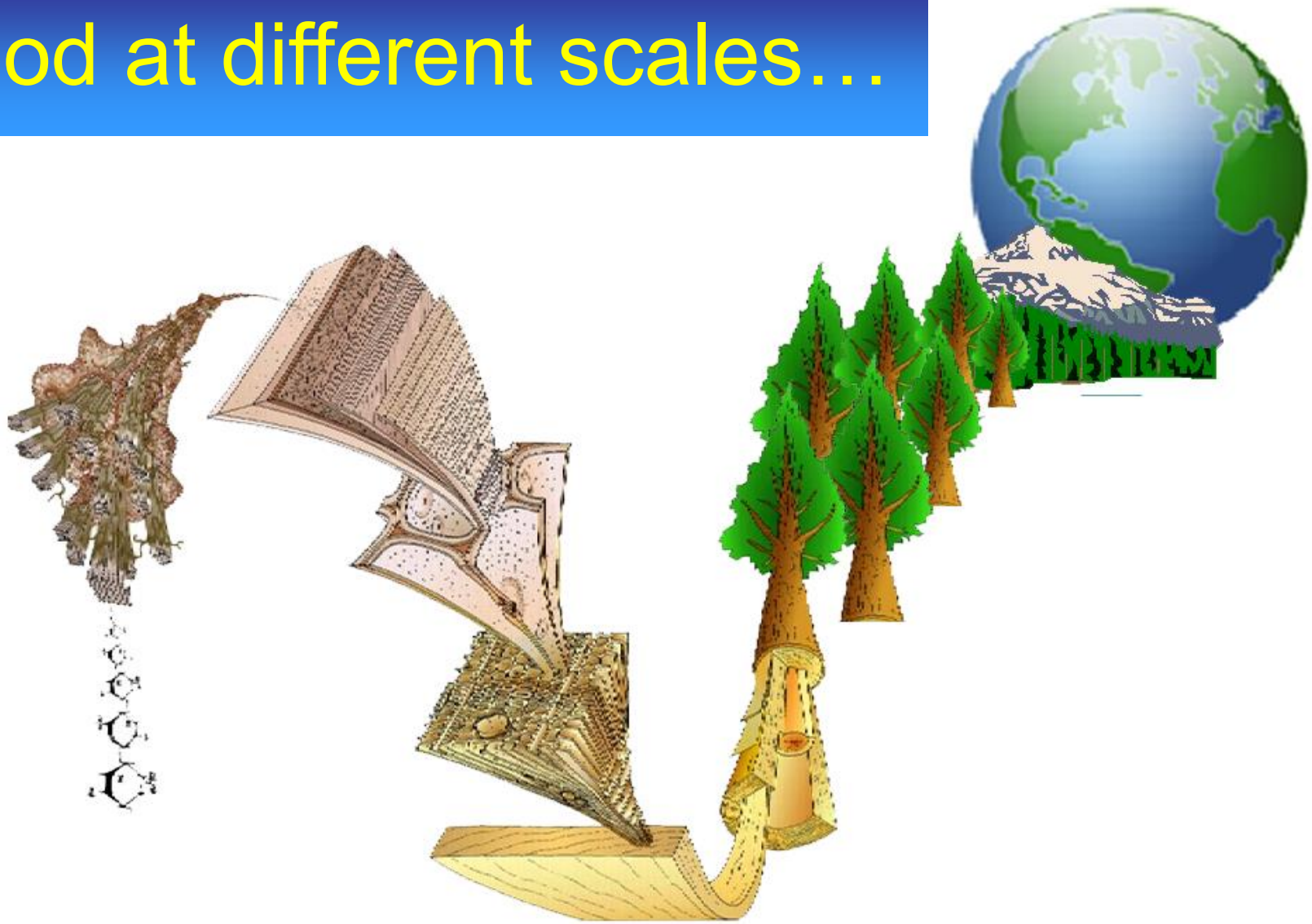
- the **hard fibrous material** that forms the main substance of the trunk or branches of a tree or shrub *(Oxford dictionary)*
- a **complex matrix of several polymers** (lignin, cellulose, hemicelluloses + extractives and minerals) [+ *resins* + *additives*]
- heterogeneous & anisotropic
- a highly hygroscopic material, responding to the humidity changes of surrounding air

surface:

- the **outer or the topmost boundary** of an object
- the outward **appearance** of someone or something

4

wood at different scales…

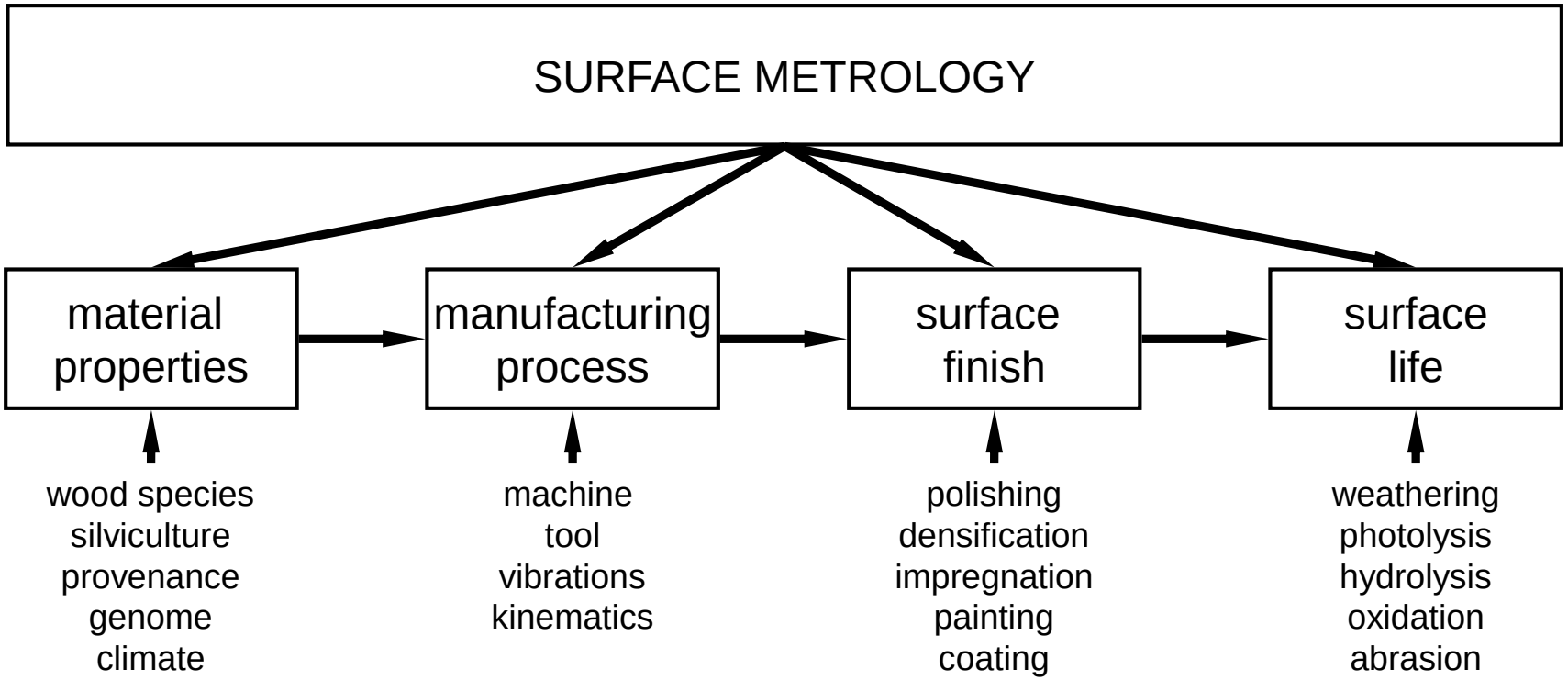


Inspired by artwork by Mark Harrington (http://www.nzwood.co.nz)

the variability of wood properties is very high in the level of one wood species, same forest, single tree, or even within one piece of wood

complexity of the wood surface

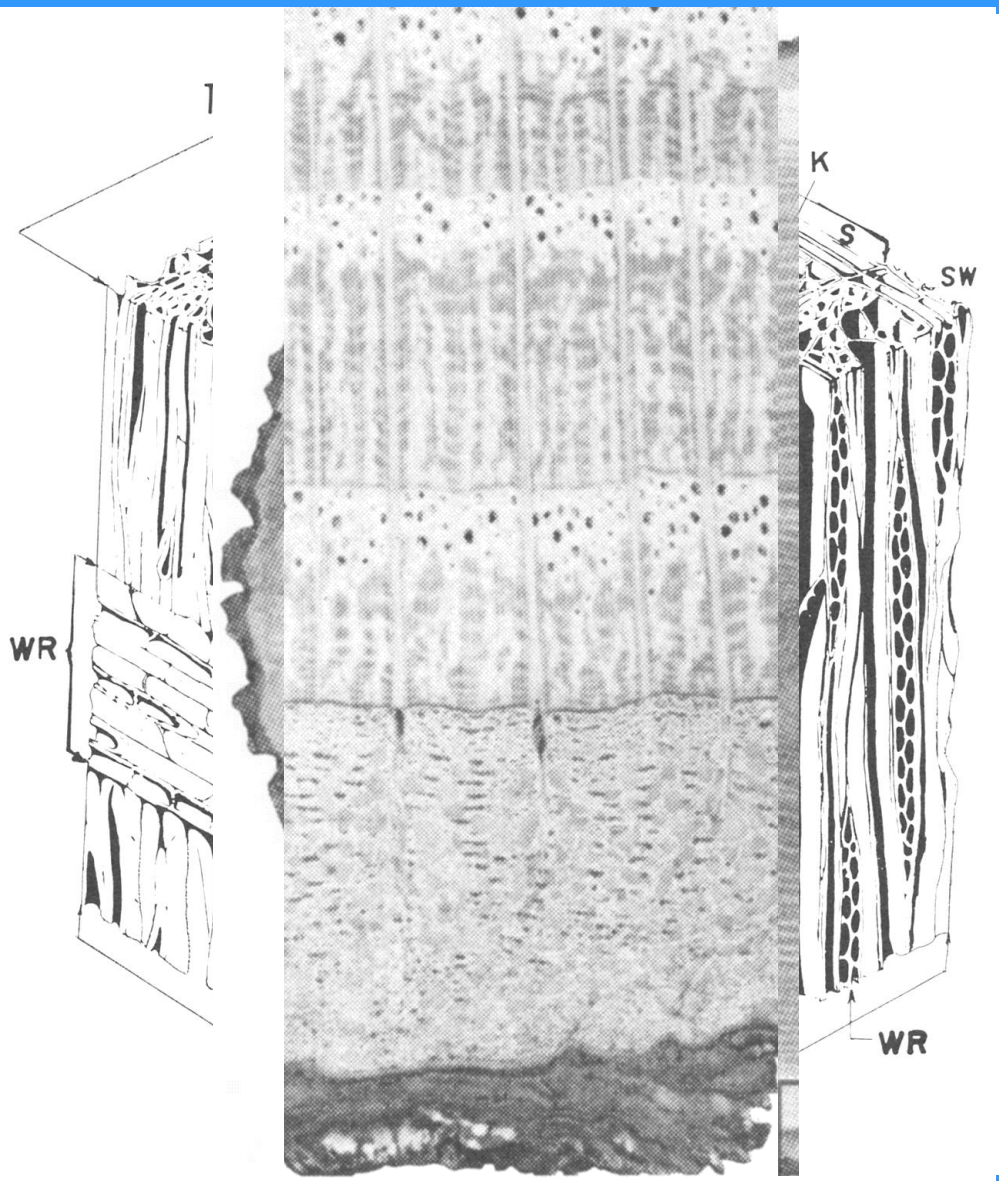
- differing anatomical elements - *cut by the tool during machining*
- anisotropy of wood
- wood density
- moisture
- kinematics of the cutting process
- machine conditions
- … and other variables



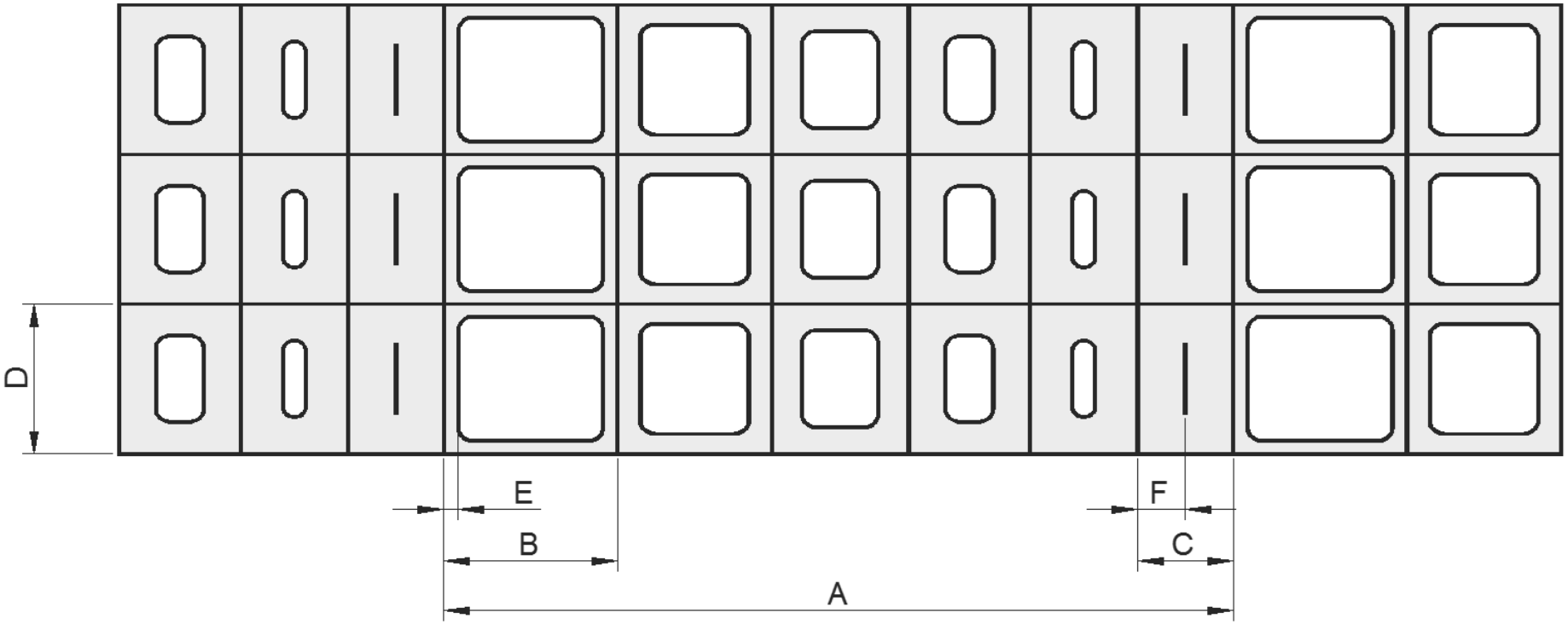
wood anatomy

macrostructure:

- bark
- cambium
- sapwood
- heartwood
- pith
- knots
- cracks
- earlywood
- latewood

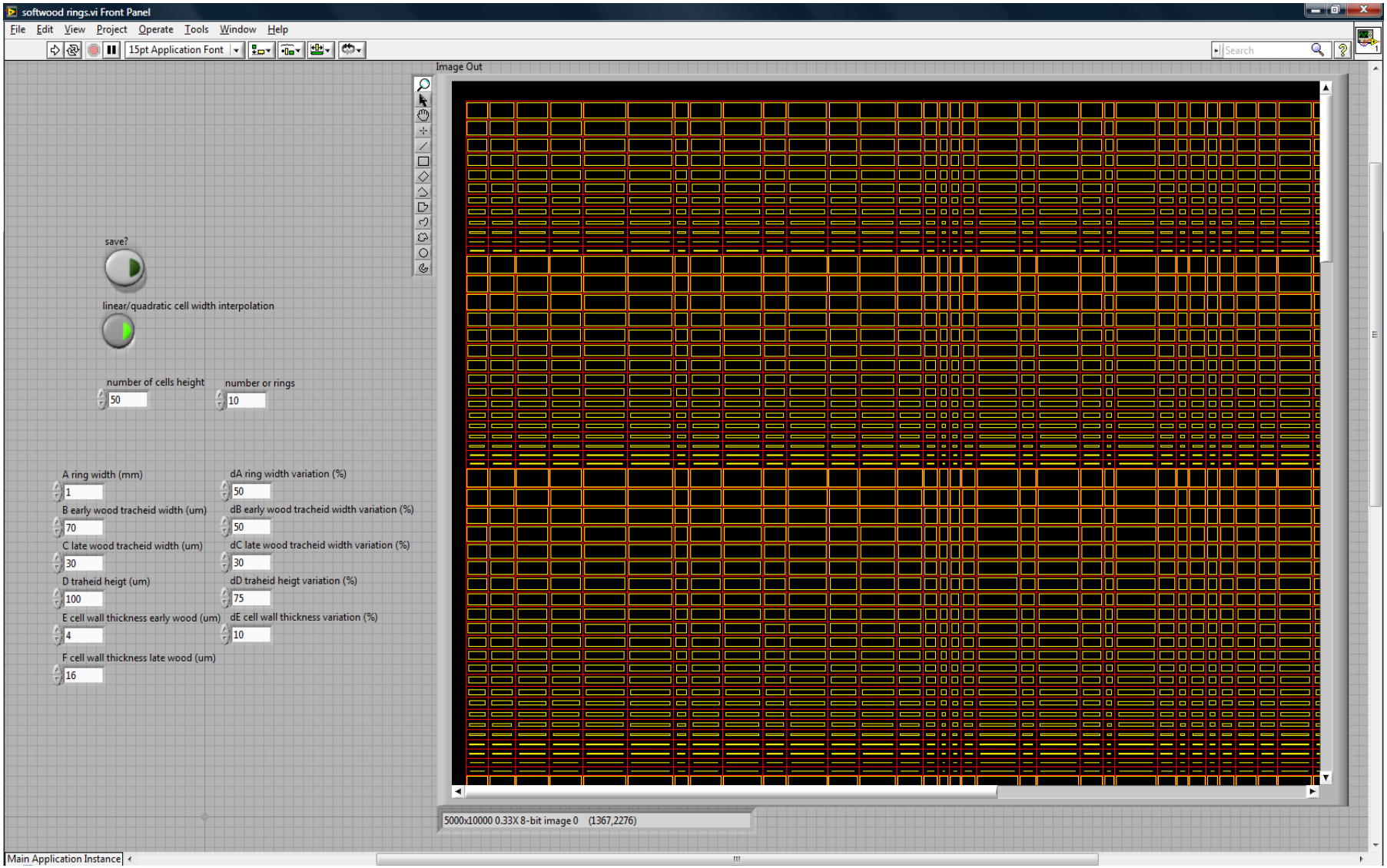


parameters characterizing anatomical structure of softwood



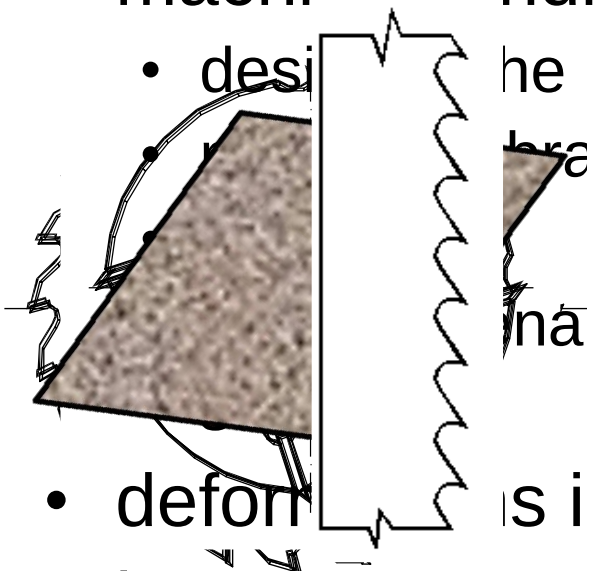
***A* – yearly ring width, *B* – early wood tracheid width, *C* – late wood tracheid width, *D* – tracheid height, *E* – early wood cell wall thickness, *F* – late wood cell wall thickness**

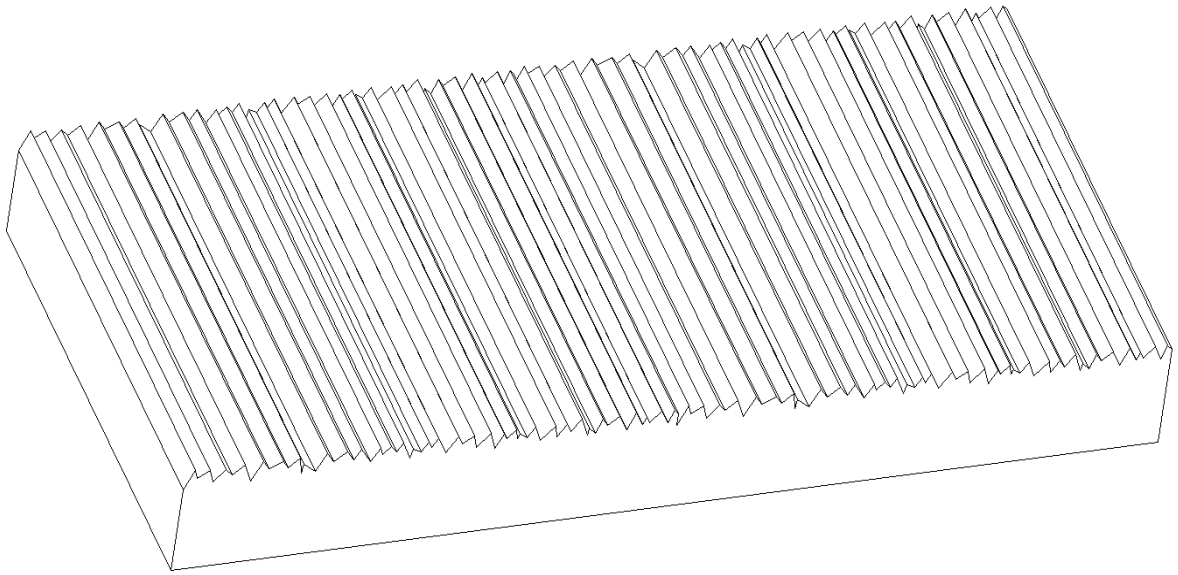
softwood section generated with LabView



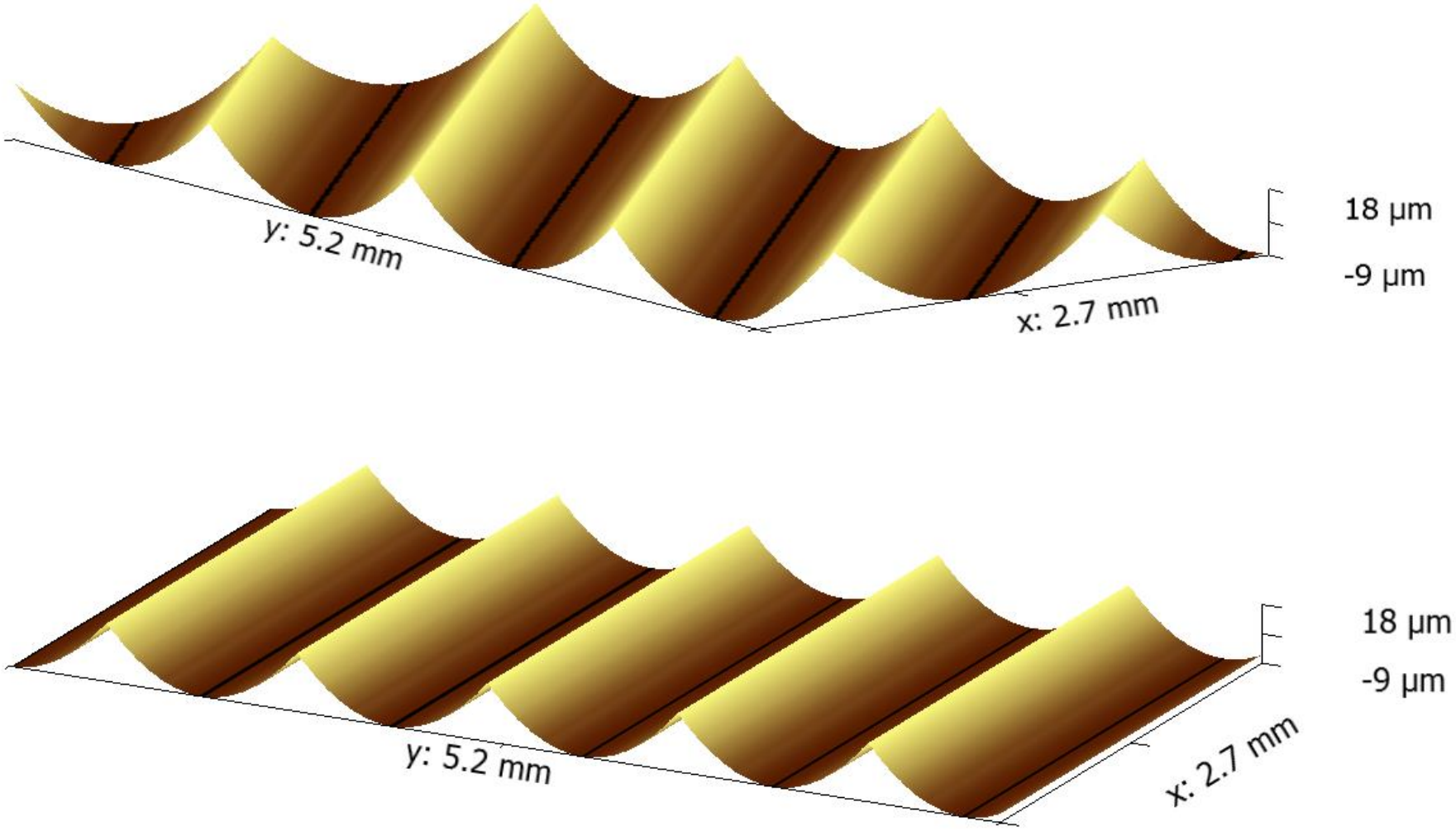
machining process

- kinematics of the cutting process
- machine condition:
  - desi he
  - ra
  - na
- defor s i
- heat treatment

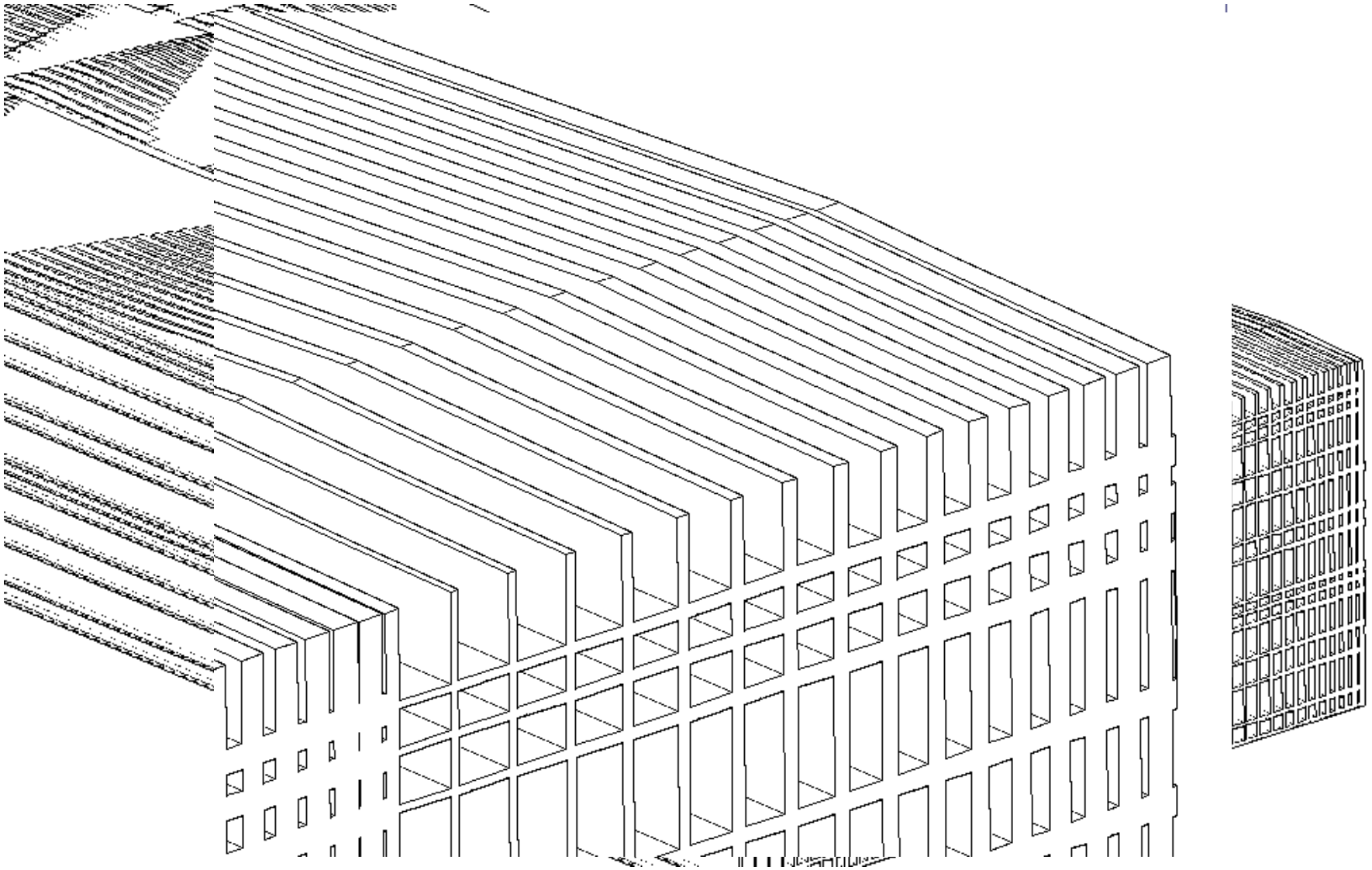




cutting edge path models



wood structure 3D models in CAD



assesment of surface properties

sight

hearing

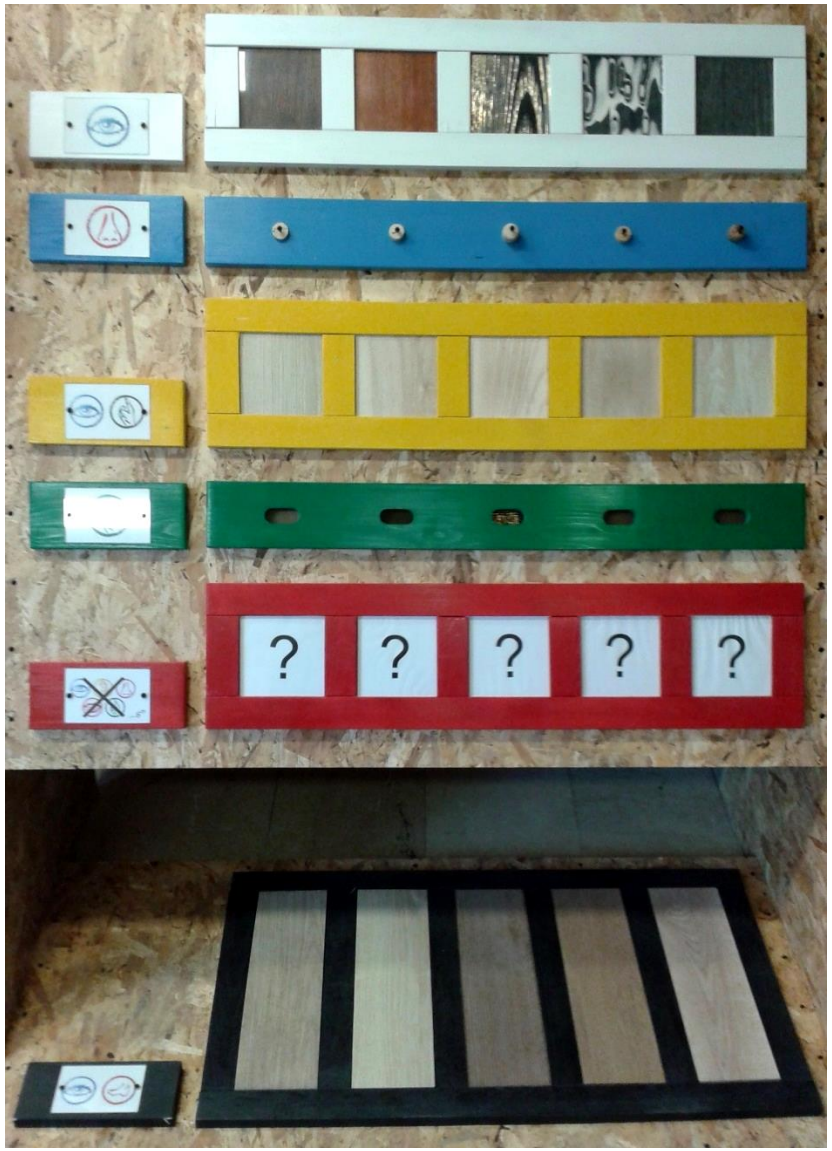
taste

smell

touch

+6th sense

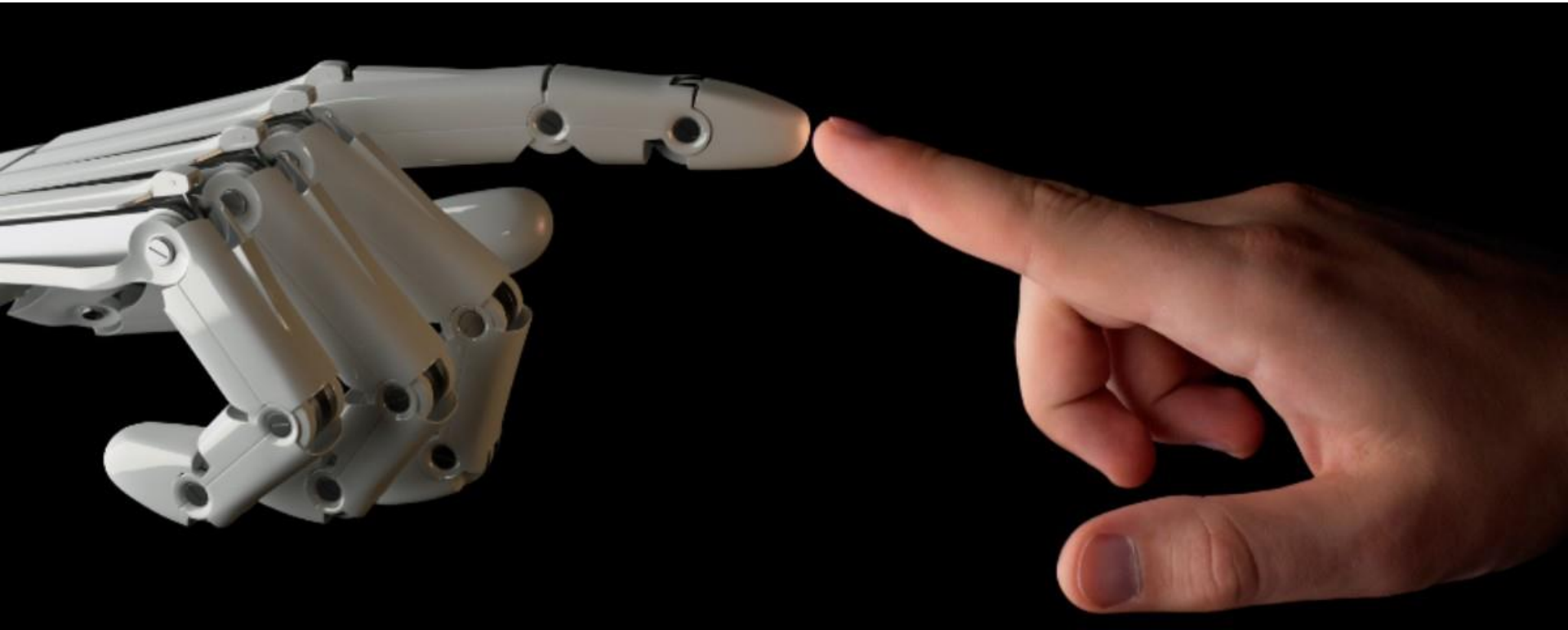
testing ≠ senses for natural wood



testing user preferences (SWORFISH project)

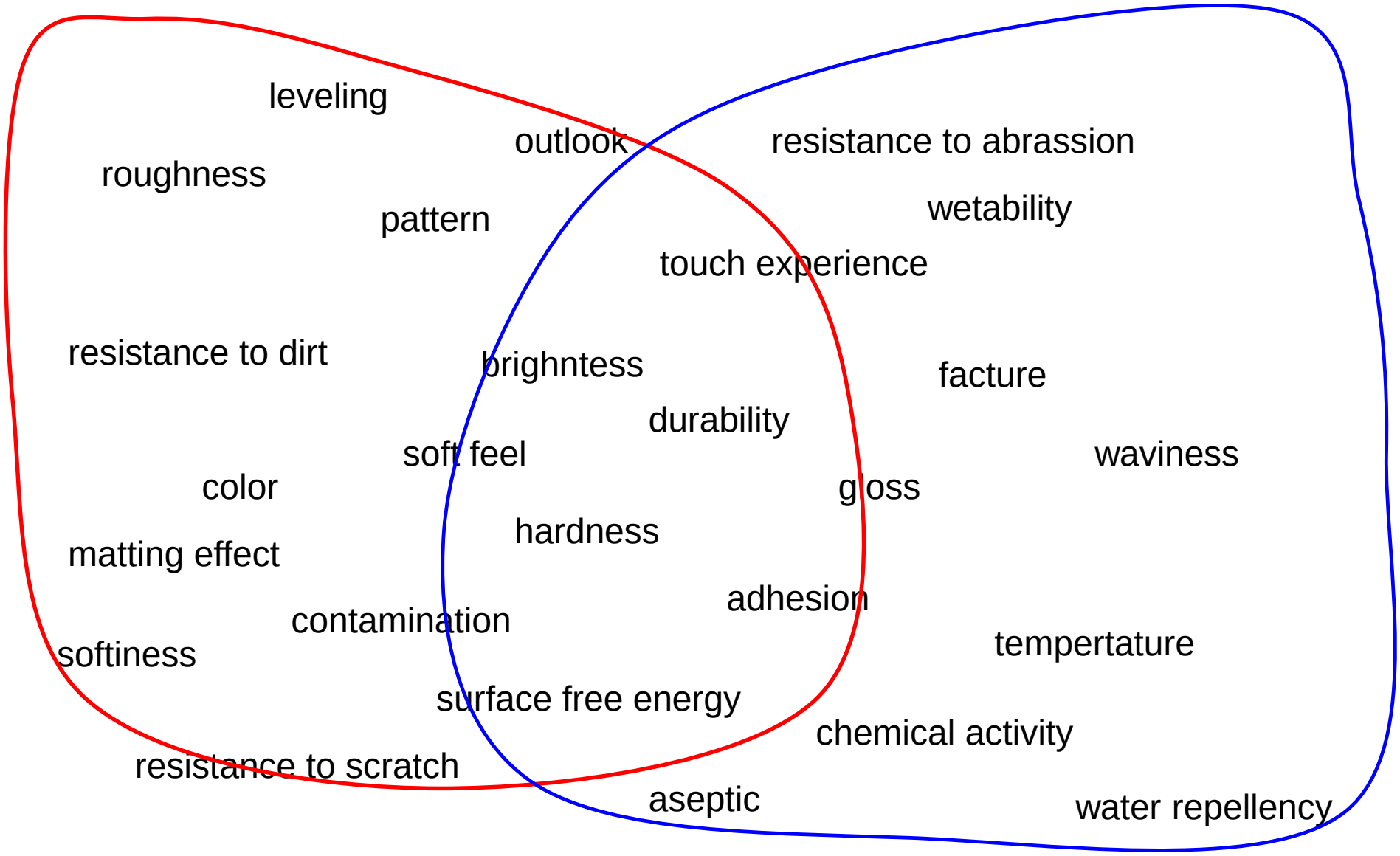
problems with personal assesment

- subjectivity
- person/time/training dependatnt
- repeatability
- …reliability



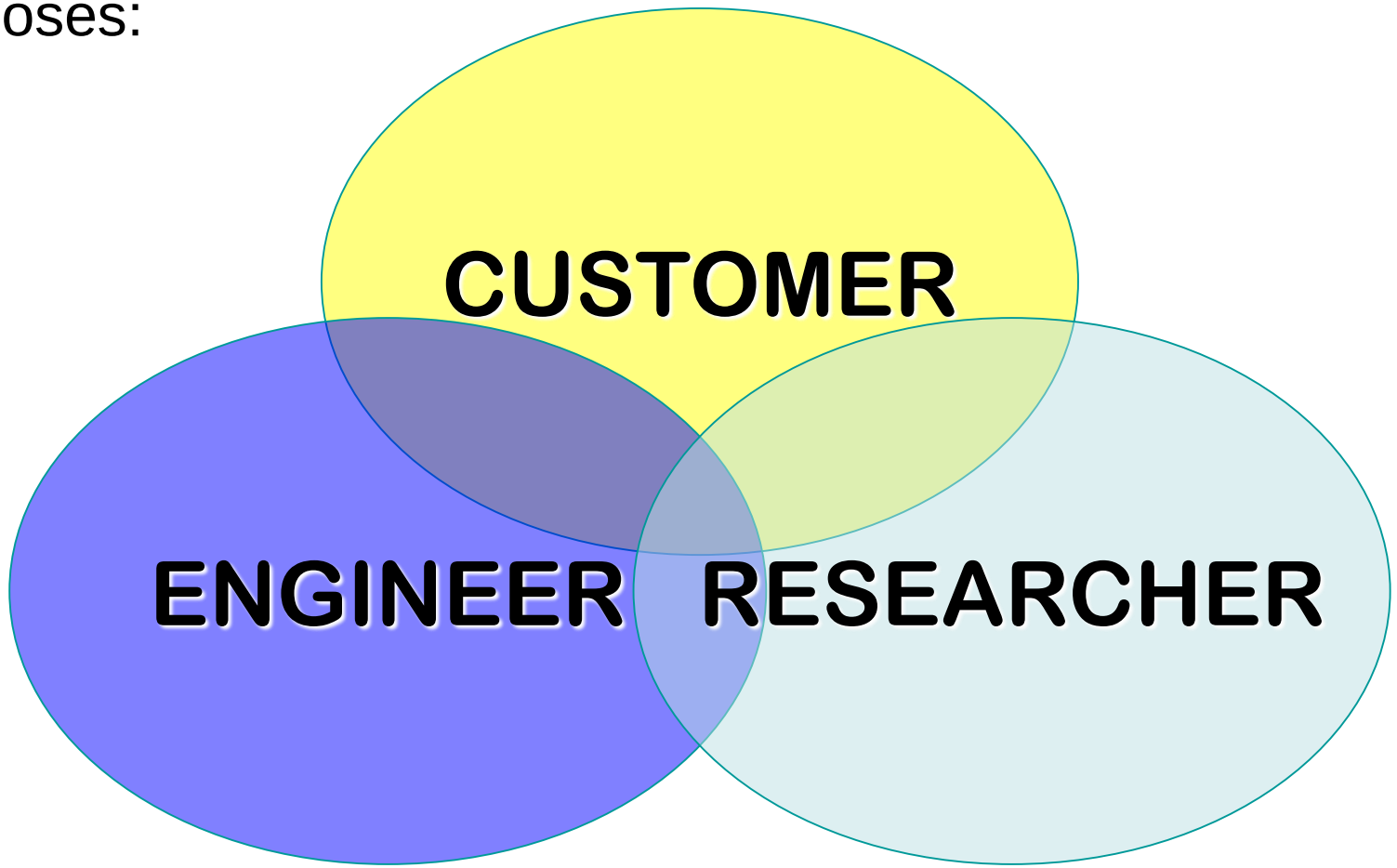
how to assess properties “objectively”?

surface properties



what is then “superb surface” of wood?

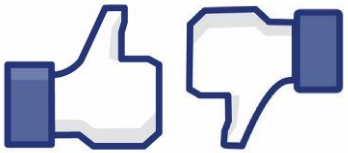
The meaning of *wood surface quality* differs relating to diverse purposes:



customer

surface is an **impression** related to the senses of touch and vision:

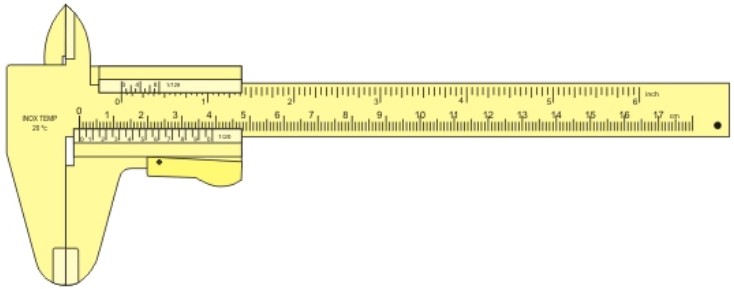
- classification of products in to *smooth* - *rough glossy* – *matt* is subjective and fuzzy, without numerical quantification
- any standardized “parameters” have no importance
- separation of the anatomical and machining component of the surface has no sense…



engineer

Surface properties/qualities are **numerical quantifications**:

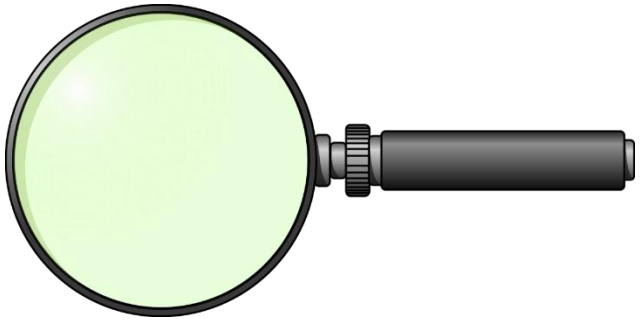
- various parameters can be used to adjust process variables or to monitor finishing
- each parameter must be within certain limits
- properties affected by the anatomical structure are sometimes ignored, as are non-related to the process itself



researcher

surface quality is a significant **material property** to be evaluated:

- varied aspects of the surface can be under investigation (anisotropy, statistical height distribution, chemical composition, physical prperties…)
- the most indeterminate and flexible
- giving so far a field for the development of new and flexible methods for its evaluation, interpretation and information extraction



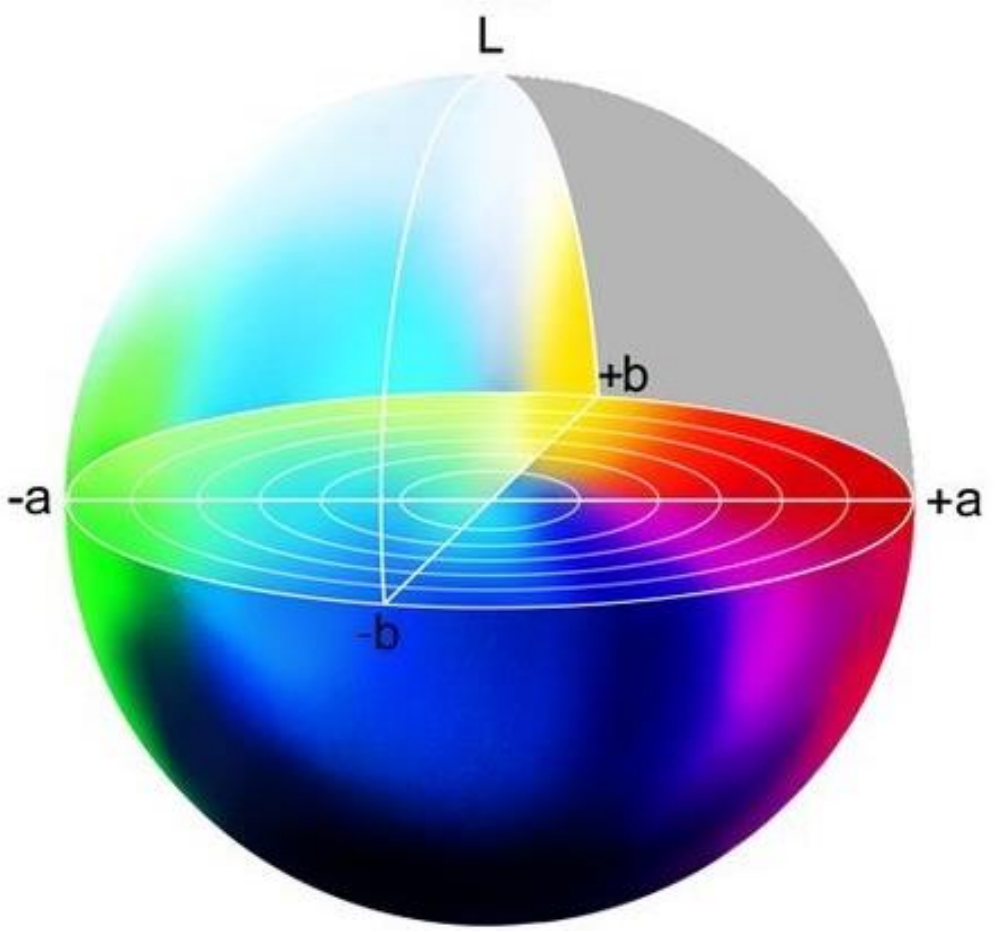
color: what is it?

- is the **visual perceptual property** corresponding to the categories called red, blue, yellow, etc.

  how to measure impression?

- Color derives from the **spectrum** of light (distribution of light power versus wavelength)

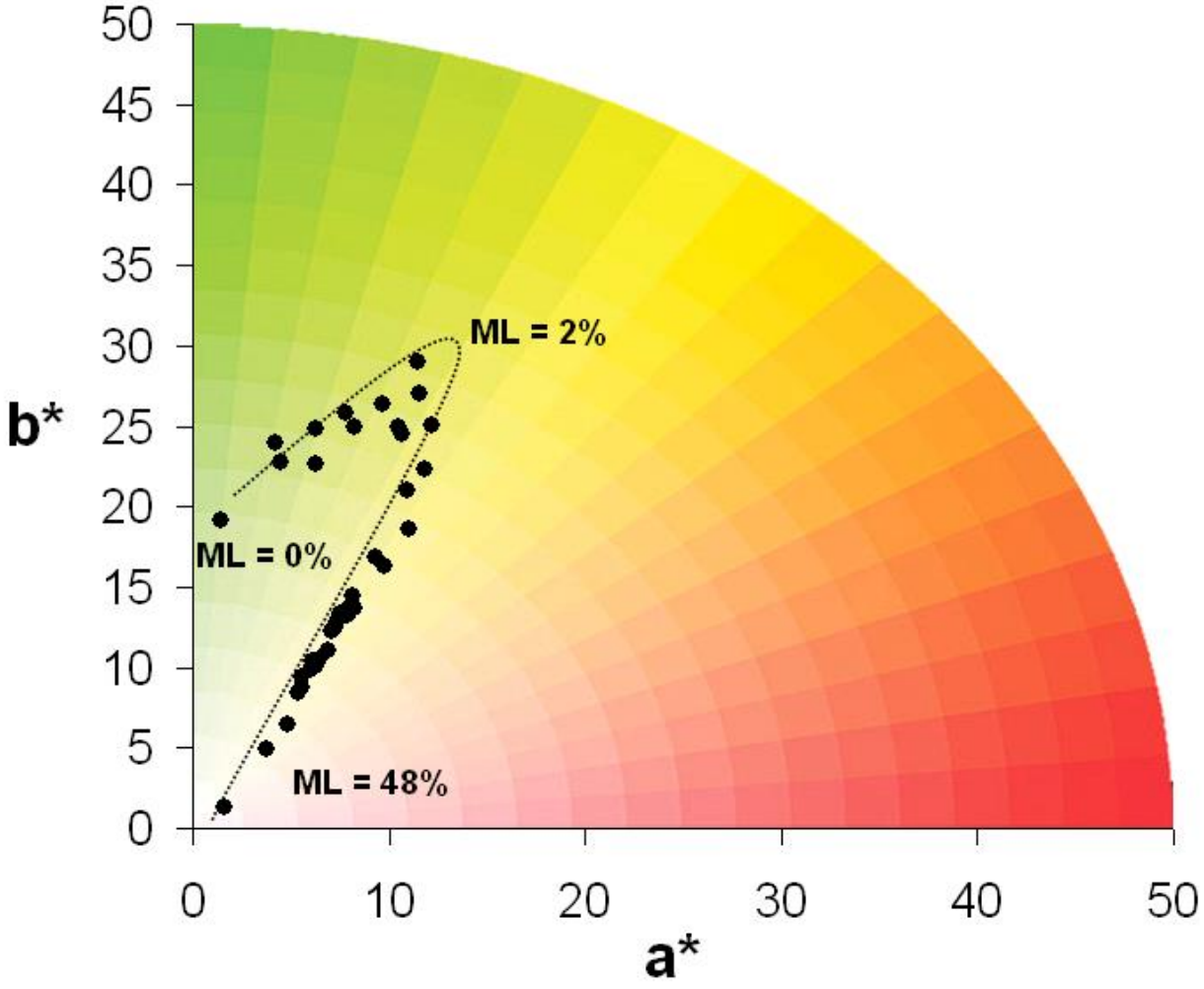
  how to interpret spectra?



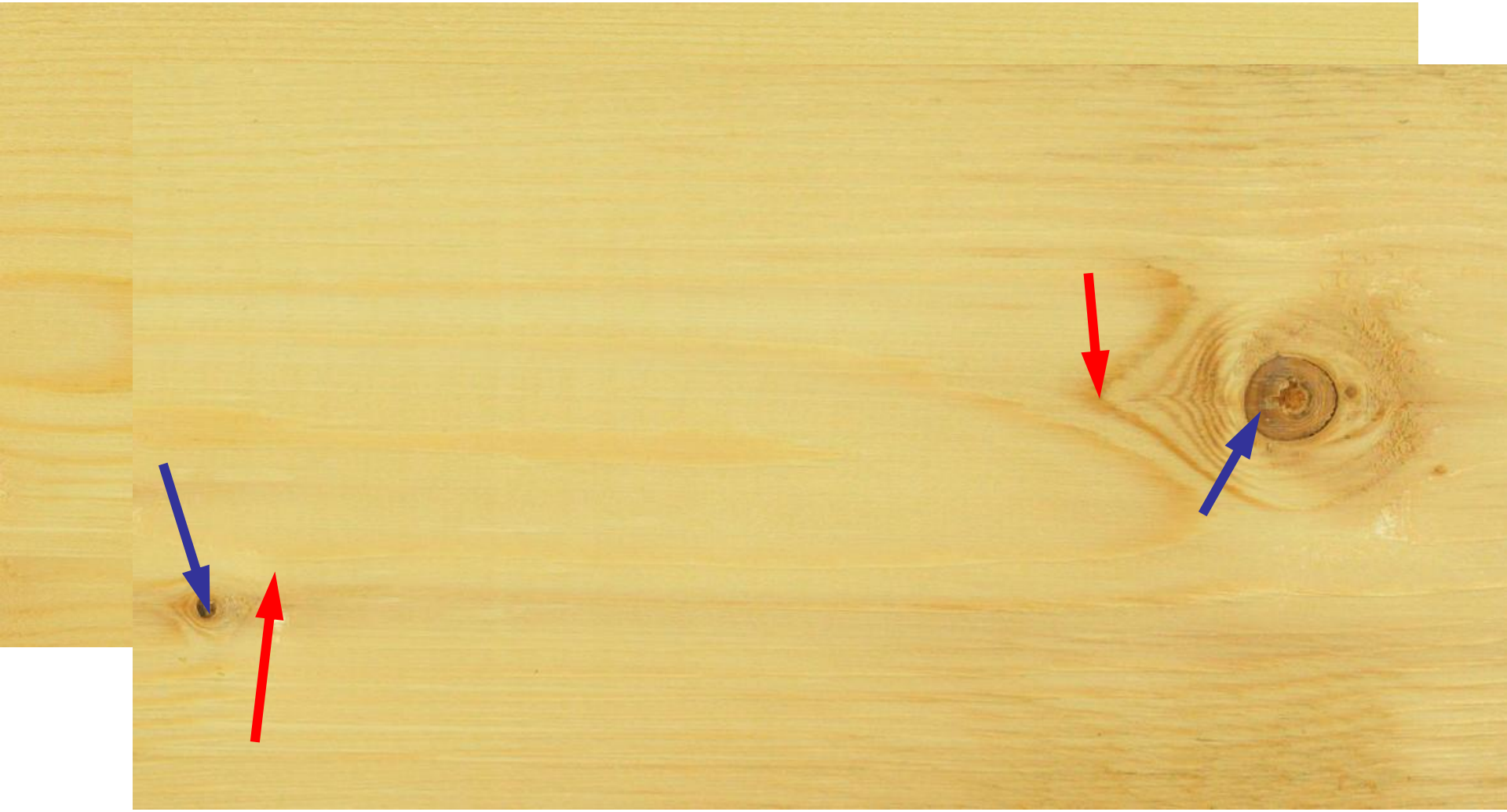
CIE Lab

measuring color

Color change with ML of TMW

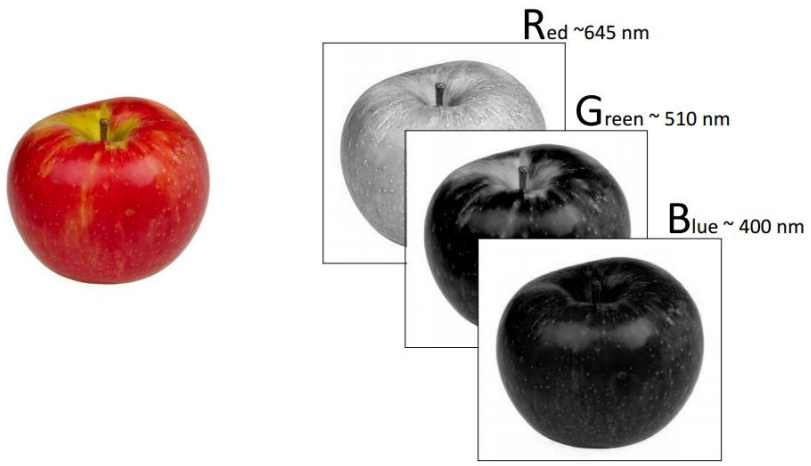


problem: *an average value over certain area*

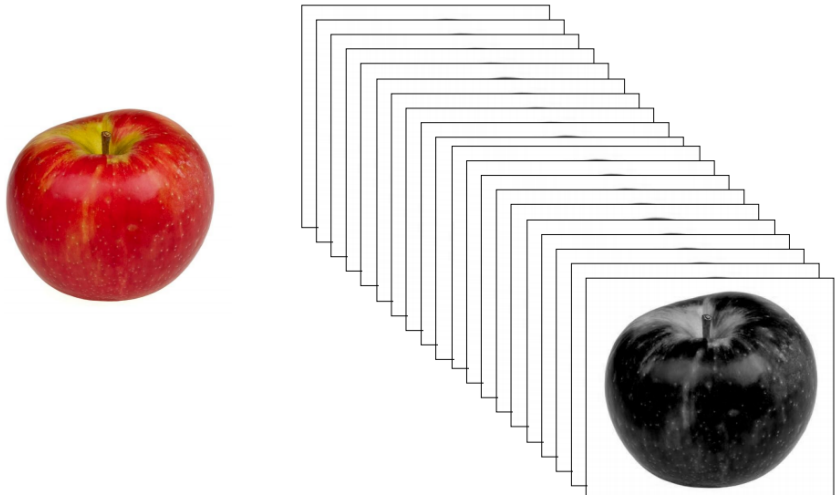


Hyperspectral imaging

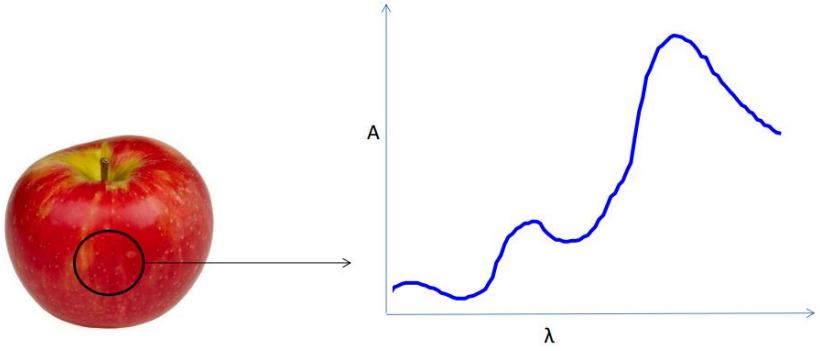
Conventional Imaging



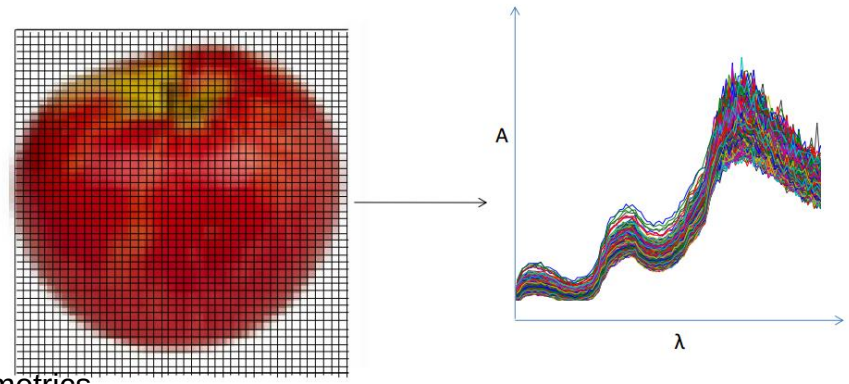
Hyperspectral Imaging



Conventional spectroscopy

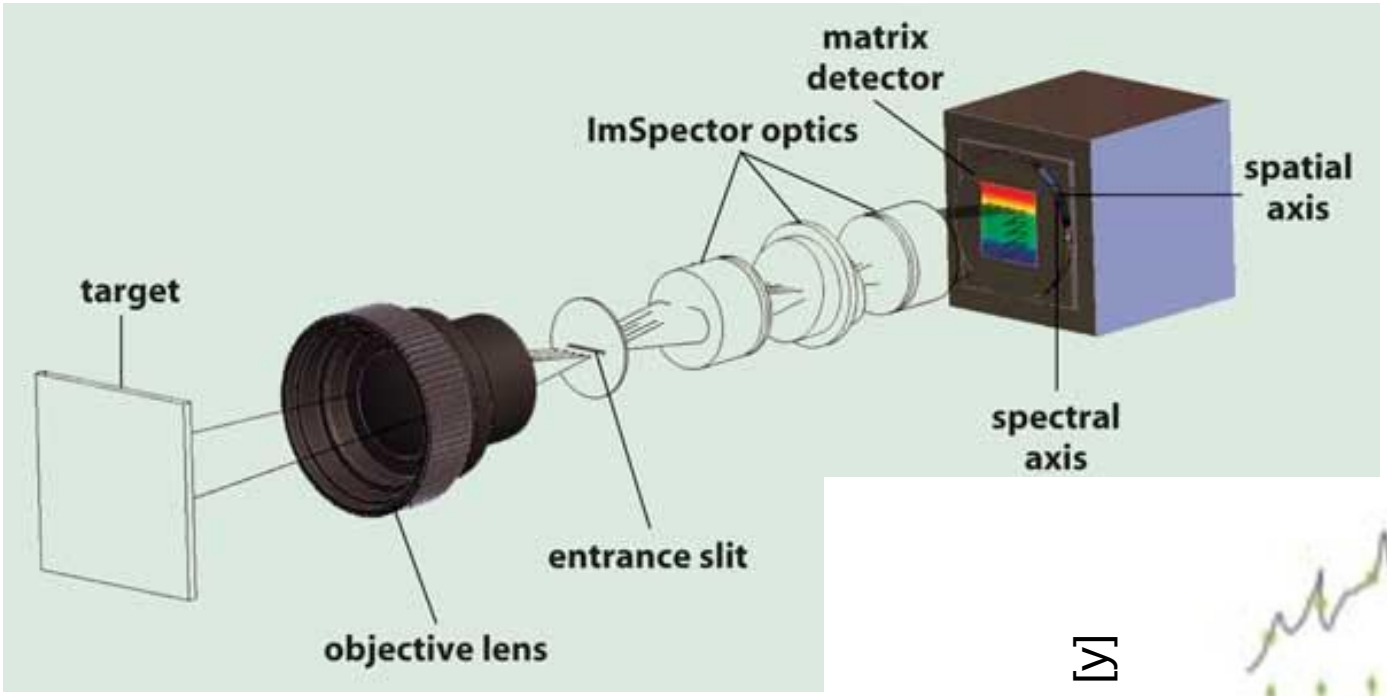


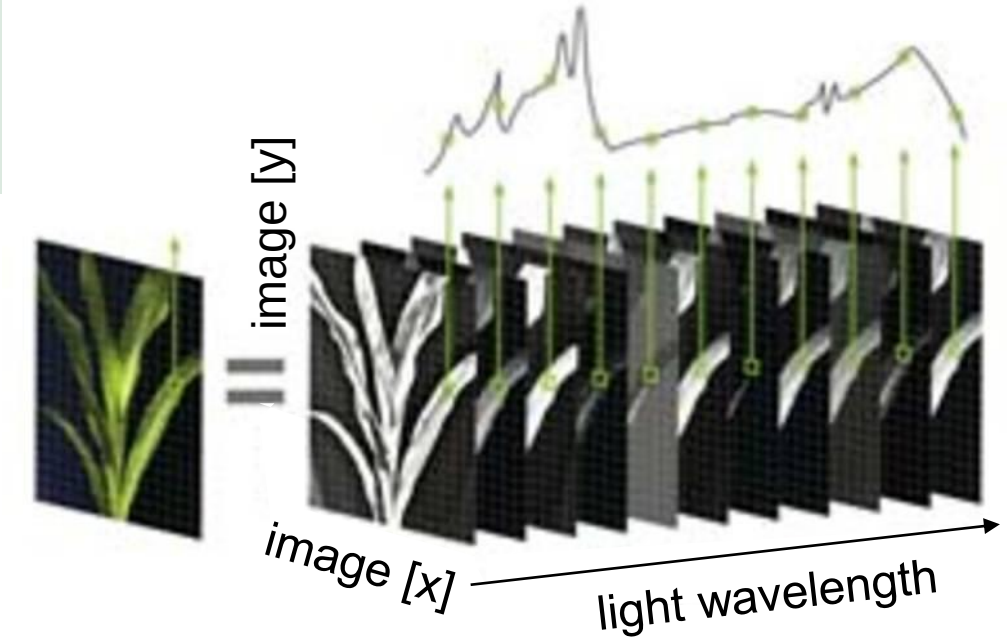
Hyperspectral imaging



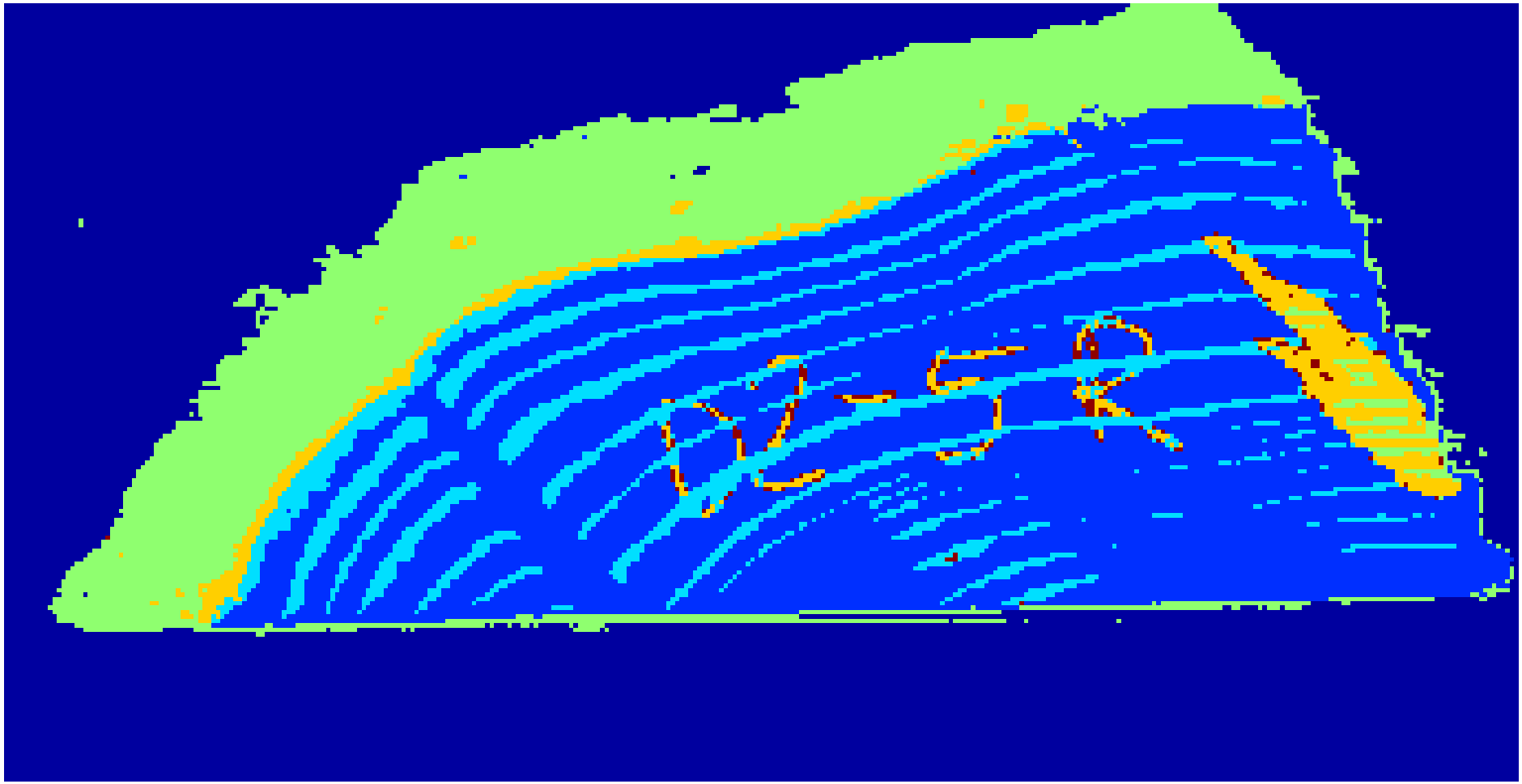
A Gowen, Hyperspectral Chemical Imaging: principles and Chemometrics

hyperspectral imaging

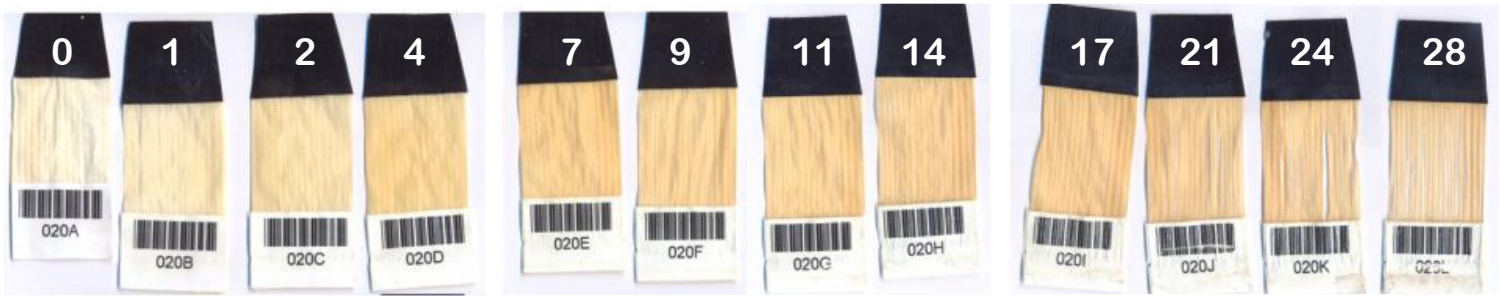


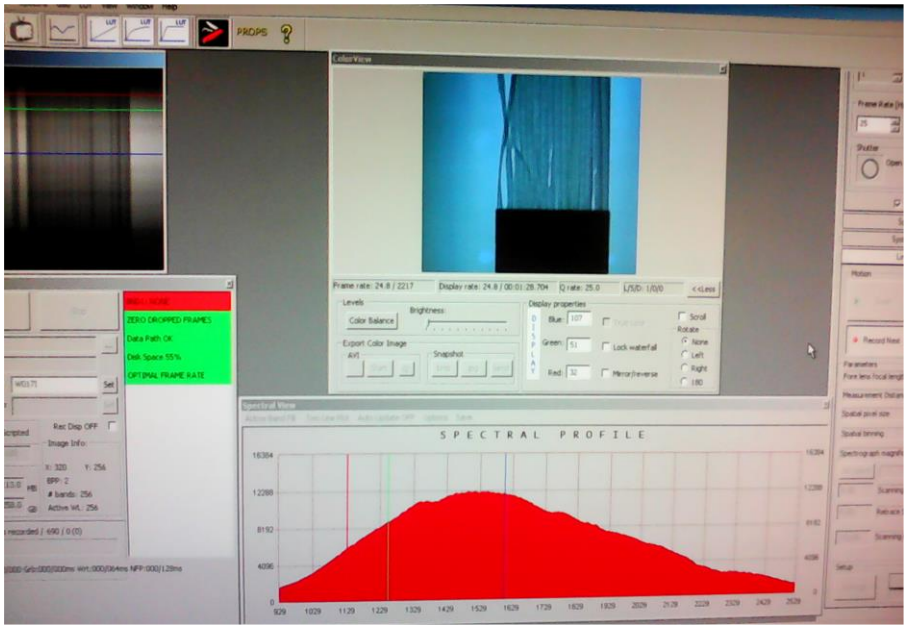


Case #1: “demo wood”

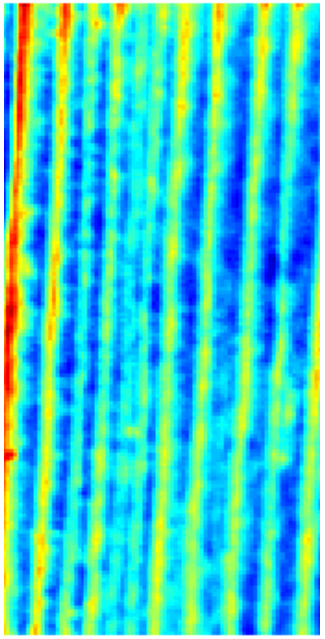


Case #2: weathered wood

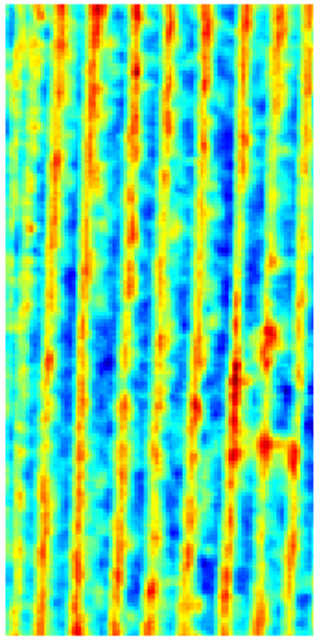




a)

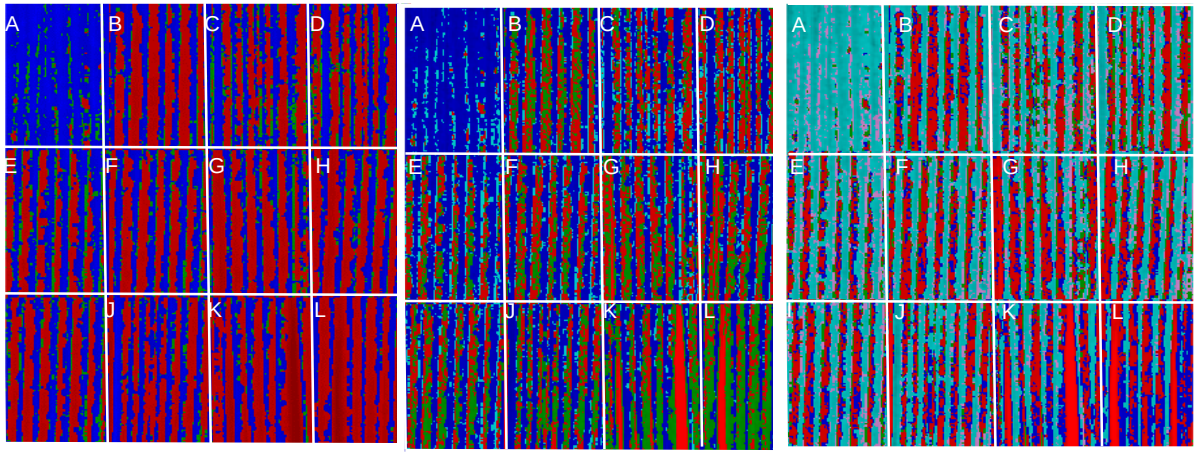


b)

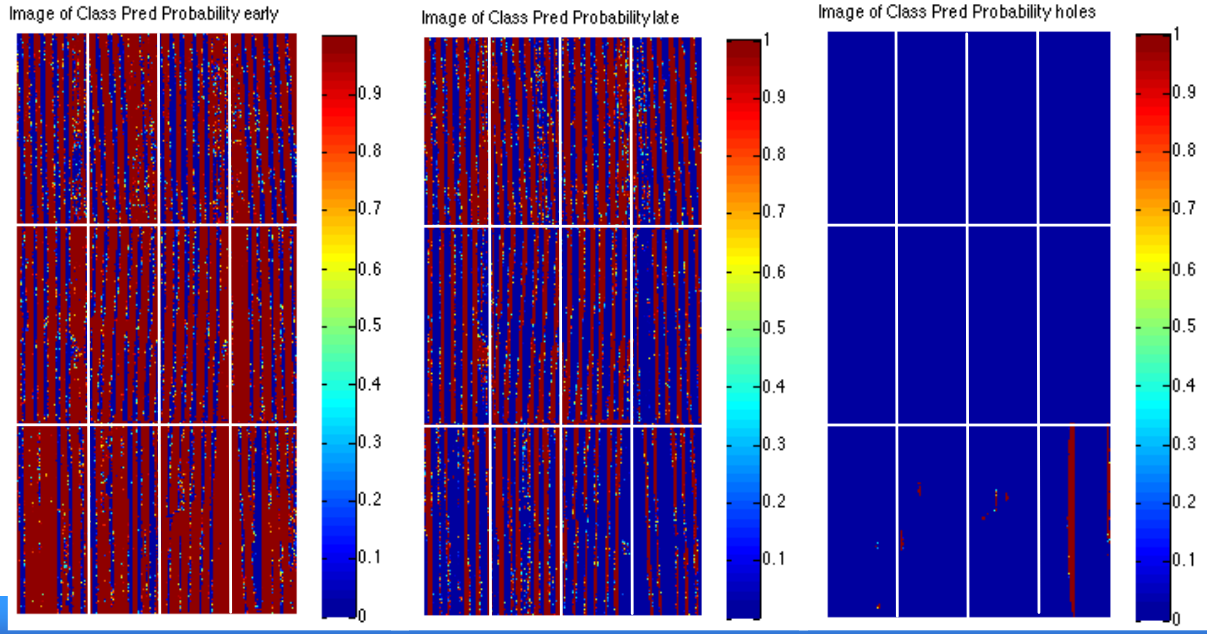


PCA analysis performed on not weathered (a) and sample after 28 days of weathering (b)

Classification - clustereing

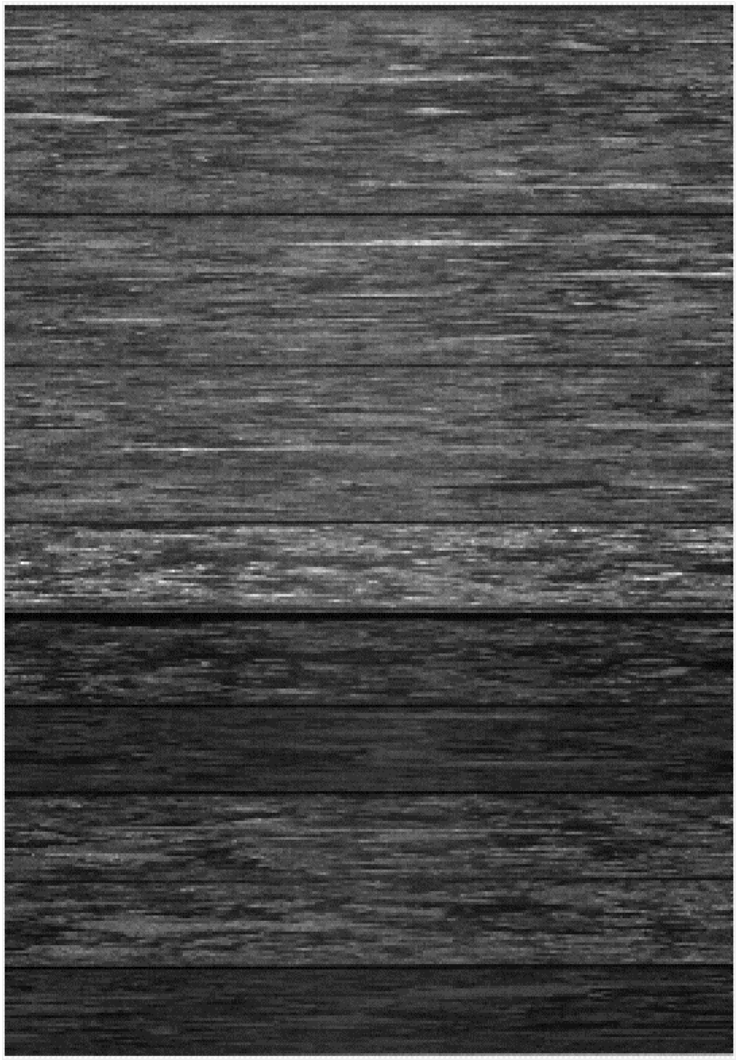


unsupervised:
K-means clustering on the mosaic of weathered wood after pre-selecting 3, 4 and 5 classes

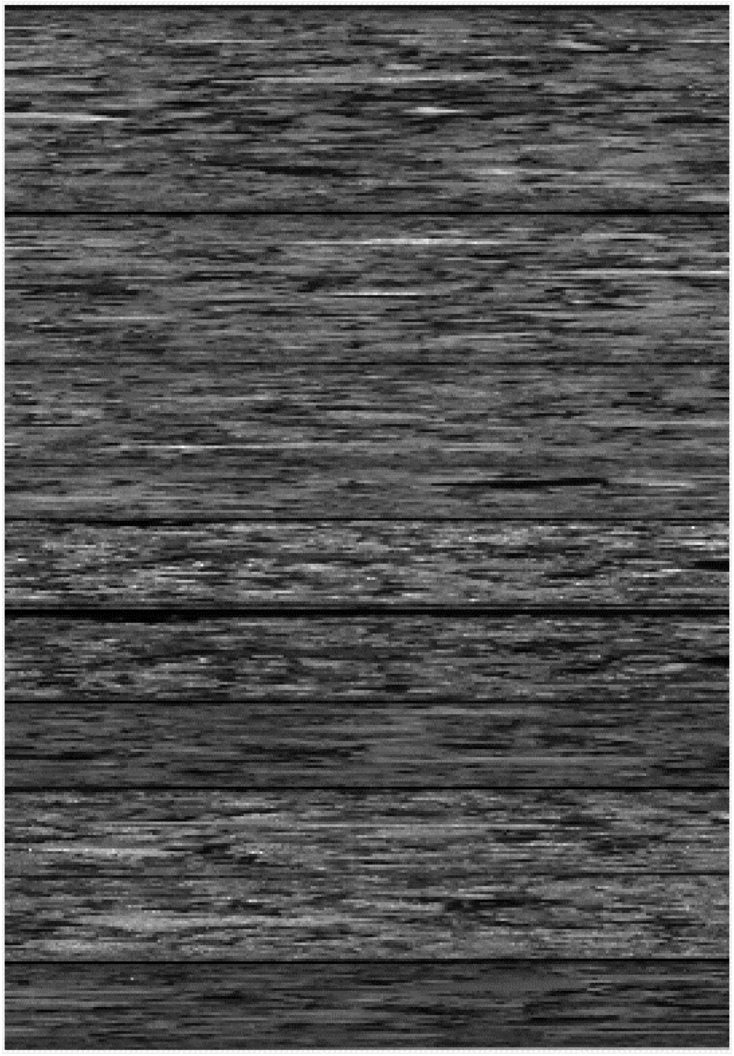


supervised:
PLS-DA on the mosaic of weathered wood used for discrimination of early and late wood and crack detection

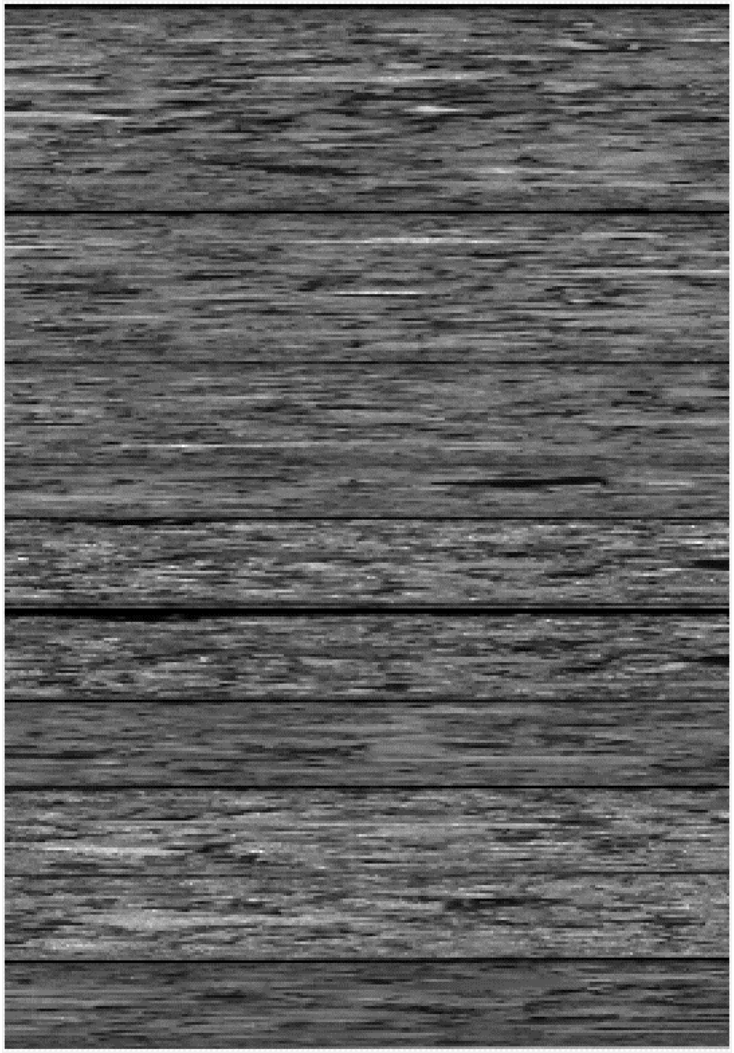
hyperspectral image: 420nm



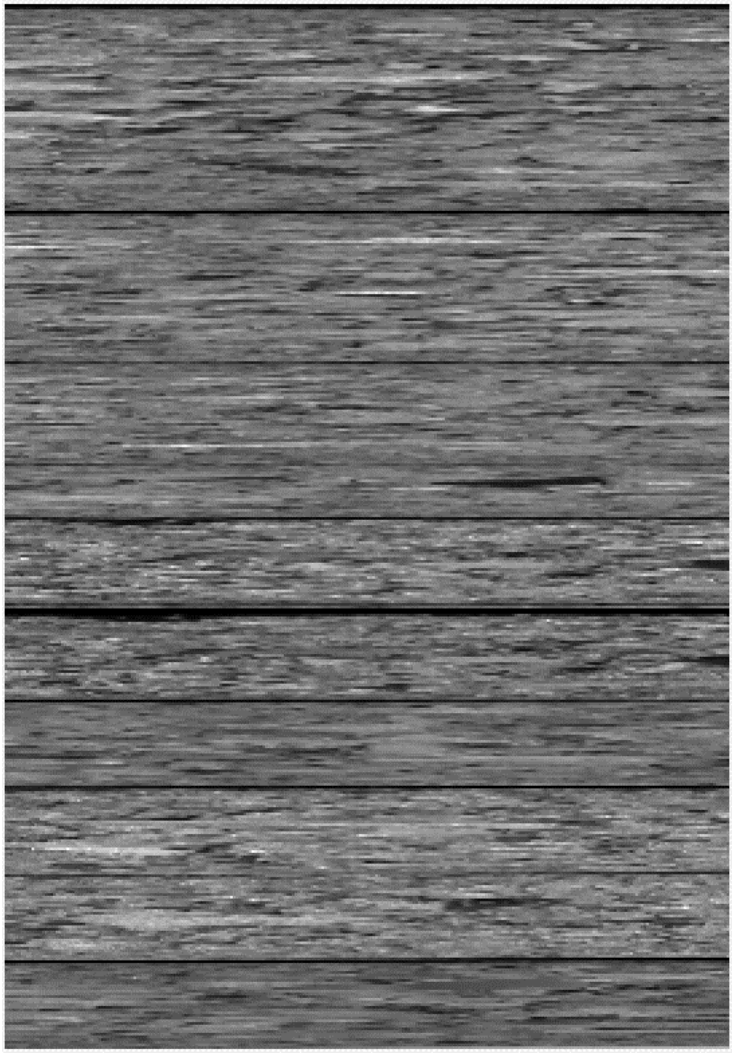
hyperspectral image: 550nm



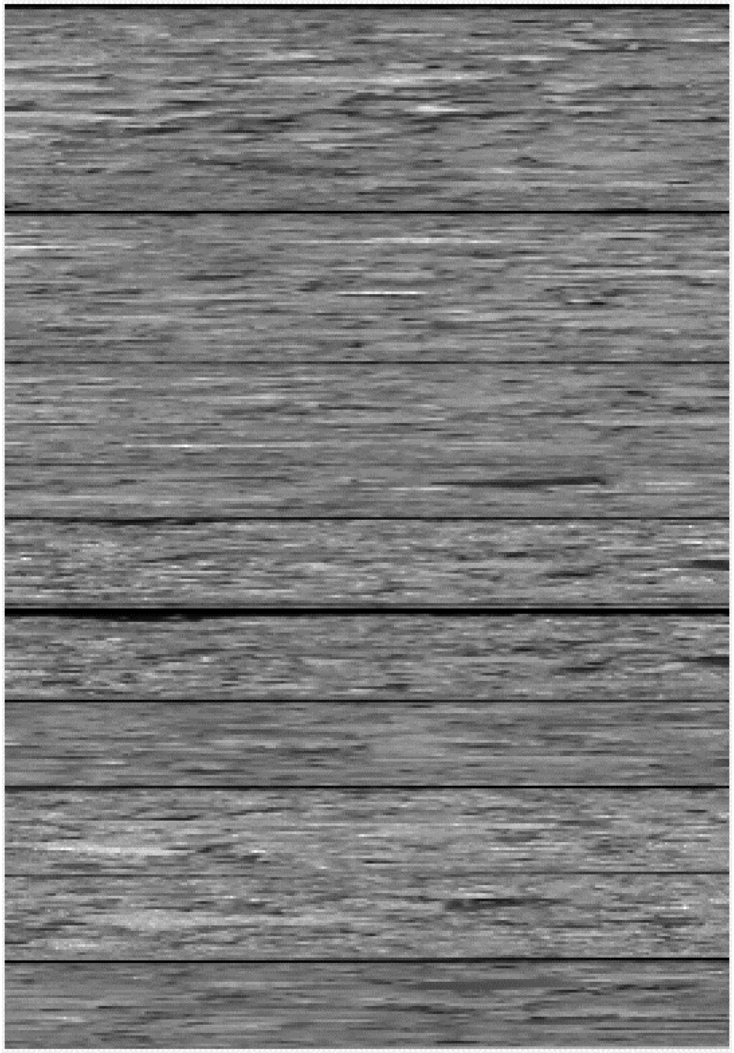
hyperspectral image: 650nm



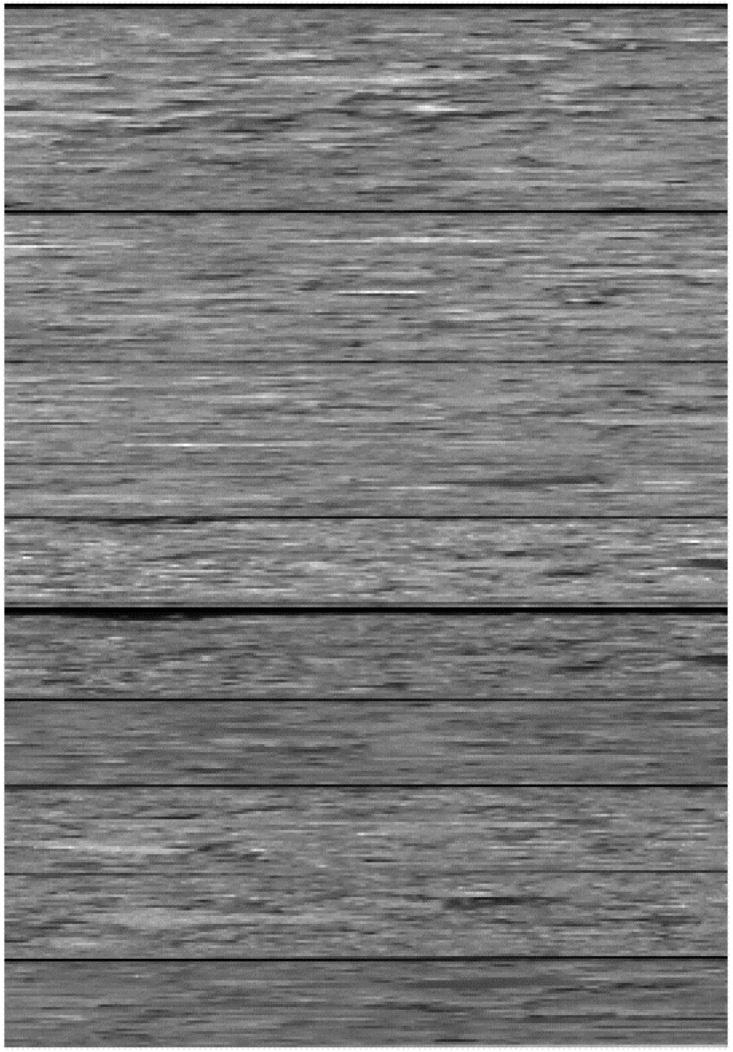
hyperspectral image: 750nm



hyperspectral image: 850nm



hyperspectral image: 950nm



hyperspectral imaging scanner

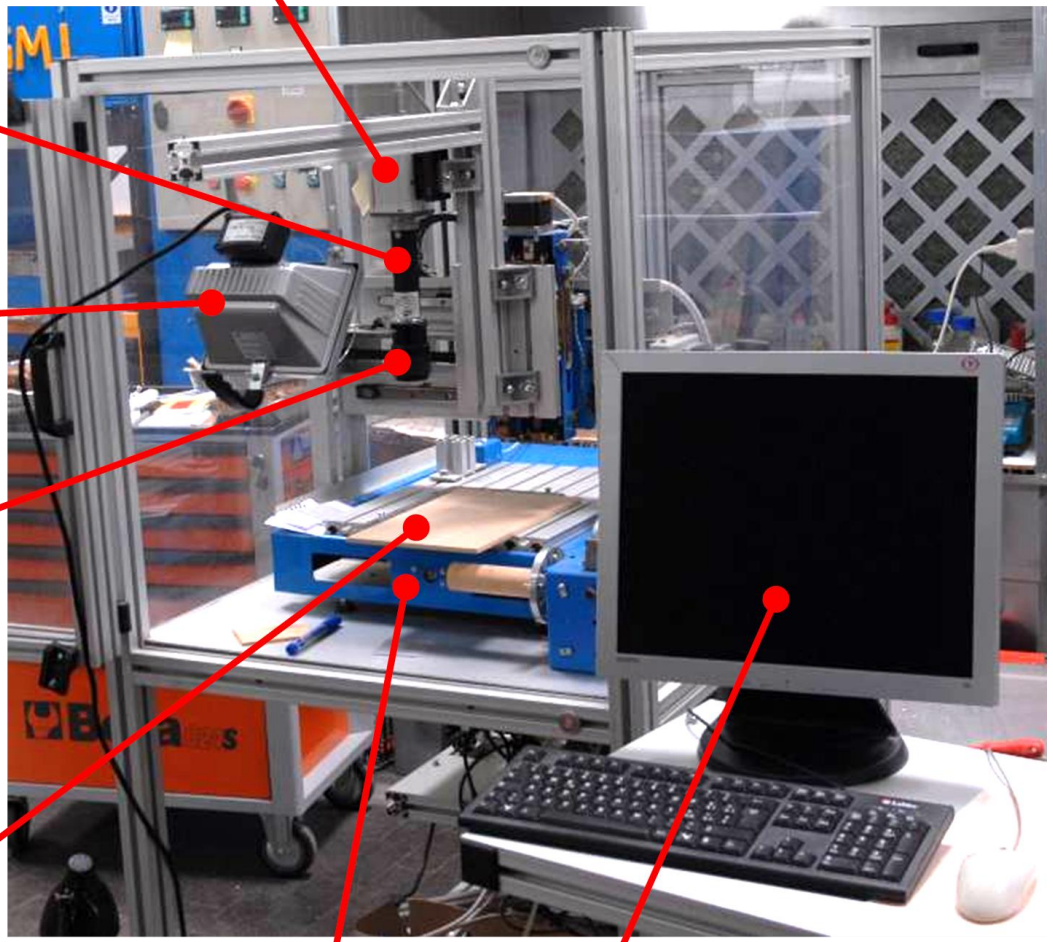
high sensitivity CCD camera (Hamamatsu ORCA-5)

spectrograph
(Specim V10)

light source

telecentric lenses
(Computar TEC-55)

sample



laboratory CNC machine

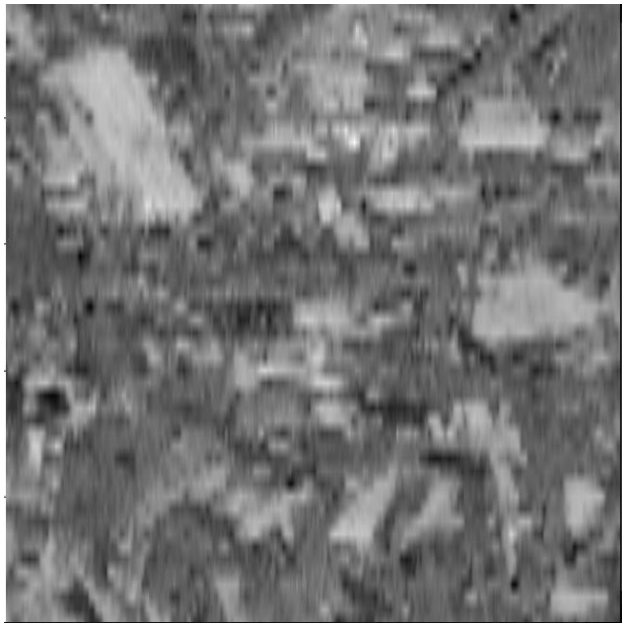
computer

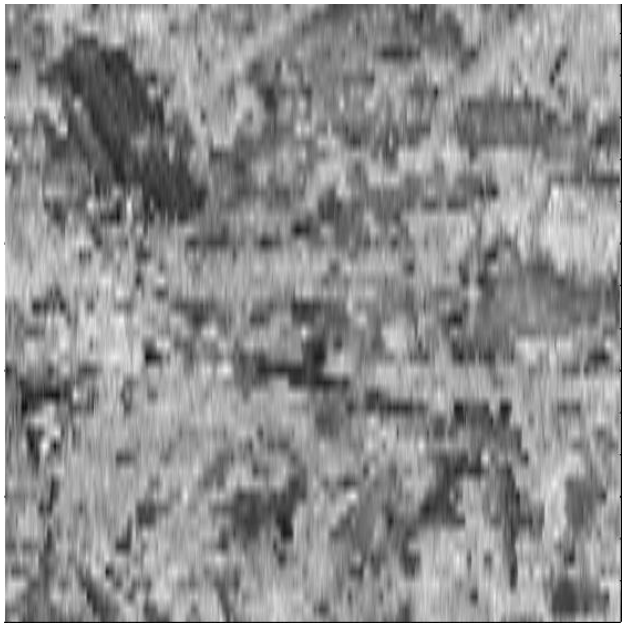
The data are in a form of the 12-bit **gray images** analyzed with a **custom software**

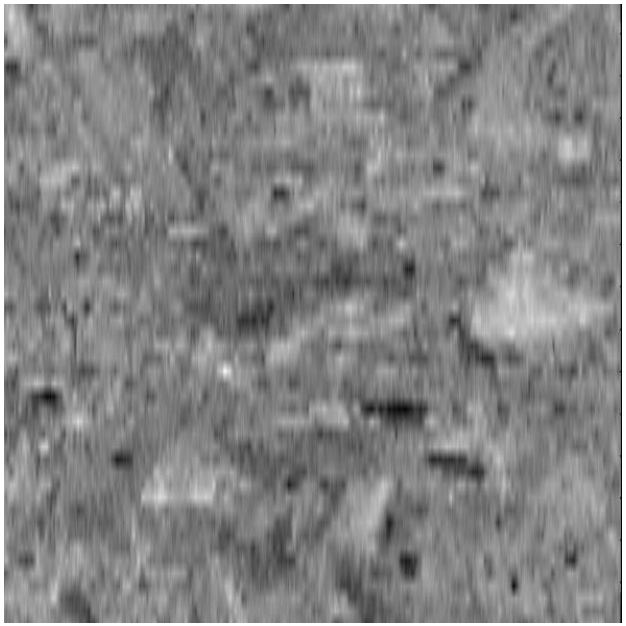
CIE Lab color maps

as measured with hyperspectral imaging

CIE Lab colour coordinates (even if possessing important limitations)
are considered as most suitable indicators characterizing colour properties







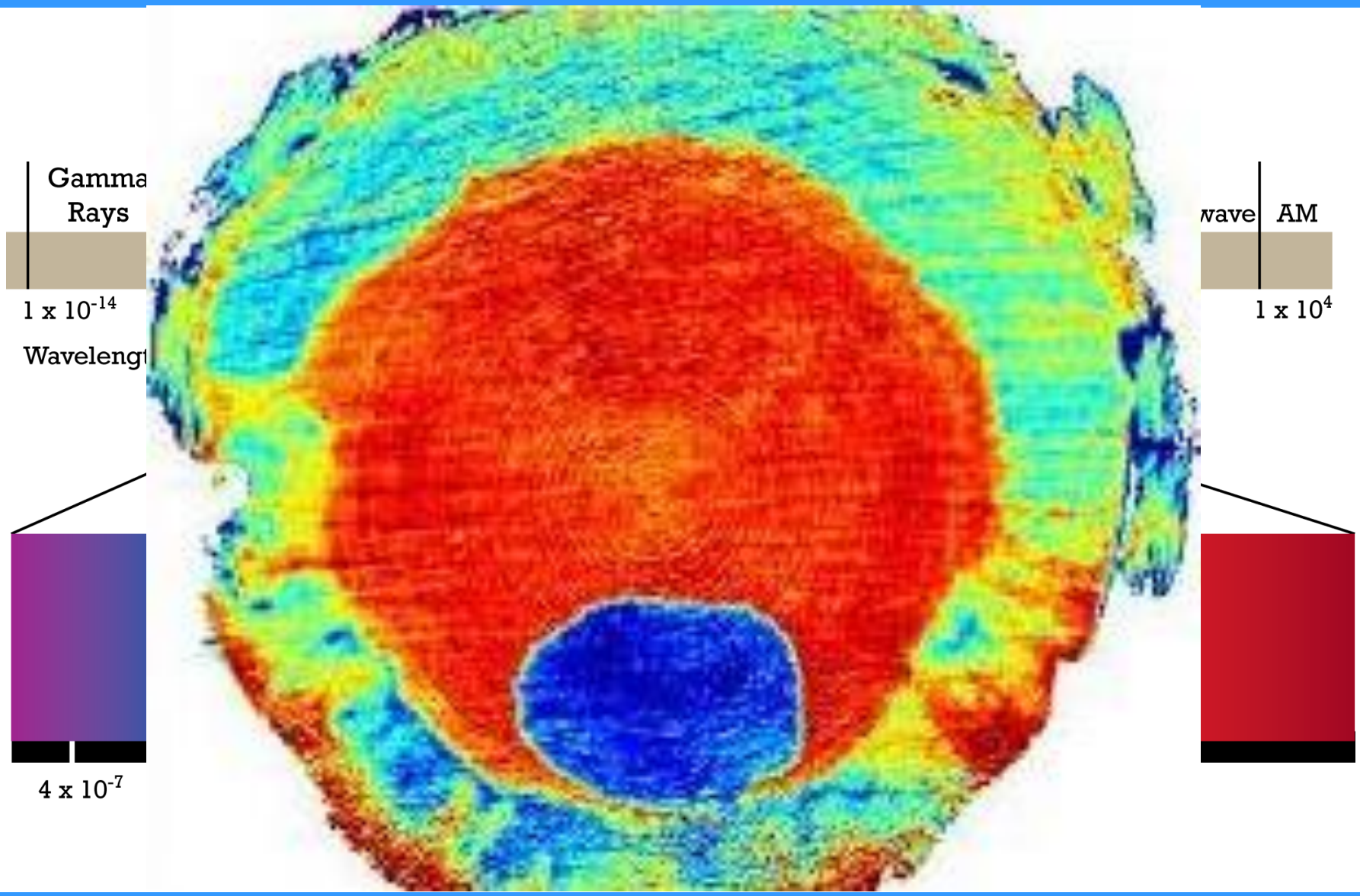
CIE L*

CIE a*

CIE b*

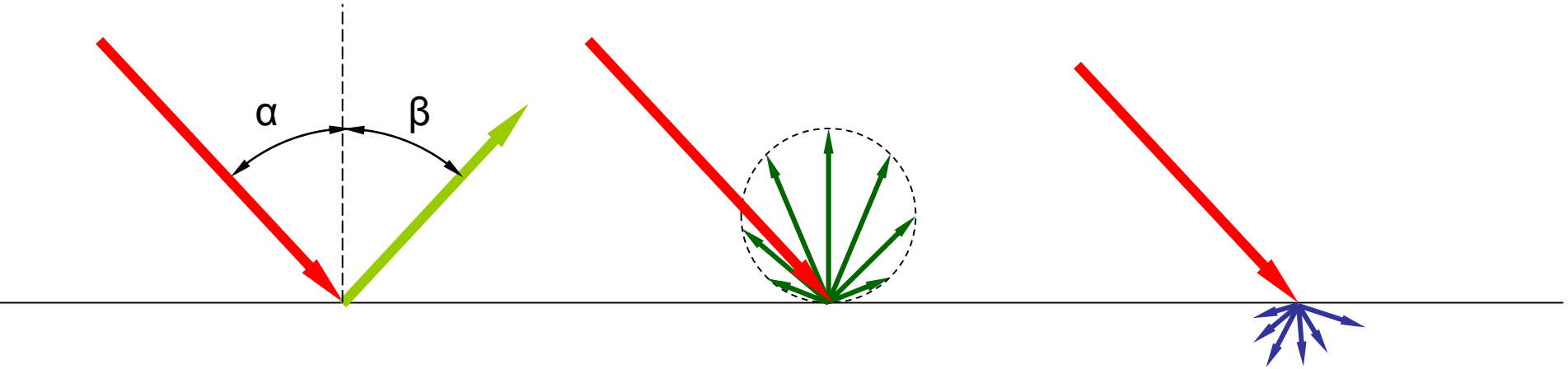
the color pattern of particleboard surface is very complex:
the composite includes various types of particles.

how about not visible “colors”



is color the only important impression?...

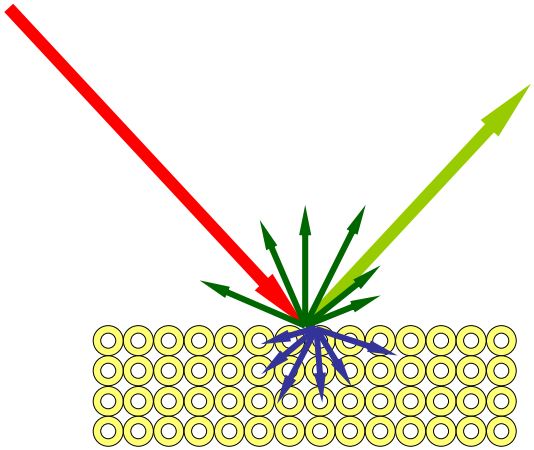
reflection of light from the surface



directional (specular)

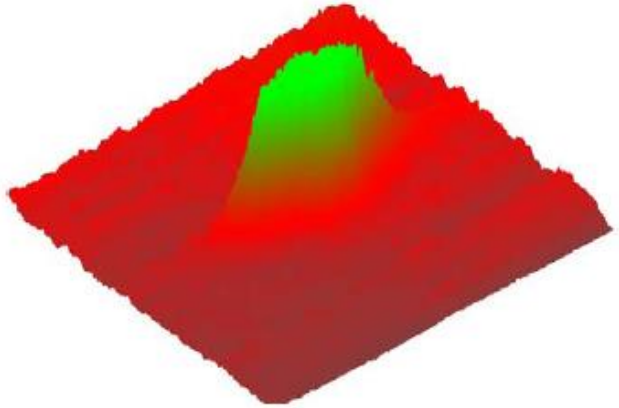
diffuse (Lambertian)

absorption/transmission

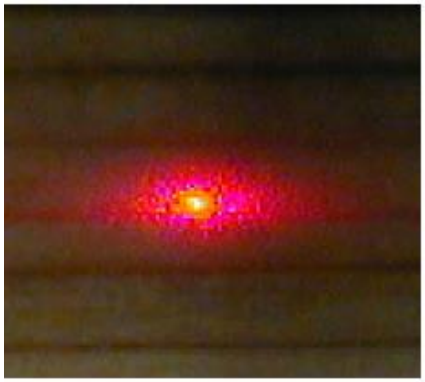


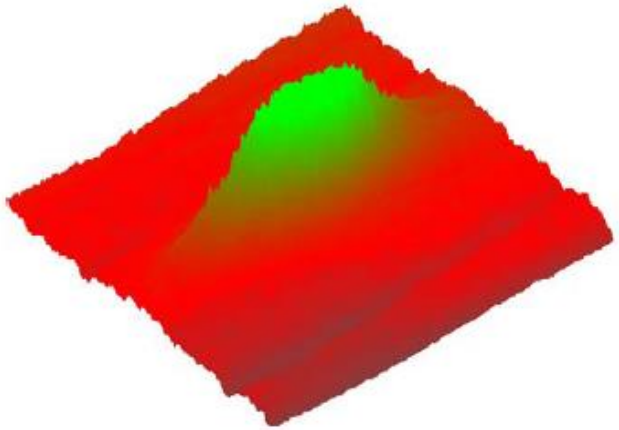
light on wood…

sakura

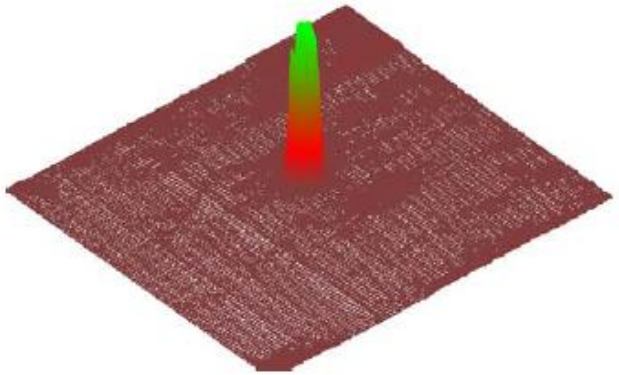


hinoki

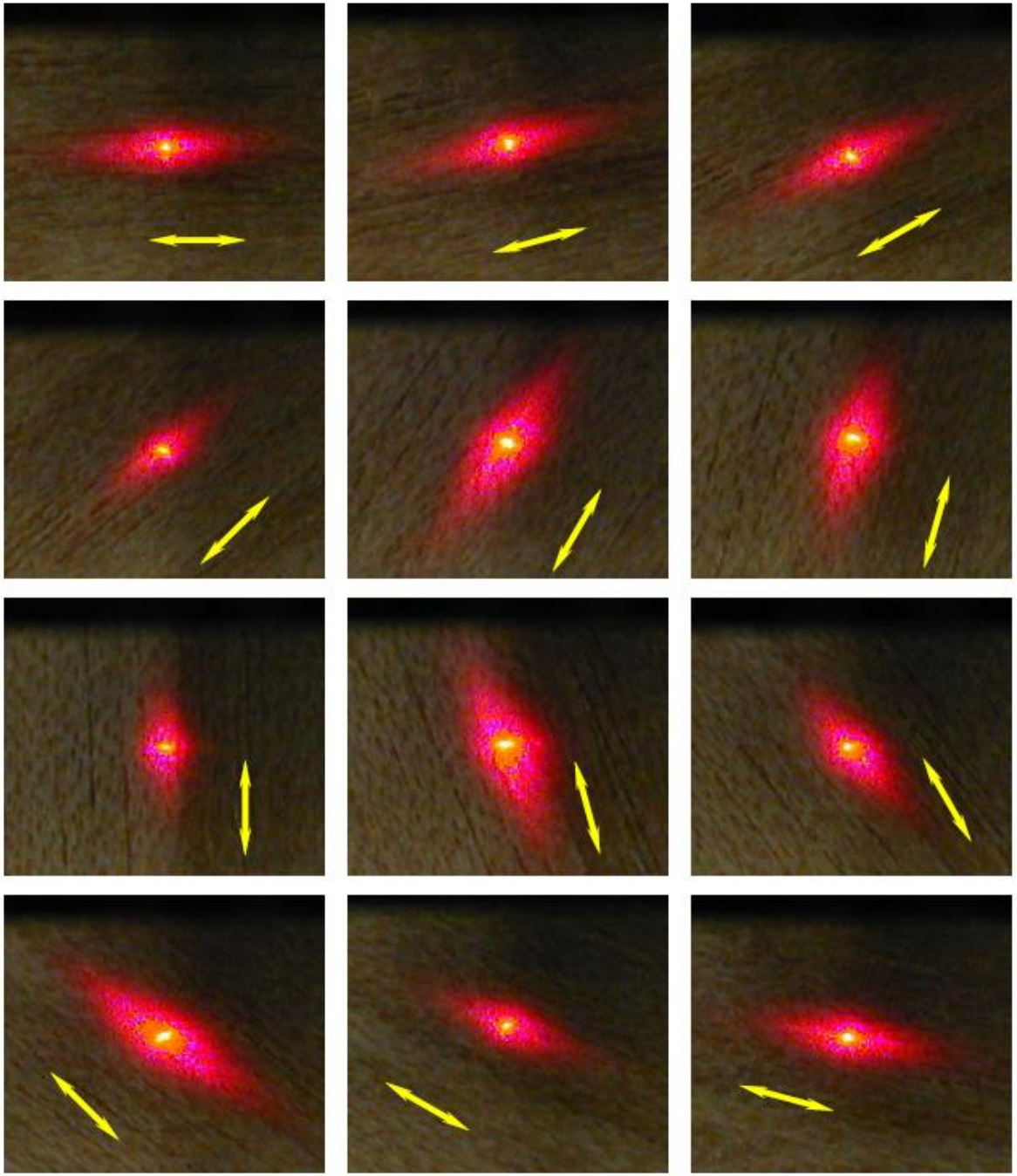




ebony



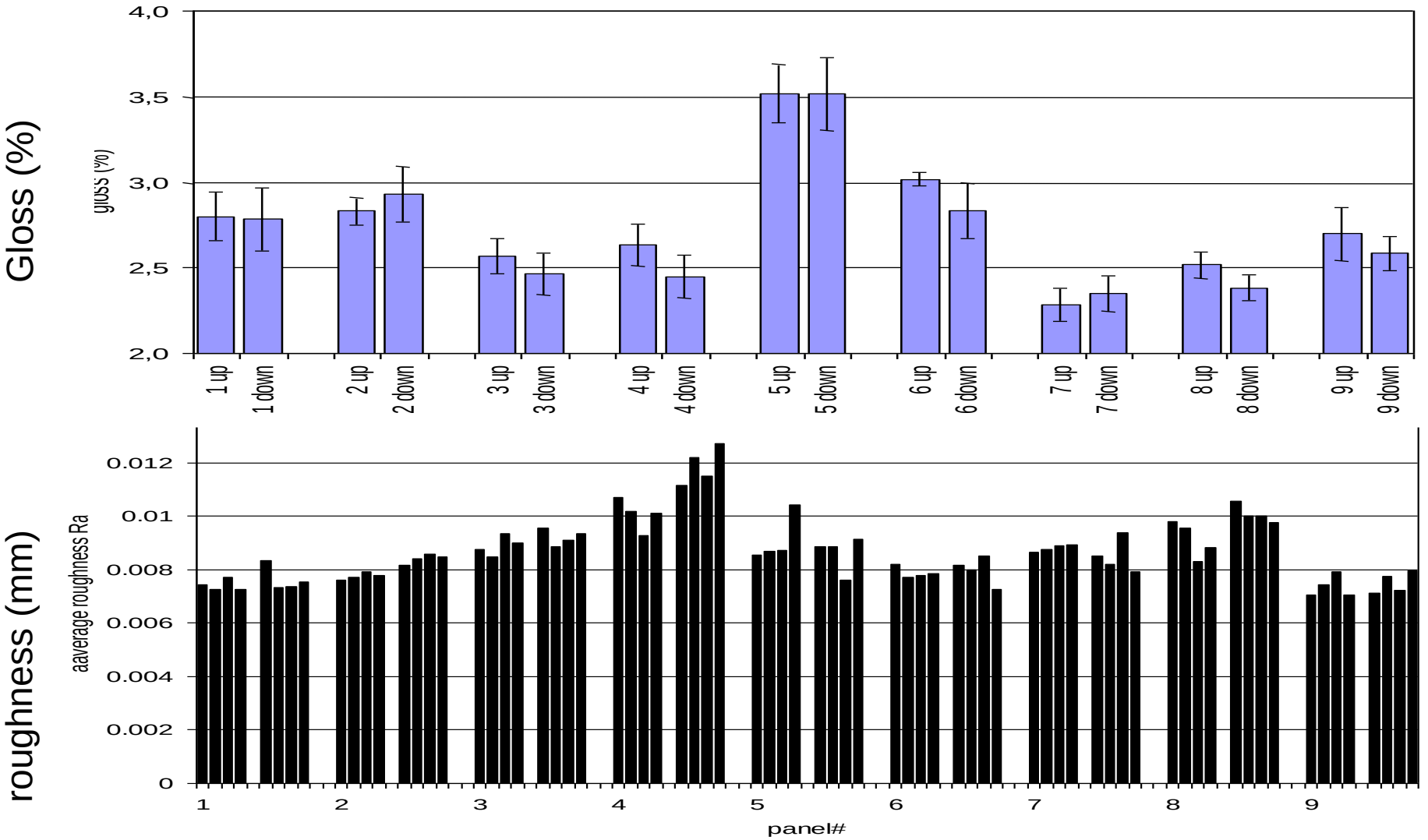
shape of the laser spot
illuminating surface
of different wood species



shape of the laser spot affected by the grain direction

measuring gloss

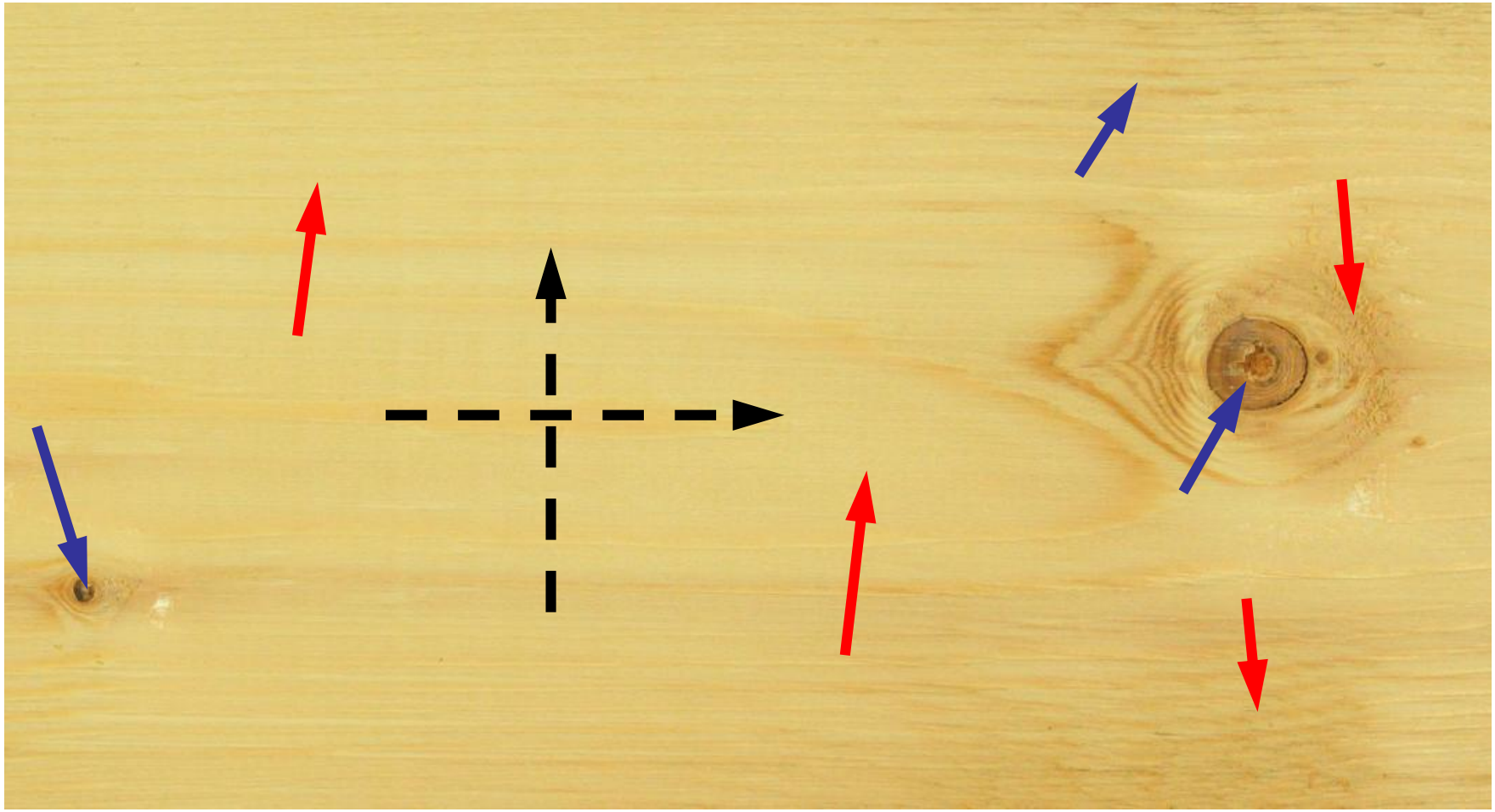
gloss <=> roughness



problems:

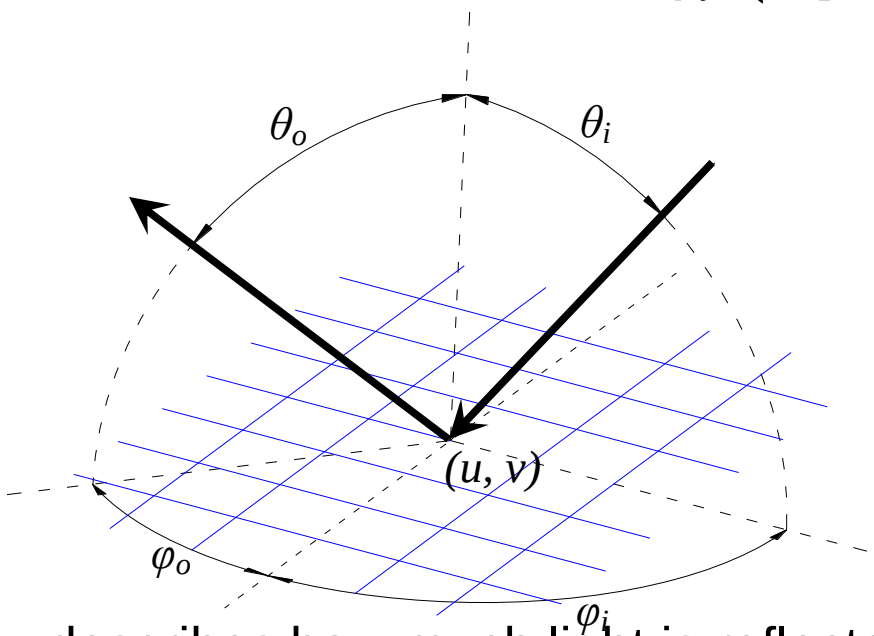
is the value of gloss same at each point over the surface?

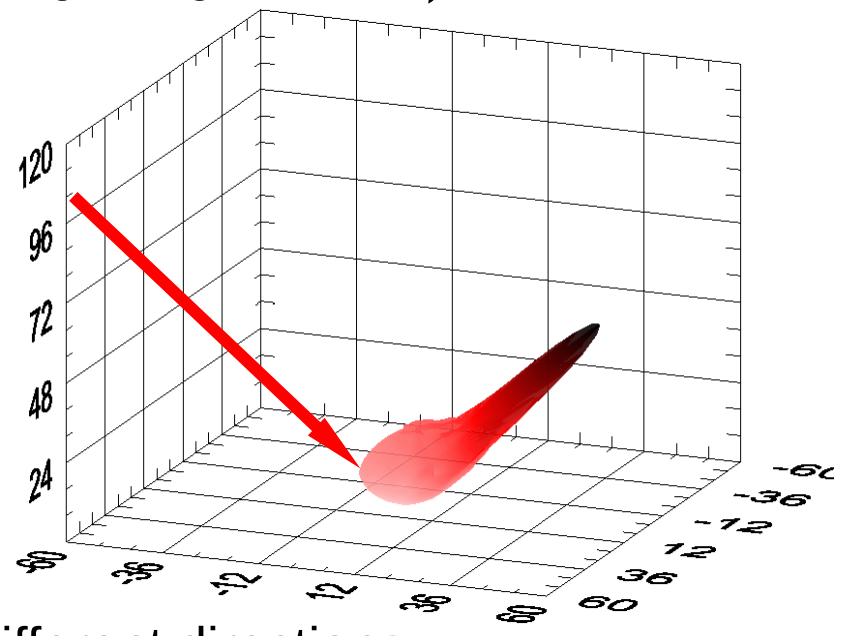
is the gloss same along and perpendicular to the fiber direction?



Bi-Directional Reflectance Function

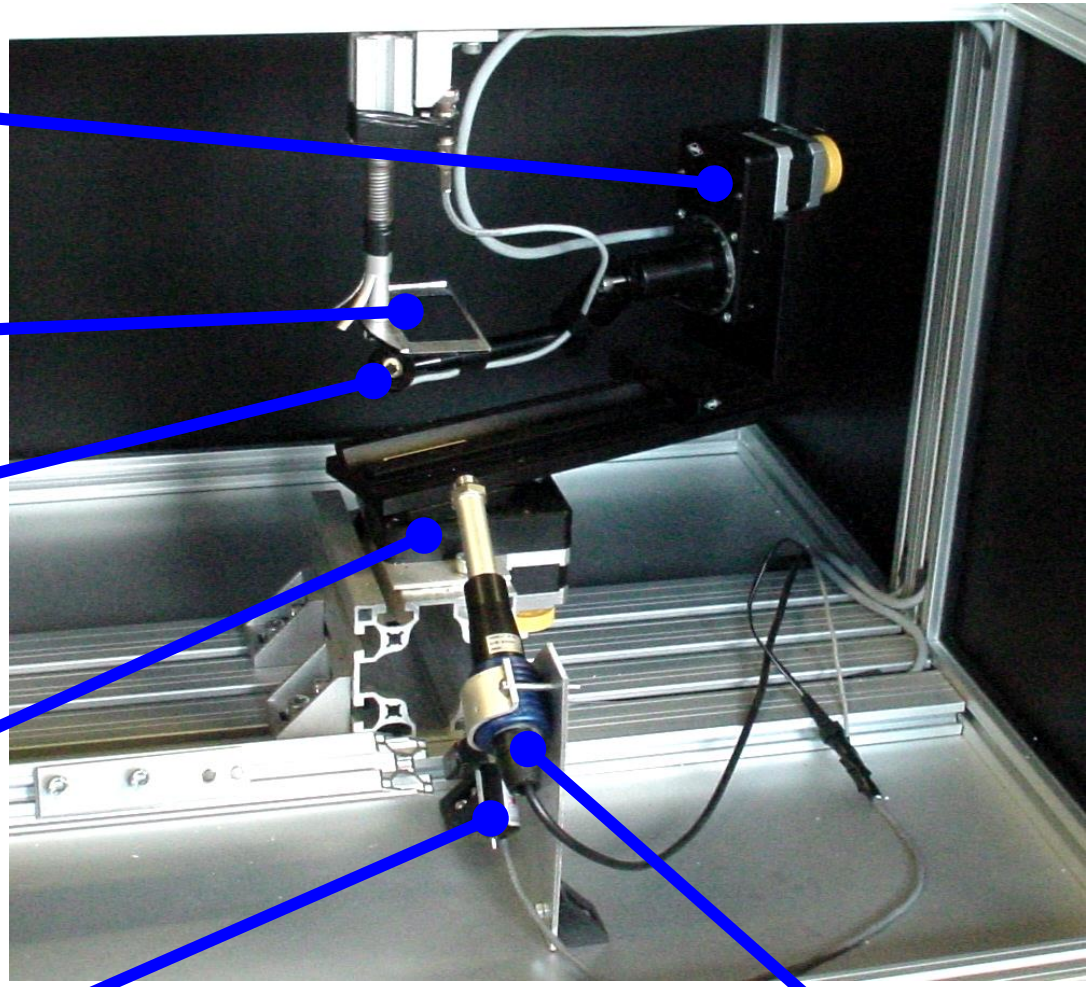
$$BRDF_\lambda(\theta_i, \phi_i, \theta_o, \phi_o, u, v)$$





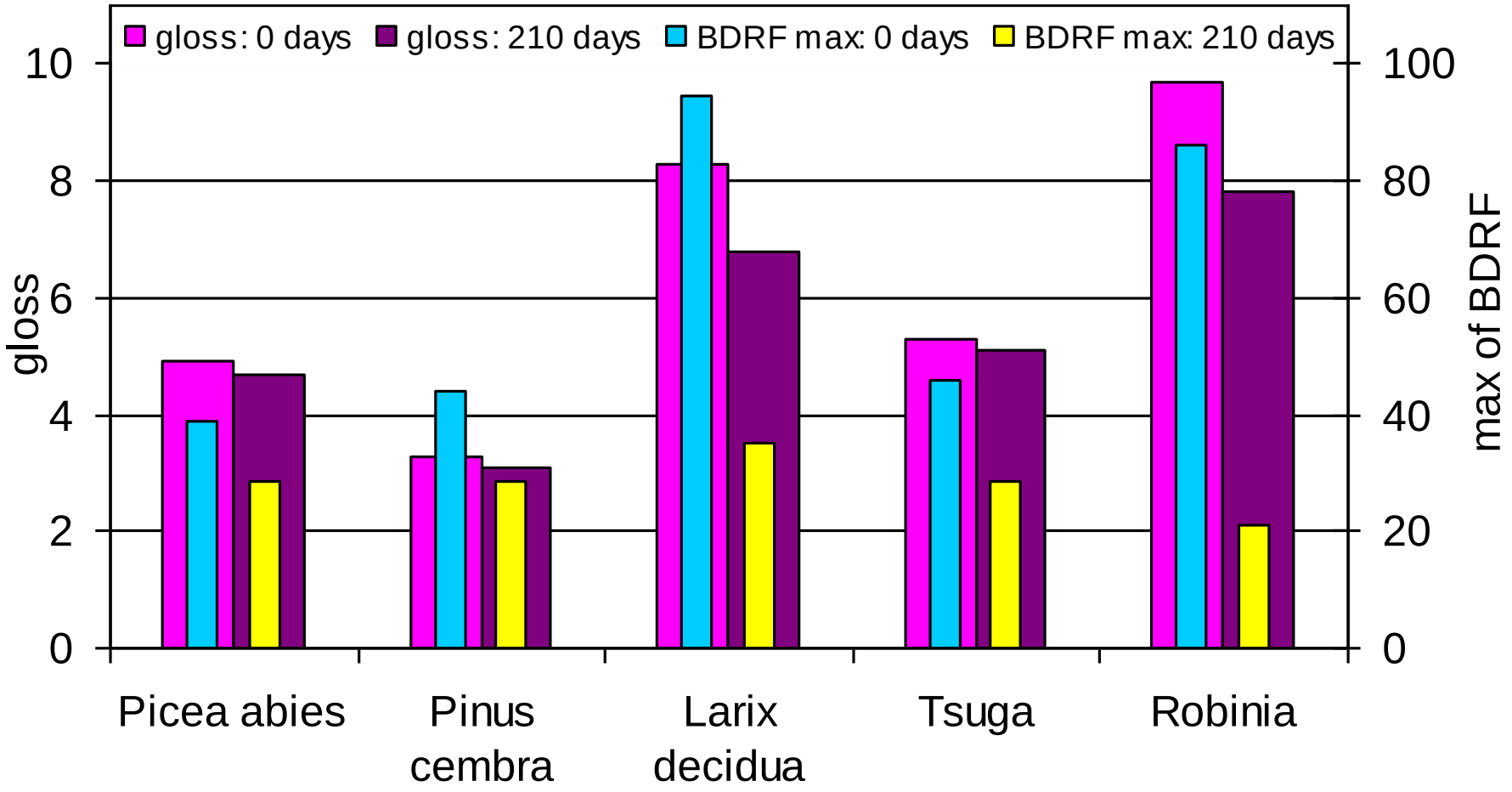
- describes how much light is reflected in different directions
- BRDF is a function of incoming light direction (θ_I and ϕ_i) and outgoing (view) direction (θ_o and ϕ_o) relative to a local orientation at the light interaction point
- light interacts differently with different regions of the surface (*u* and *v*), this is know as positional variance
- BDRF is a function of wavelength λ

3D gloss/BDRF scanner



The data are in a form of the 3 column matrix analyzed with a **custom software**

gloss <=> BDRF

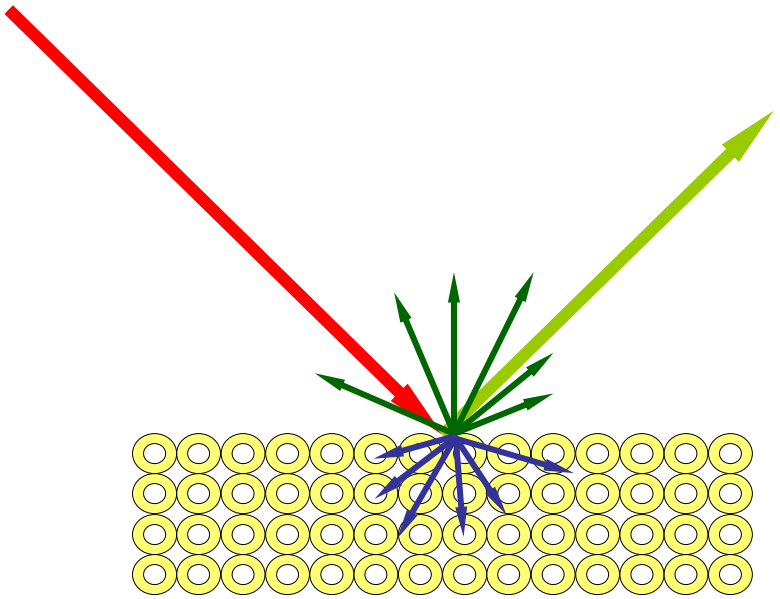


Measurement of gloss with “standard” device and 3D scanner (laser).
Different wood species coated with the same finish. Time of exposure: 210days.

problems:

why gloss (BDRF) is varying on the wood surface?

why it is so much space dependatnt?



wood surface roughness

I can't define roughness,

but I know it when I see it

(Thomas)

…roughness seems to be such a property, with the added difficulty it is not always so easy to define as a concept…

wood surface roughness: definitions

- *the **finer irregularities** of the surface texture that usually result from the inherent action of some production process, such as machining or wear*
- *the more narrowly spaced **components of surface texture***
- *each arithmetical mean value of arithmetical mean roughness (R_a)… which are **the parameters** expressing the surface roughness at each part sampled randomly from the surface of the object*
- *a **texture** that is not smooth but is irregular and uneven*
- *the **geometrical detail** of a solid surface, relating particularly to variations in height*
- *the **deviation** of the actual surface topography from an ideal atomically smooth and planer surface*

what is a smooth surface?

- customer:

  surface giving good/pleasant impression

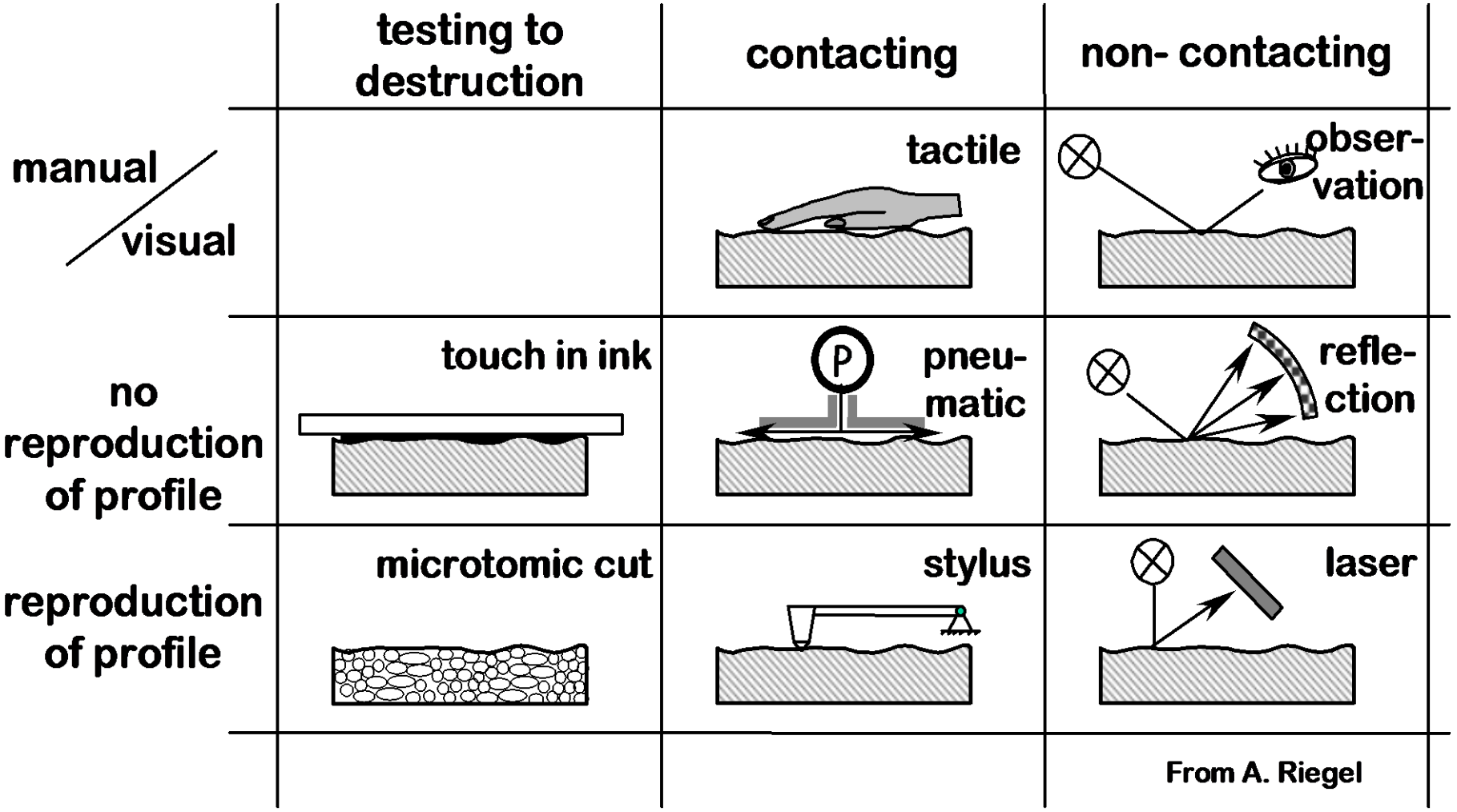
- engineer:

  surface which is characterized with parameters being within certain limits

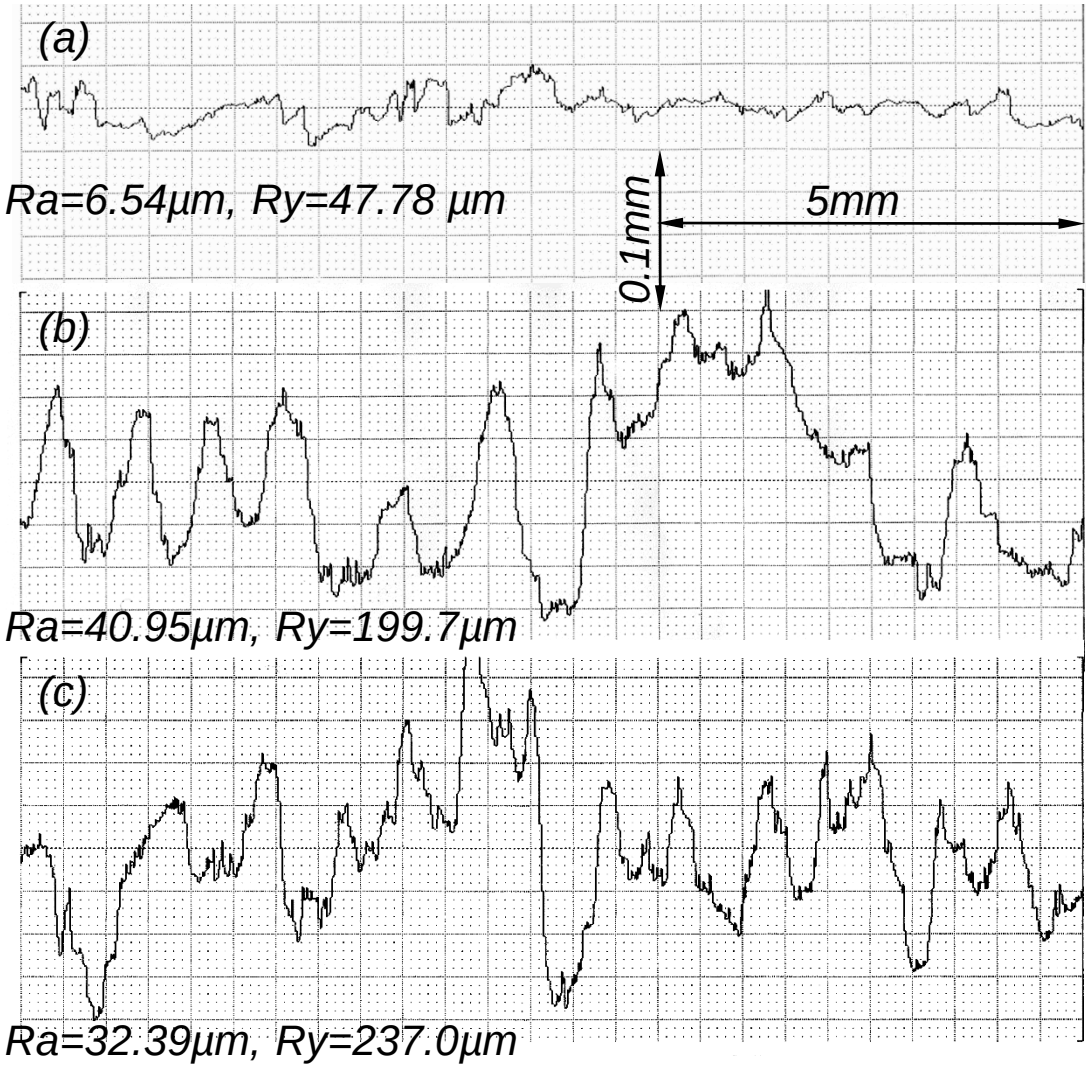
- researcher:

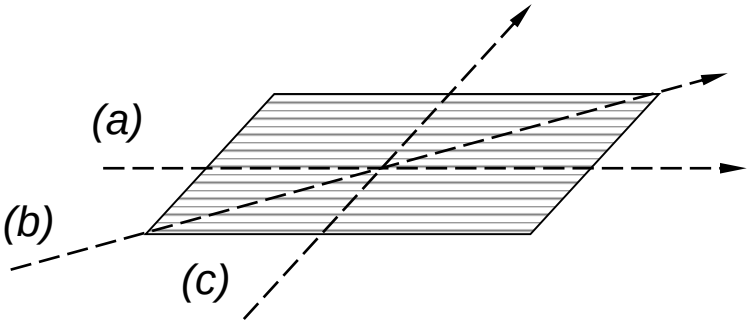
  surface where geometrical deviations approach zero (microtome cut?)

surface roughness: evaluation methods

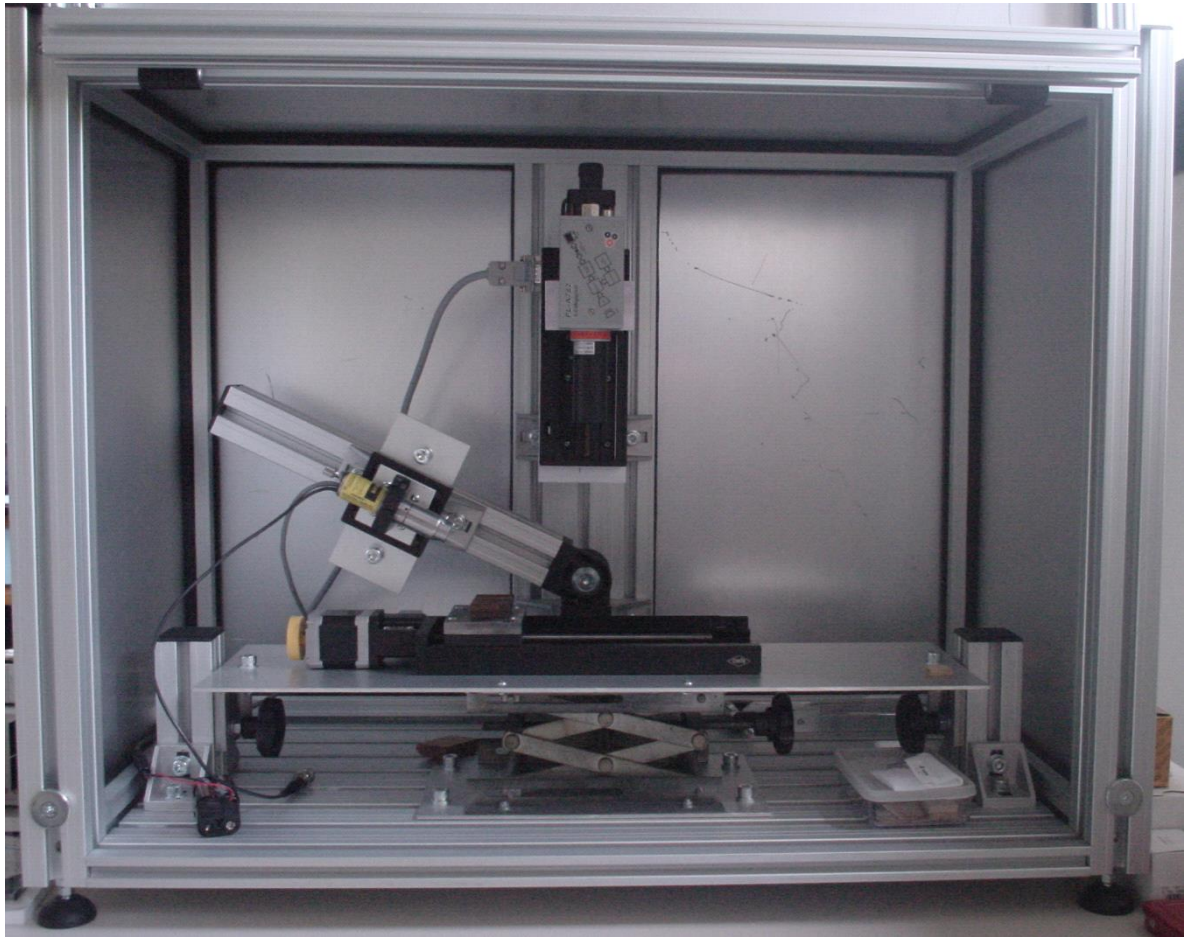


surface in 2D



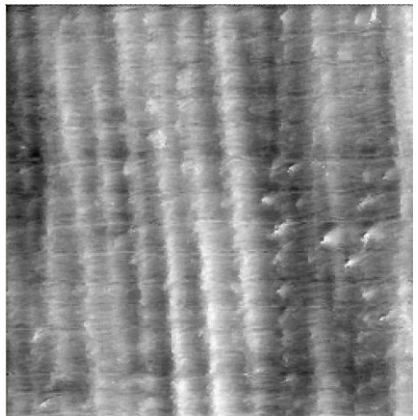


triangulation experimental platform

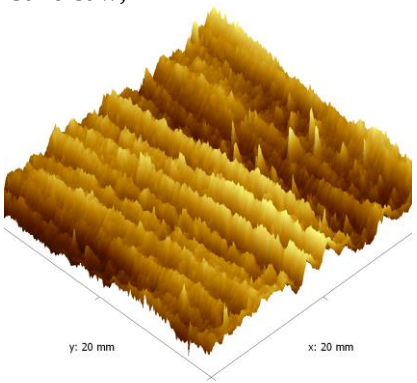


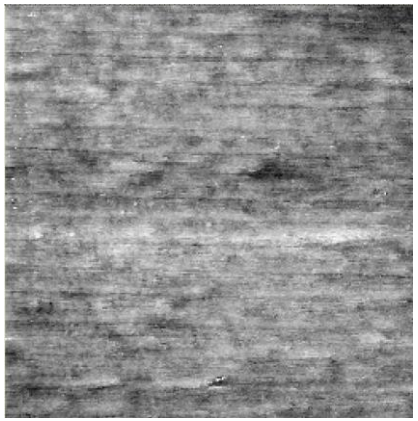
Configurations:

- structured light:
  - laser line
  - shadow
- light sources:
  - laser
  - fiber optics
  - LED
- lenses:
  - standard
  - macro/micro
  - telecentric
- cameras:
  - CCD
  - CMOS
- dark box
- mechanics

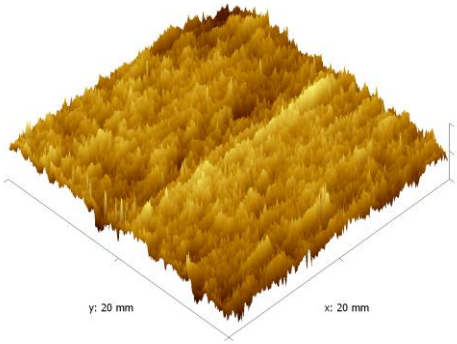


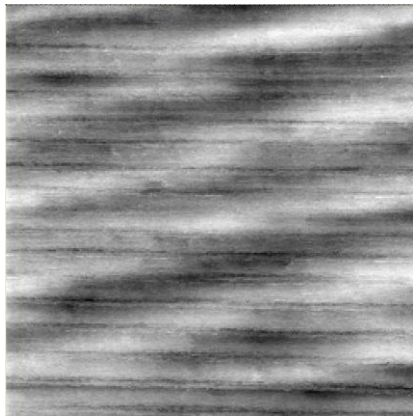
TMP; band saw, r



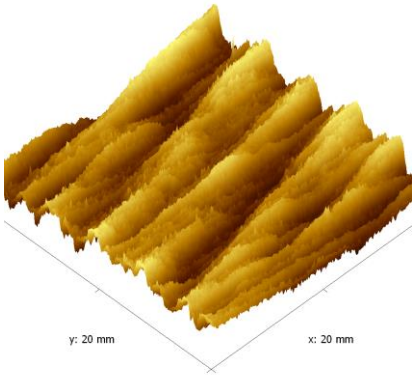


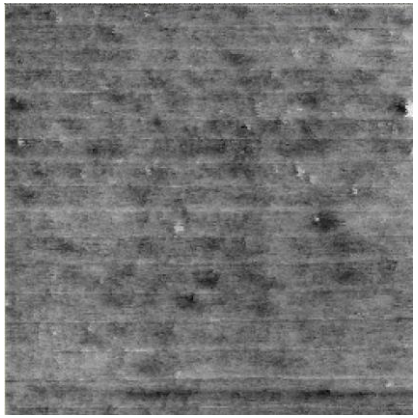
F4P; router, 4500rpm, r



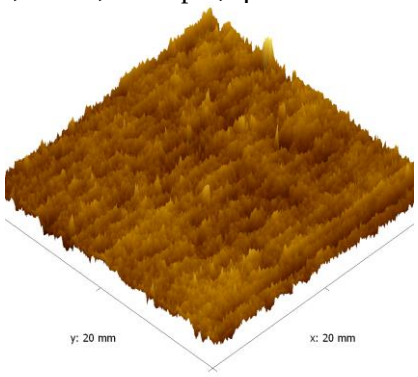


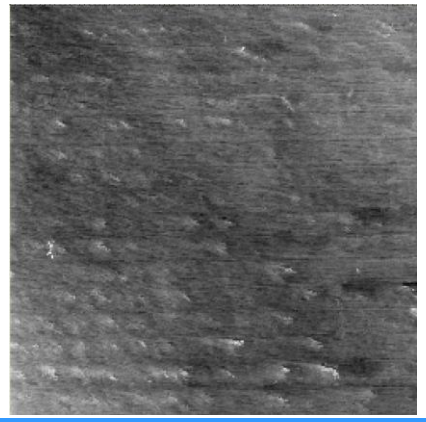
TMW; band saw, q



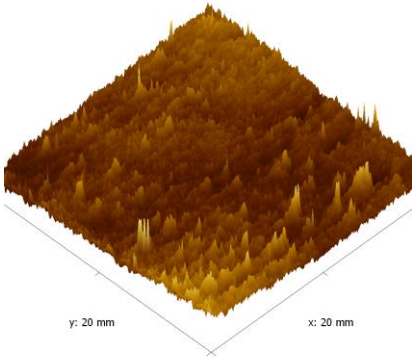


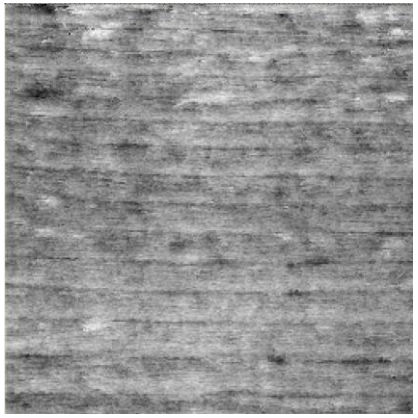
F4W; router, 4500rpm, q



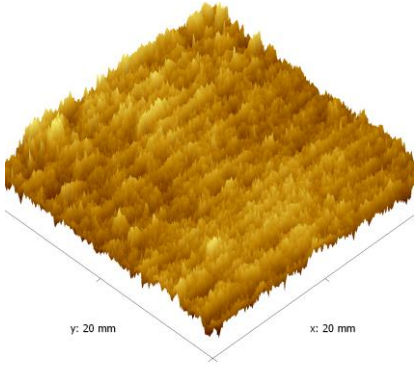


TWP; table circular saw, r



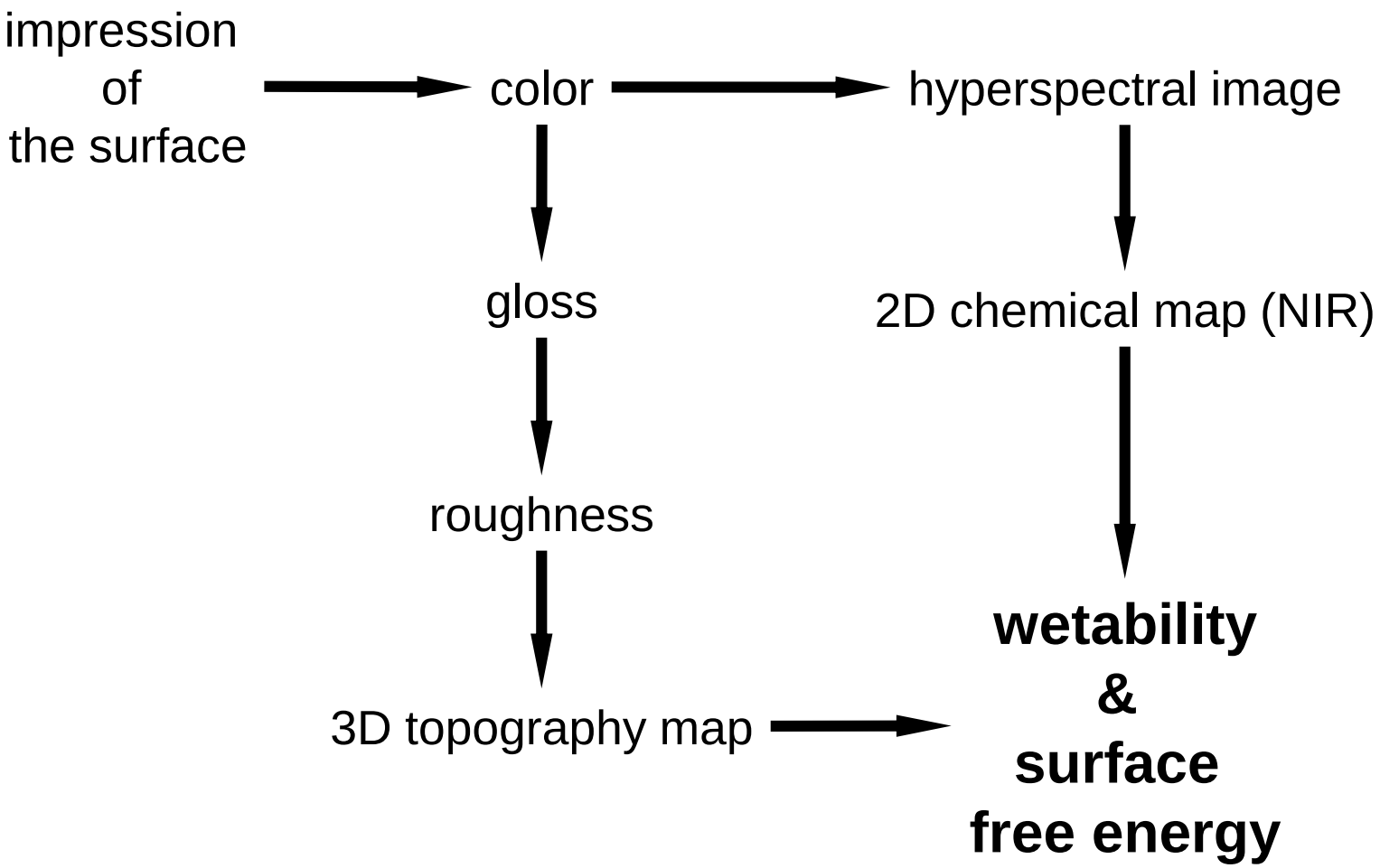


F9P; router, 9000rpm, r

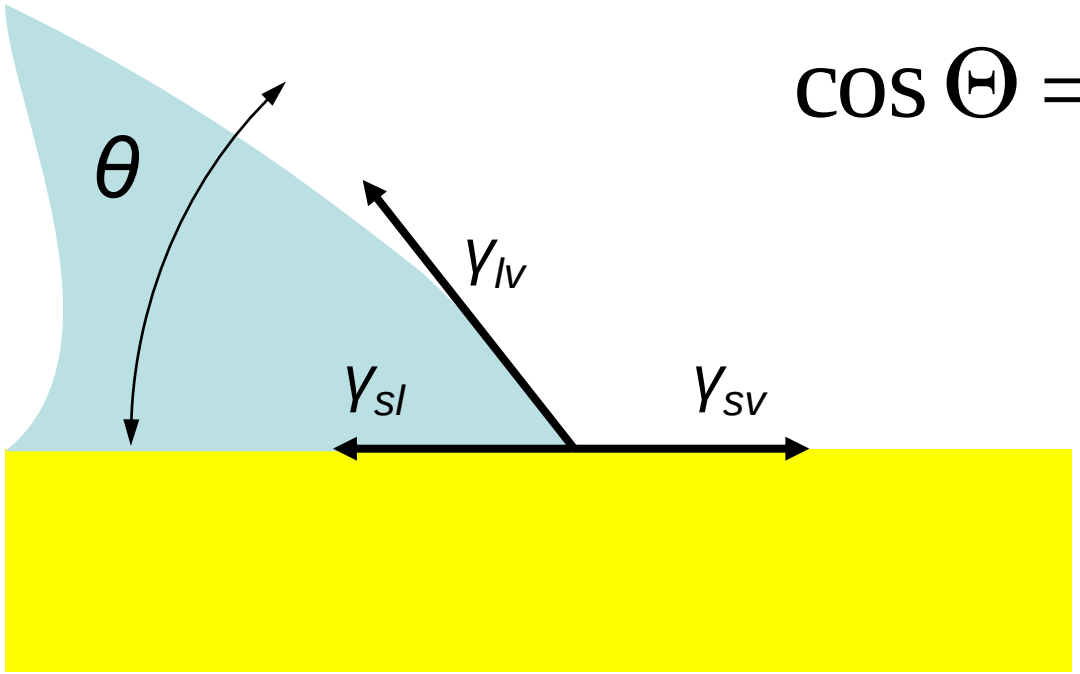


what can be done if combine

all the above information?



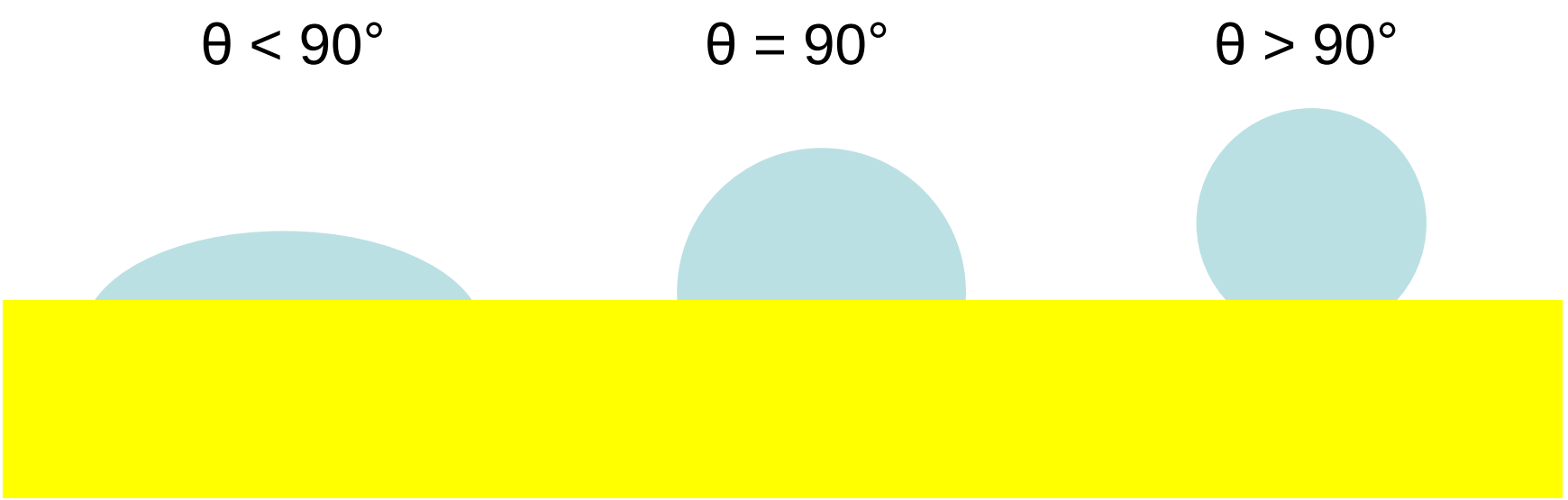
contact angle: the Young equation



$$\cos\Theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

- the contact angle θ is an indicator of the attitude of a surface to be wetted by a liquid
- it plays an important role in the wood industry and it is principally important in adhesion (coating, gluing, finishing)

surface wetting

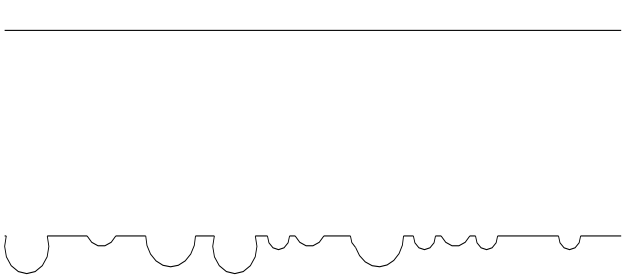


hydrophilic surface

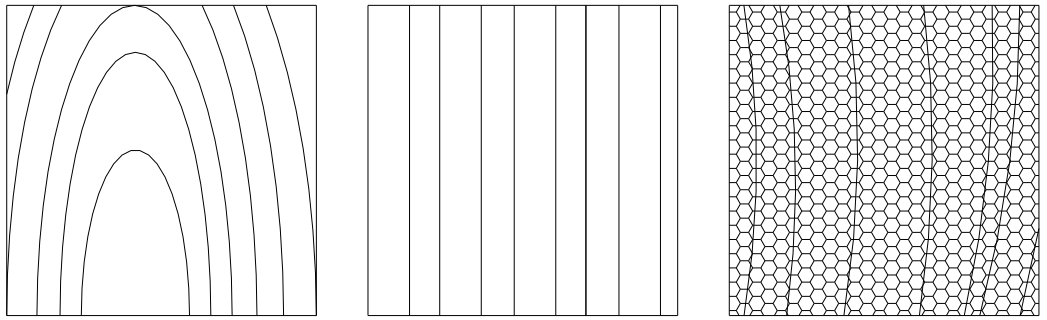
hydrophobic surface

drop on anisotropic/porous material

- the shape of the drop is influenced by the grain direction and surface (micro) roughness - that can modify the expected roundness
- the adsorption of the drop in the time providing a continuous change of the drop properties (volume) and its chemical compositin (extraction)
- the measurement can be difficulty reproducible (impossible?) at the same position on the surface

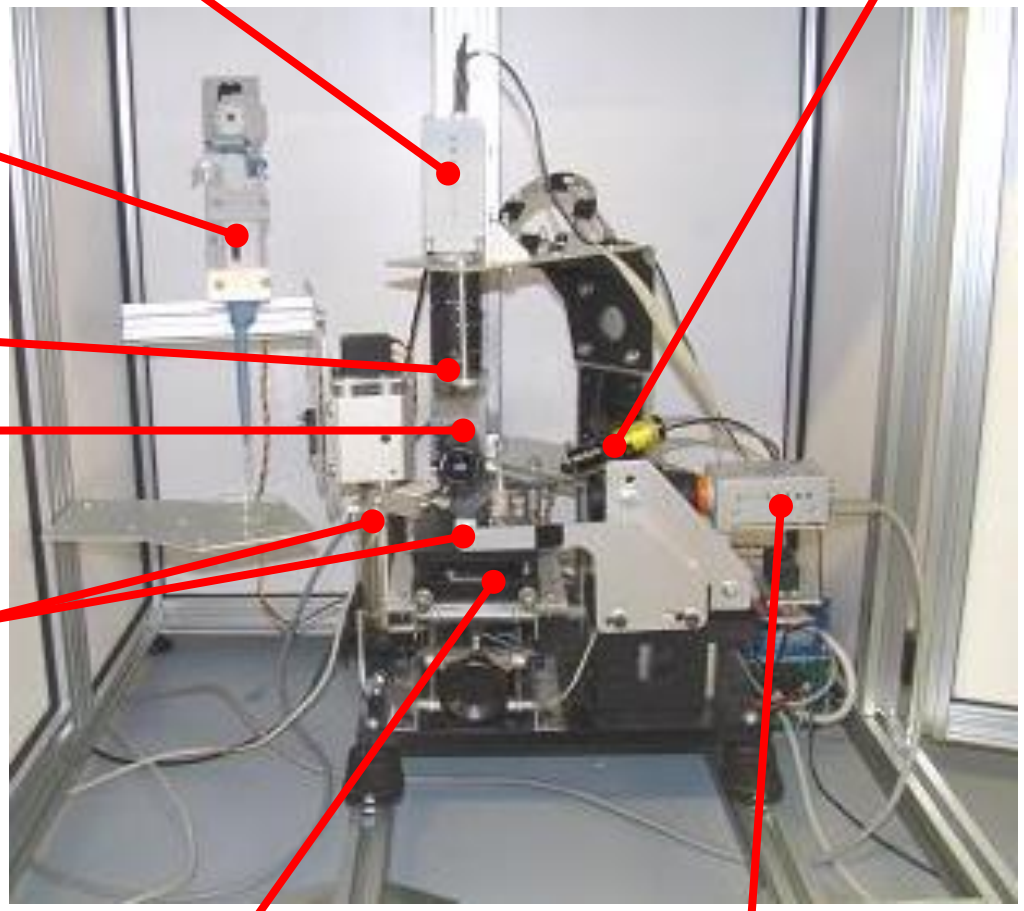


geometrical anisotropy



chemical anisotropy

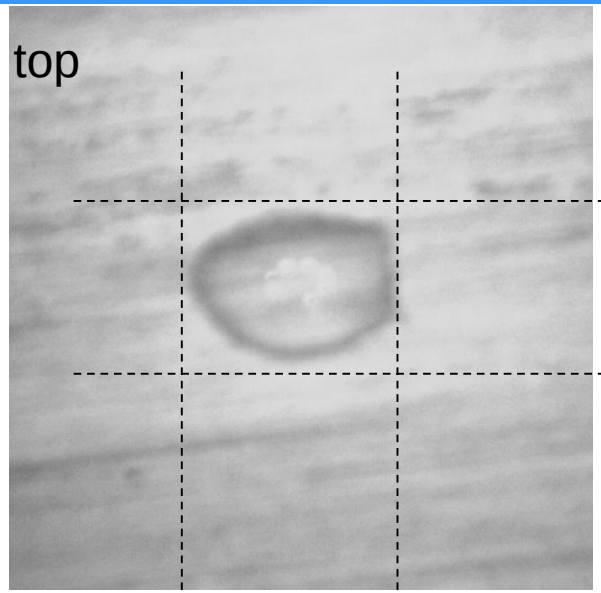
wetability scanner

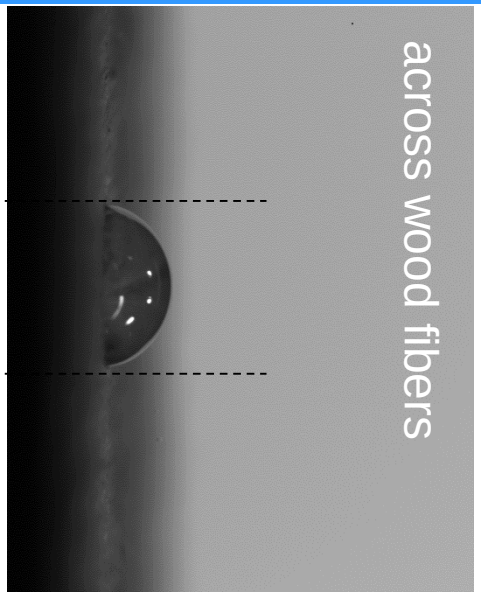


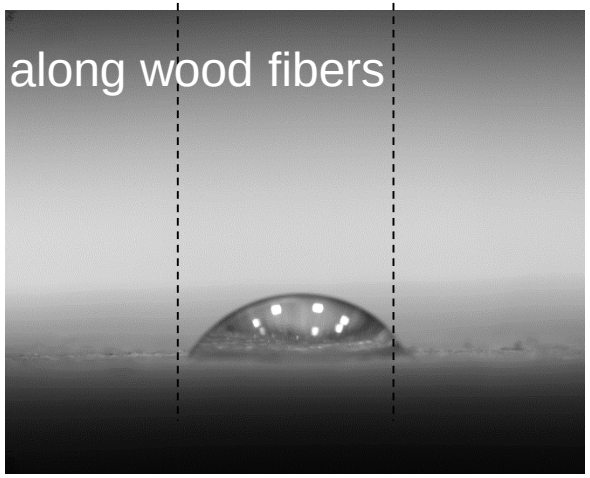
the robot is capable to put a **drop of a given volume** at focal plane of 3 cameras

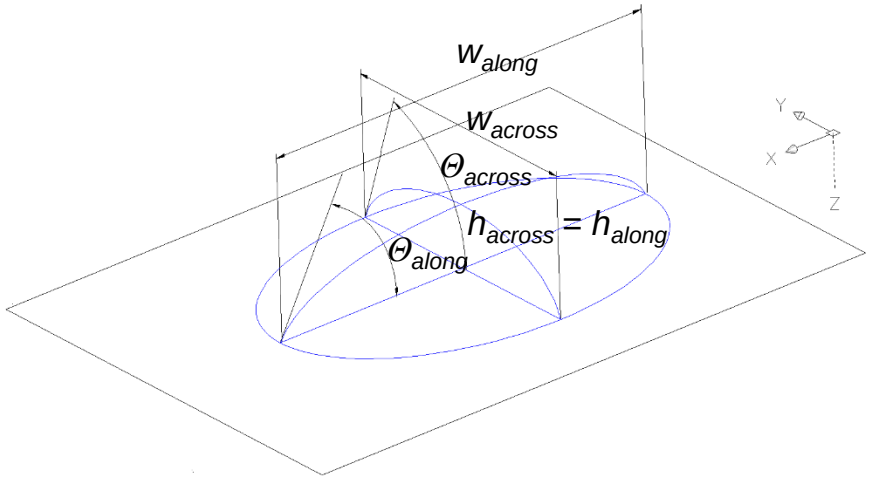
the pipette is **escaping** from the filled of view immediately after the immersing the surface

raw images

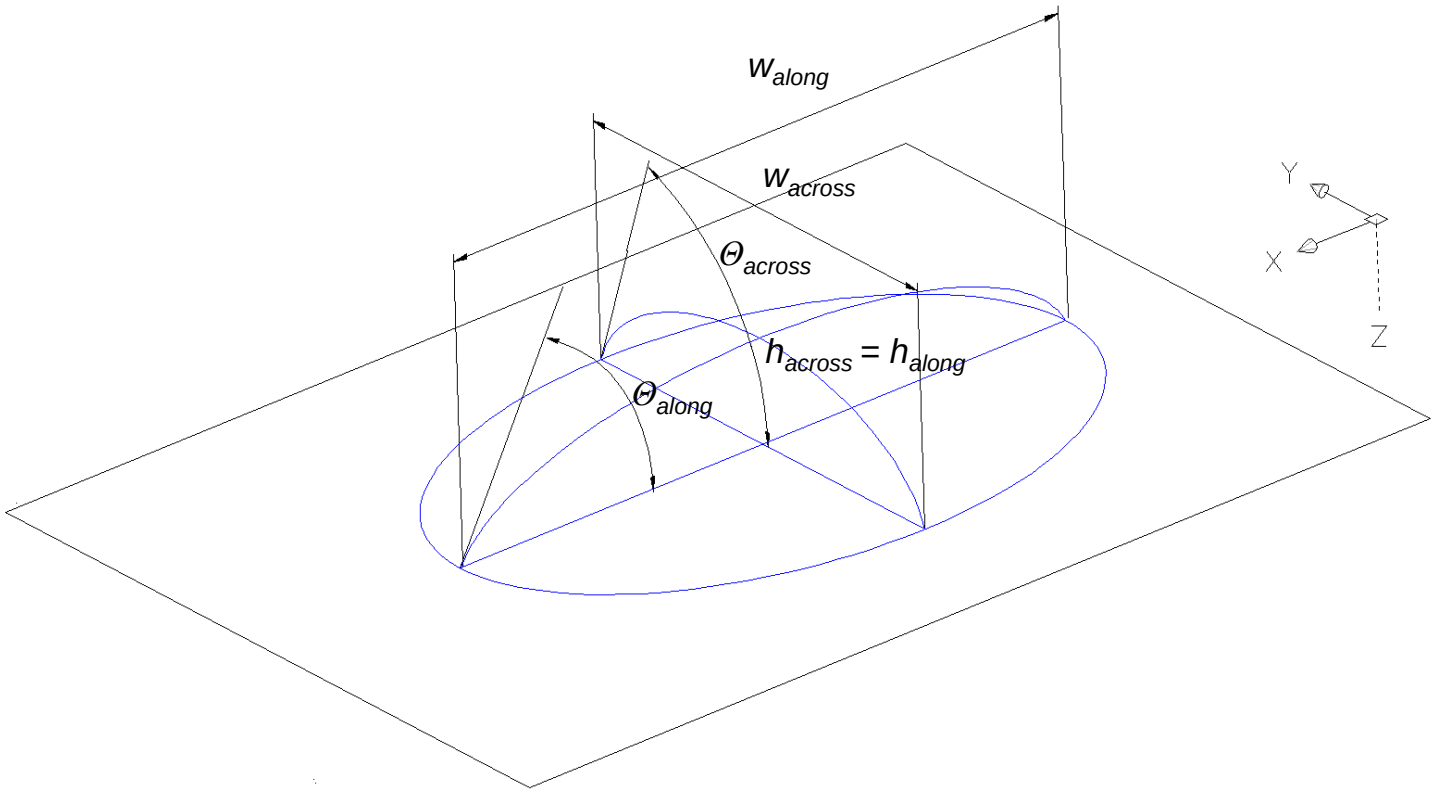

top


across wood fibers


along wood fibers

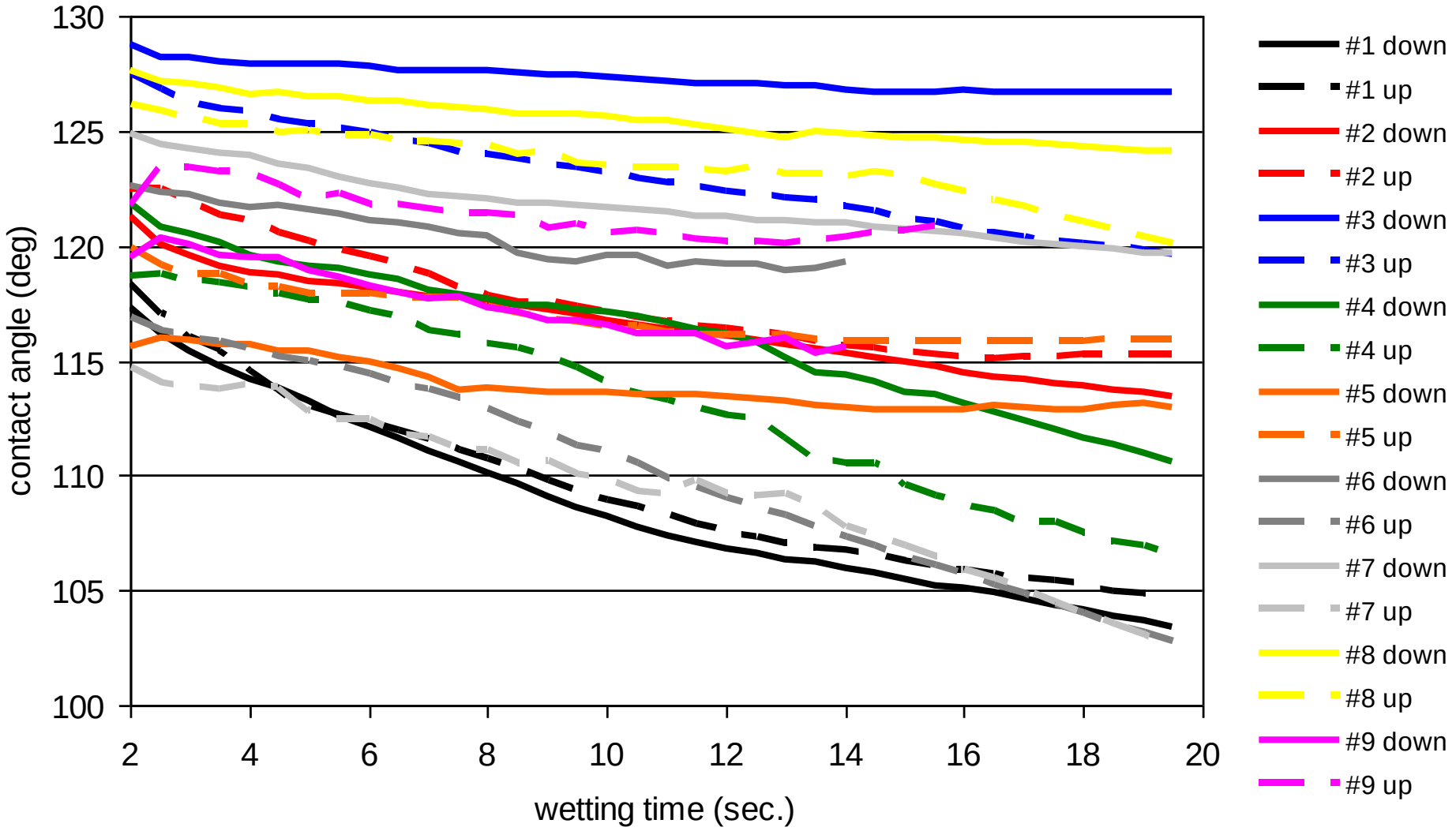

w_{along}
w_{across}
Θ_{across}
$h_{across} = h_{along}$
Θ_{along}
Y
X
Z

computation of contact angle(s)



Θ_{along} – contact angle along the fibers as seen by the camera 1
Θ_{across} – contact angle across the fibers as seen by the camera 2
h_{along} – height of the drop as along the fibers of the liquid and surface, as seen by the camera 1
h_{across} – contact height across the fibers of the liquid and surface, as seen by the camera 2
w_{along} – contact width along the fibers of the liquid and surface, as seen by the camera 1
w_{across} – contact width across the fibers of the liquid and surface, as seen by the camera 2
w_{along}/w_{across} – ratio of the contact width of the drop along and across of the fiber direction

an example of results:
contact angle on wood composite surface

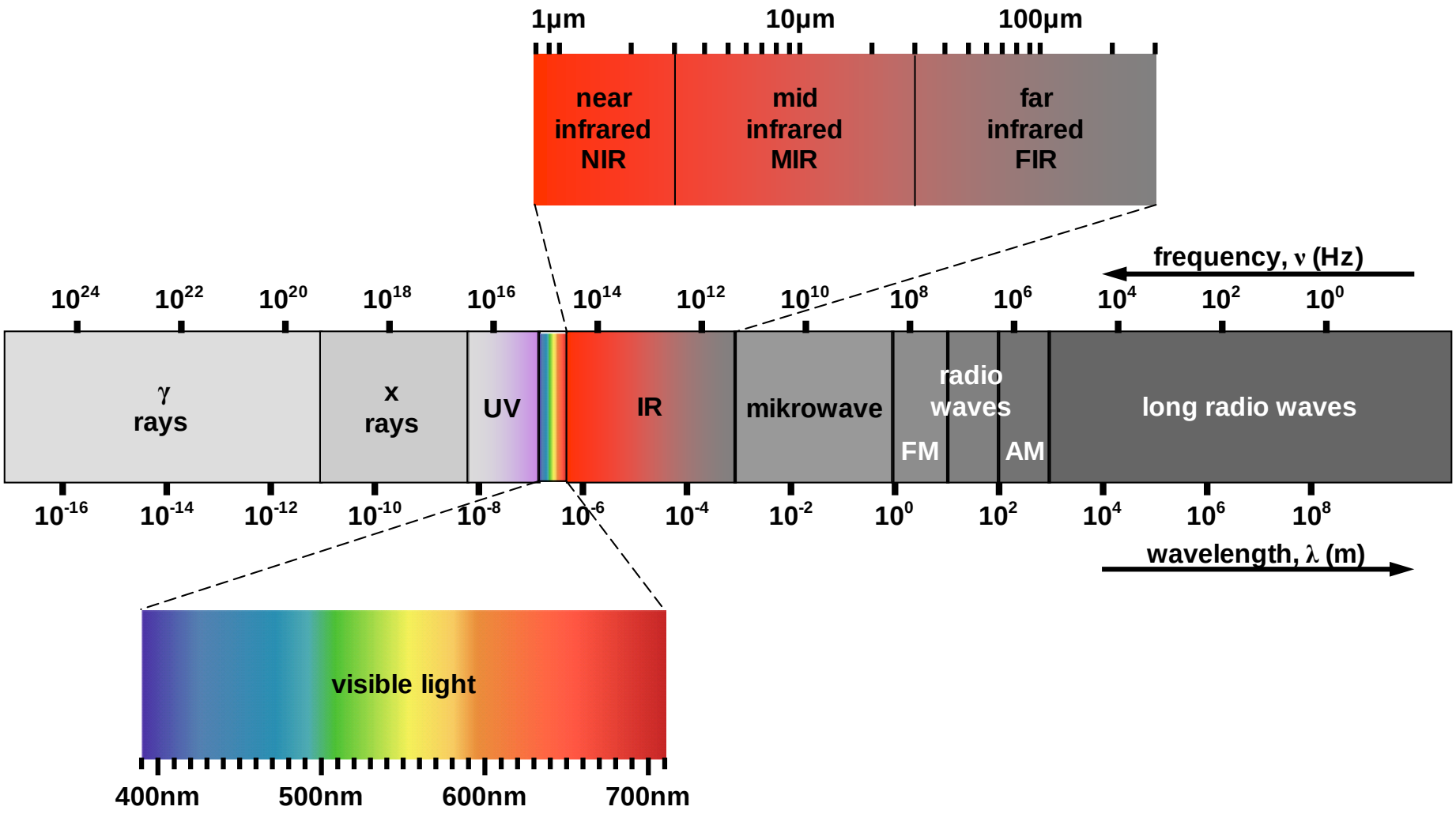


Summarizing - surface

- the surface properties of wood are still among the less known properties, although they are very important particularly in relation to psychological sensations of users of wood and wood products. Therefore more attention should be paid to these properties.
- several unconventional measurement techniques have been applied here for characterization of the particleboard surface properties:
  - **color uniformity and pattern** - *VIS-NIR hyperspectral camera*
  - **chemical characteristics of the samples** - *NIR spectroscopy and hyperspectral imaging*
  - **surface roughness** - *laser displacement sensor (3D)*
  - **surface wettability** - *prototype 3D sessile drop scanner*
- even if that methods are prototype - they have a great potential to be utilized and applied at industrial scale
- multi-sensor evaluation can be considered an efficient and effective method to determine objectively different surface properties

and bulk?…

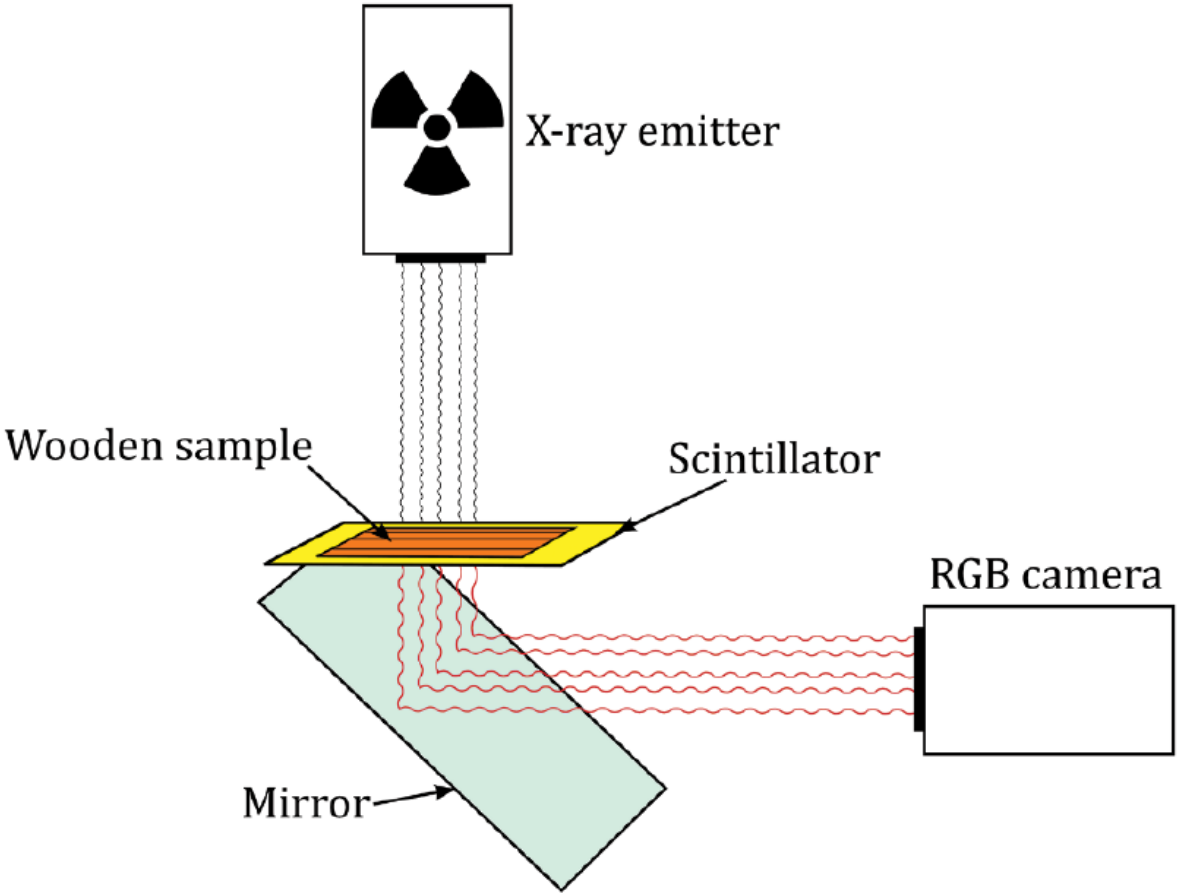
Electromagnetic spectrum



Some possibilities to characterize bulk

- X-ray:
  - radiography
  - CT
  - XRF
  - diffractometry
- UV/VIS/NIR/IR
- microwaves
- neutron imaging
- NMR
- ESR
- “wet chemistry”
- VoC/gas emissions (GC, MS, PT-RMS, dedicated sensors)
- …

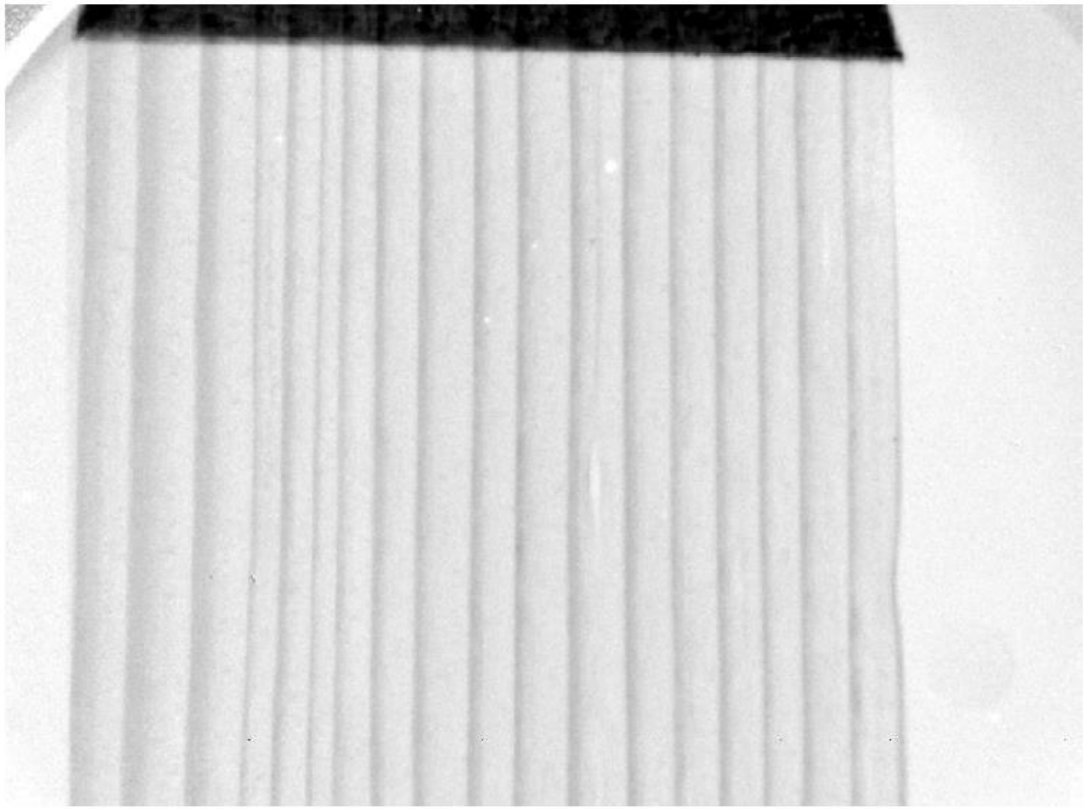
X-ray densitometry



From: COST Action FP1303 STSM report by Petter Stefansson

Computation of density from x-ray

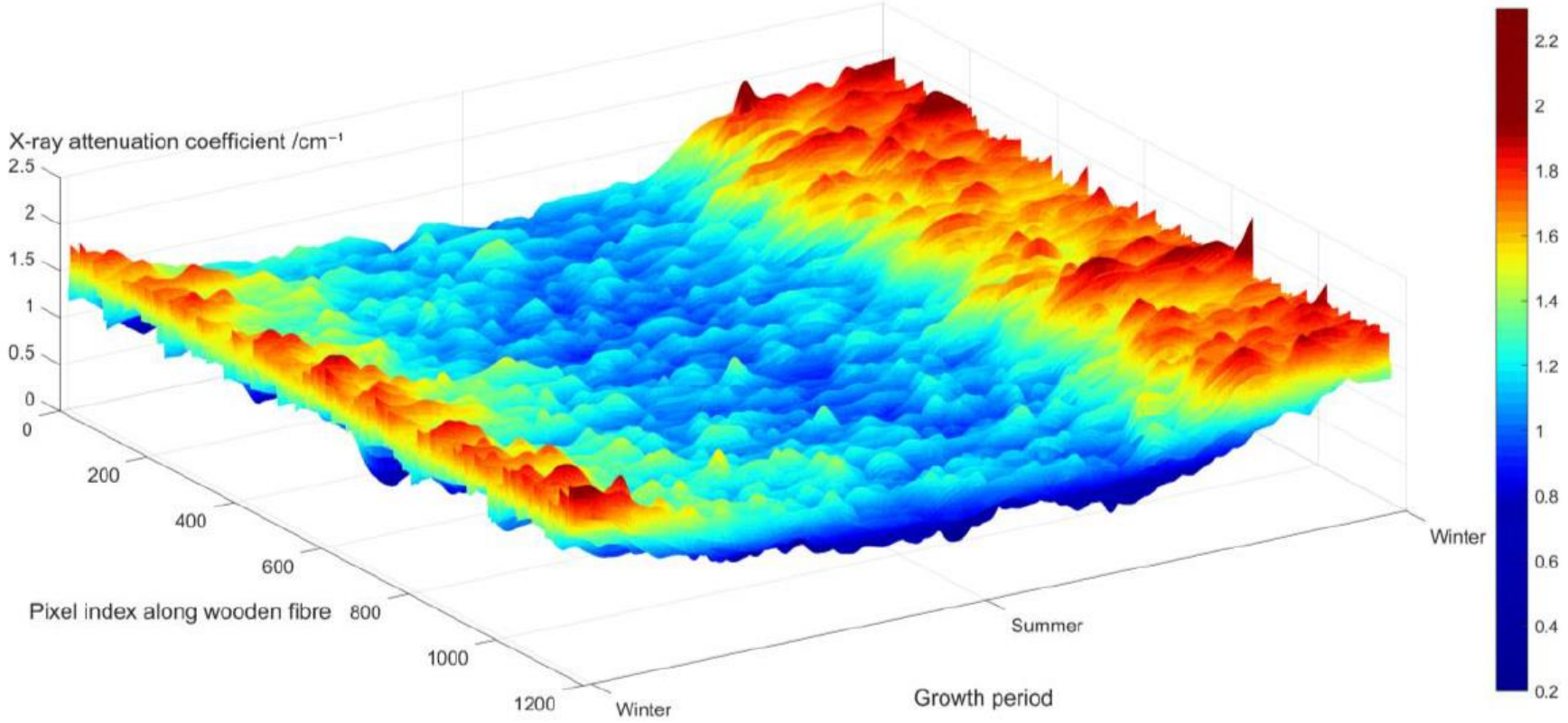
$$Image_{Preprocessed} = \frac{Image_{raw}}{Image_{white} - Image_{black}} - Image_{black}$$



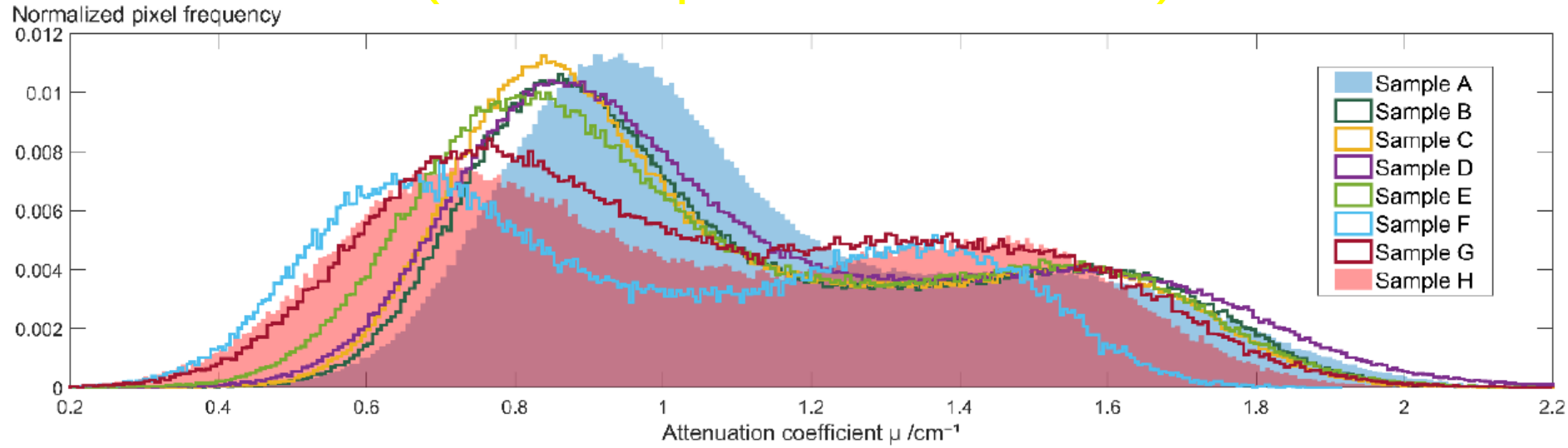
$$Transmittance = \frac{I}{I_0}$$

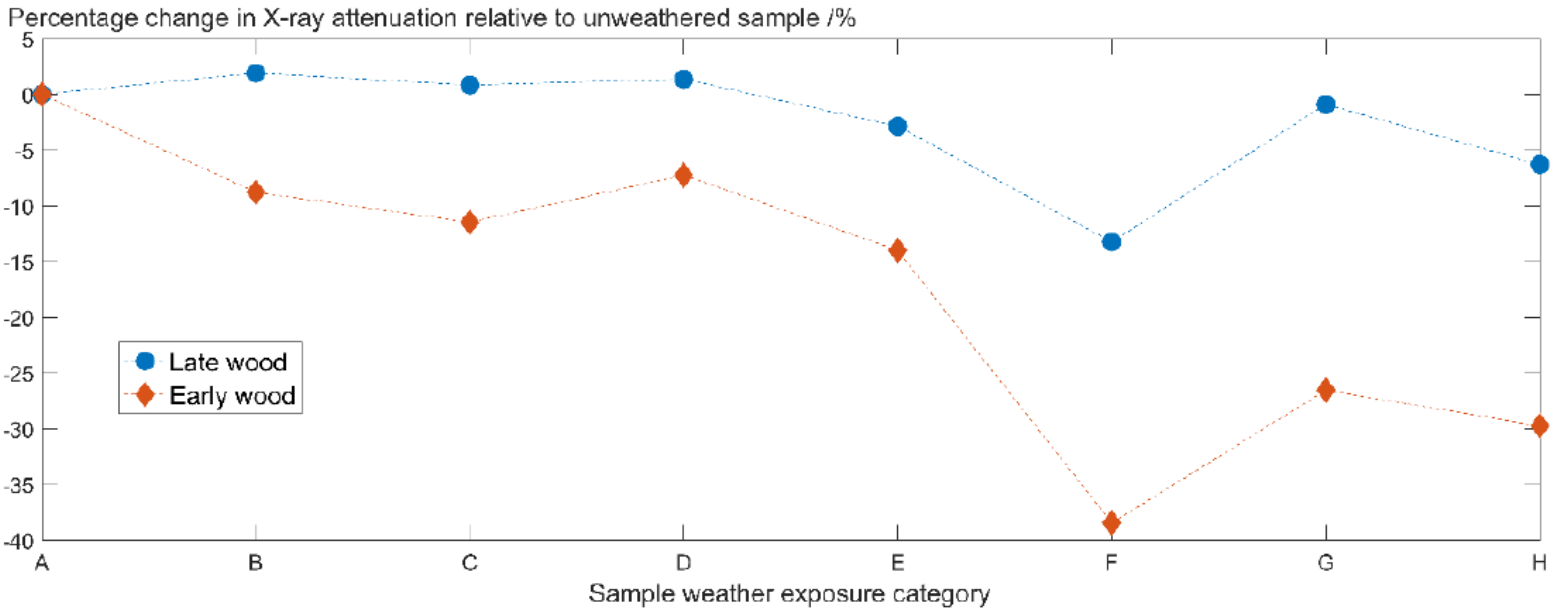
$$I = I_0 \cdot e^{-\mu \cdot t}$$

$$\mu = -\frac{\ln\left(\frac{I}{I_0}\right)}{t}$$


X-ray attenuation coefficient /cm⁻¹
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
Pixel index along wooden fibre
Winter
Summer
Winter
Growth period
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2

change of density along weathering
(thin samples from RR test)





NIR

The history of NIR begins in 1800 with **Frederick William Herschel**

Herschel directed sunlight through a glass prism to create a spectrum and measured the temperature of each color

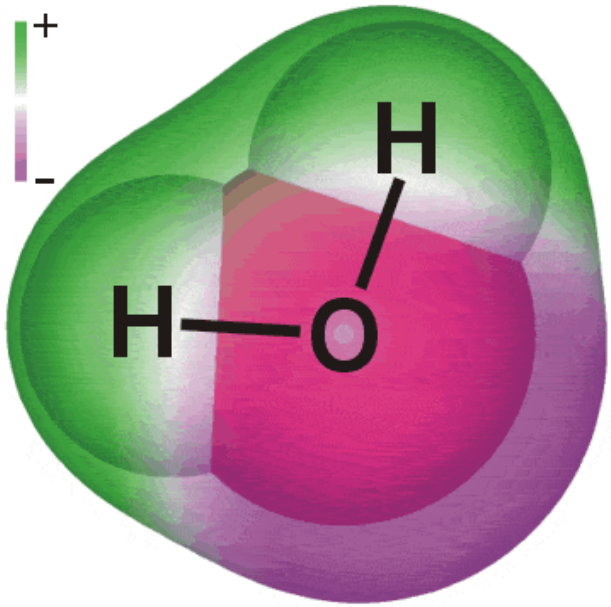
the temperature of the colors increased from the violet to the red part of the spectrum

after further studying, he concluded that there must be an invisible form of light beyond the visible spectrum

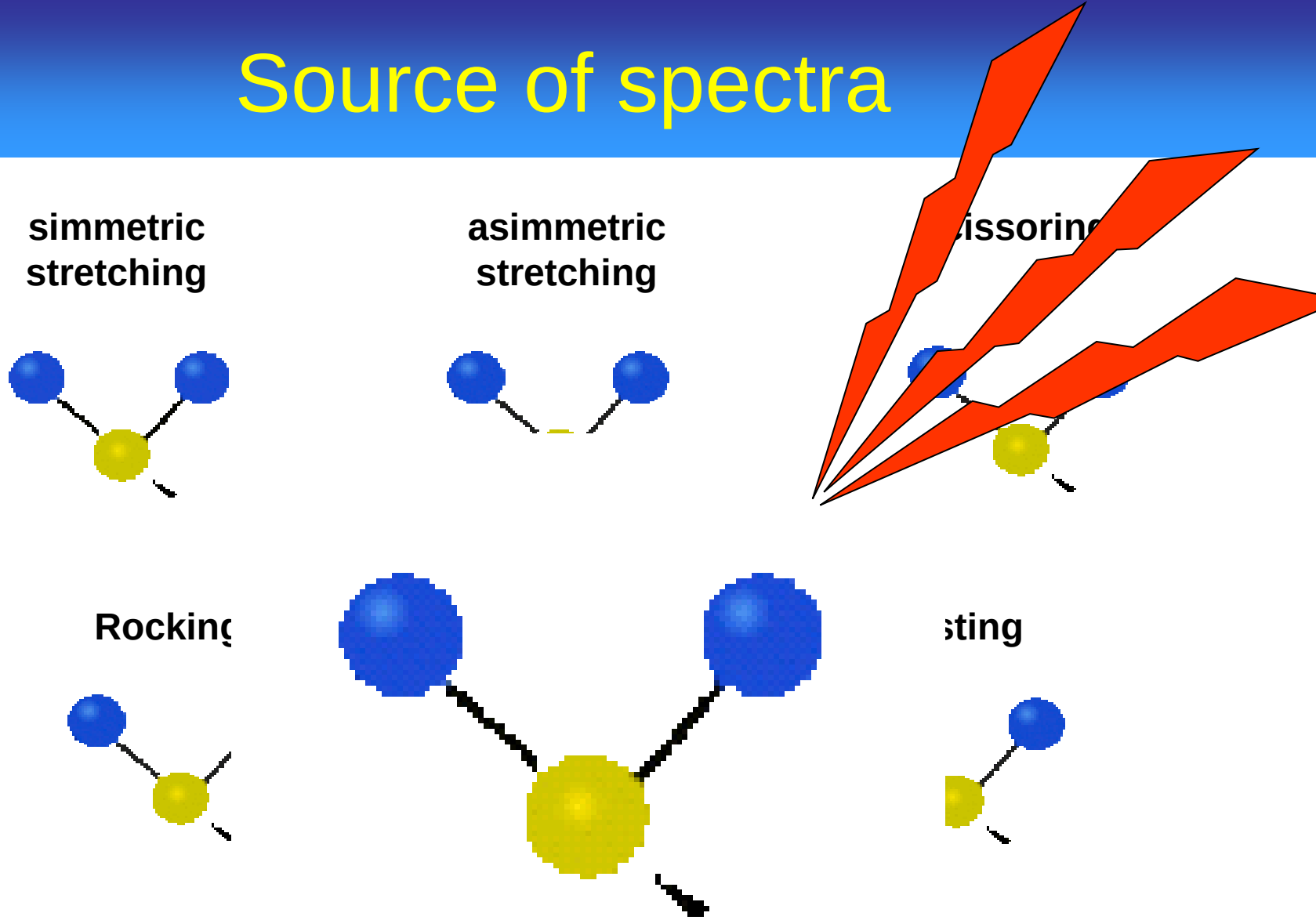
it was the first time that someone showed that there were forms of light that we cannot see with our eyes

Principle of molecular vibrations

- Spectroscopy provides information about the vibrations of functional groups in a molecule
- Every molecule has specific vibration frequencies
- When polar molecule is exposed to infrared light its starts vibrate since certain frequency is absorbed
- Consequently a change in dipol moment of the molecule occurs



Source of spectra

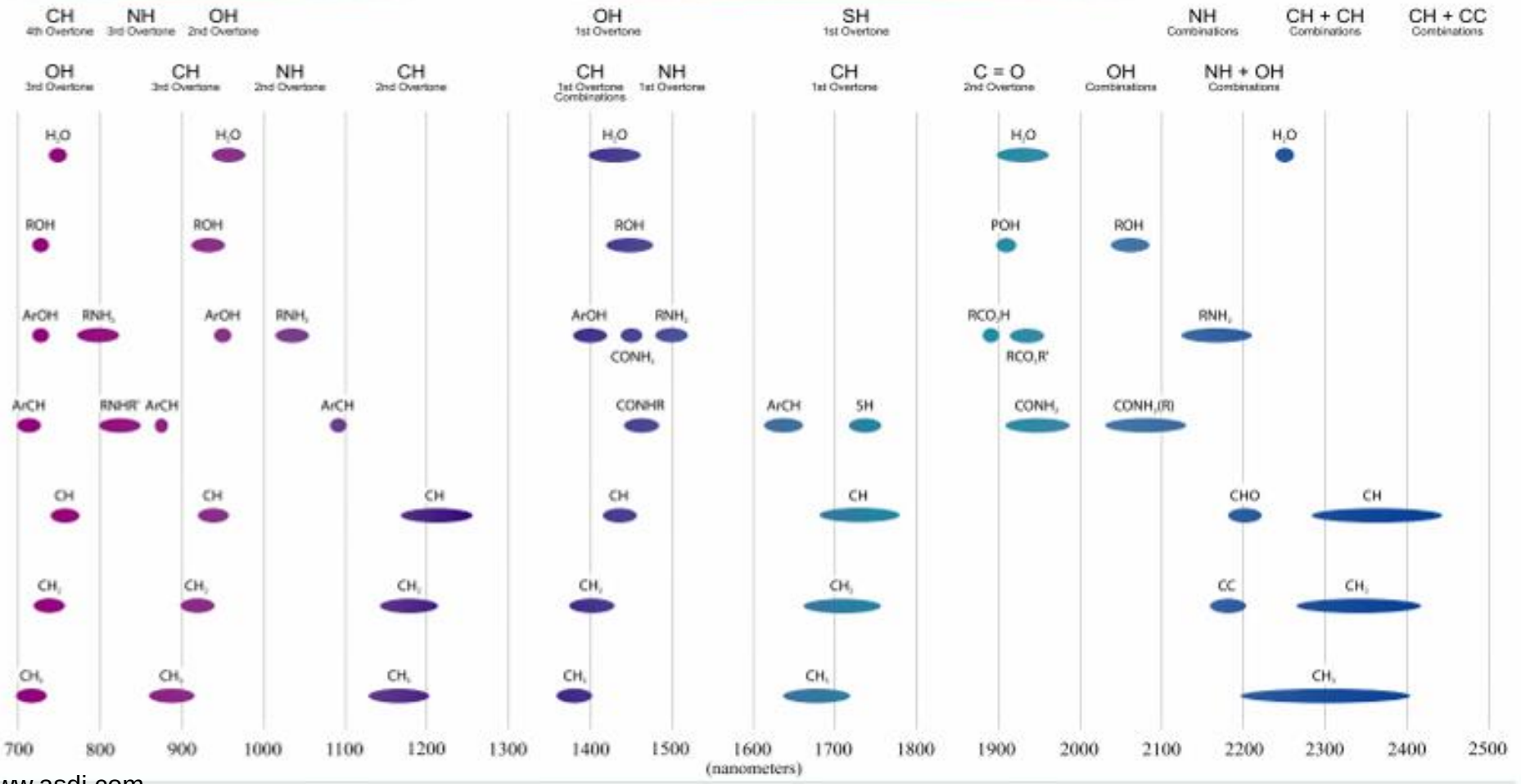


Spectra represents molecular vibrations of chemical molecules exposed to infrared light.

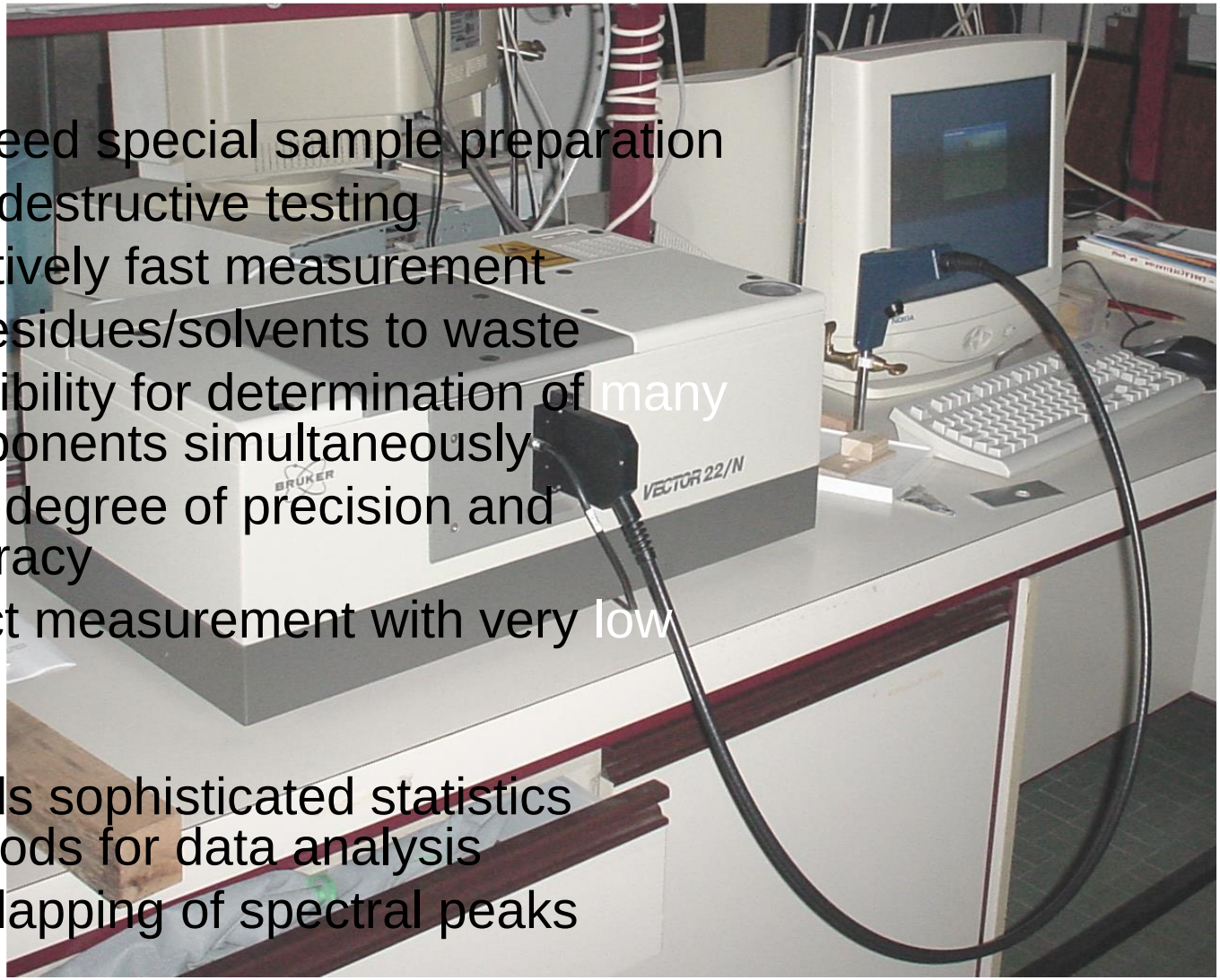
http://en.wikipedia.org/wiki/Infrared_spectroscopy

Spectrum NIR

third overtones **second overtones** **first overtones** **combinations bands**



NIR technique



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

- Needs sophisticated statistics methods for data analysis
- Overlapping of spectral peaks

NIR application

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

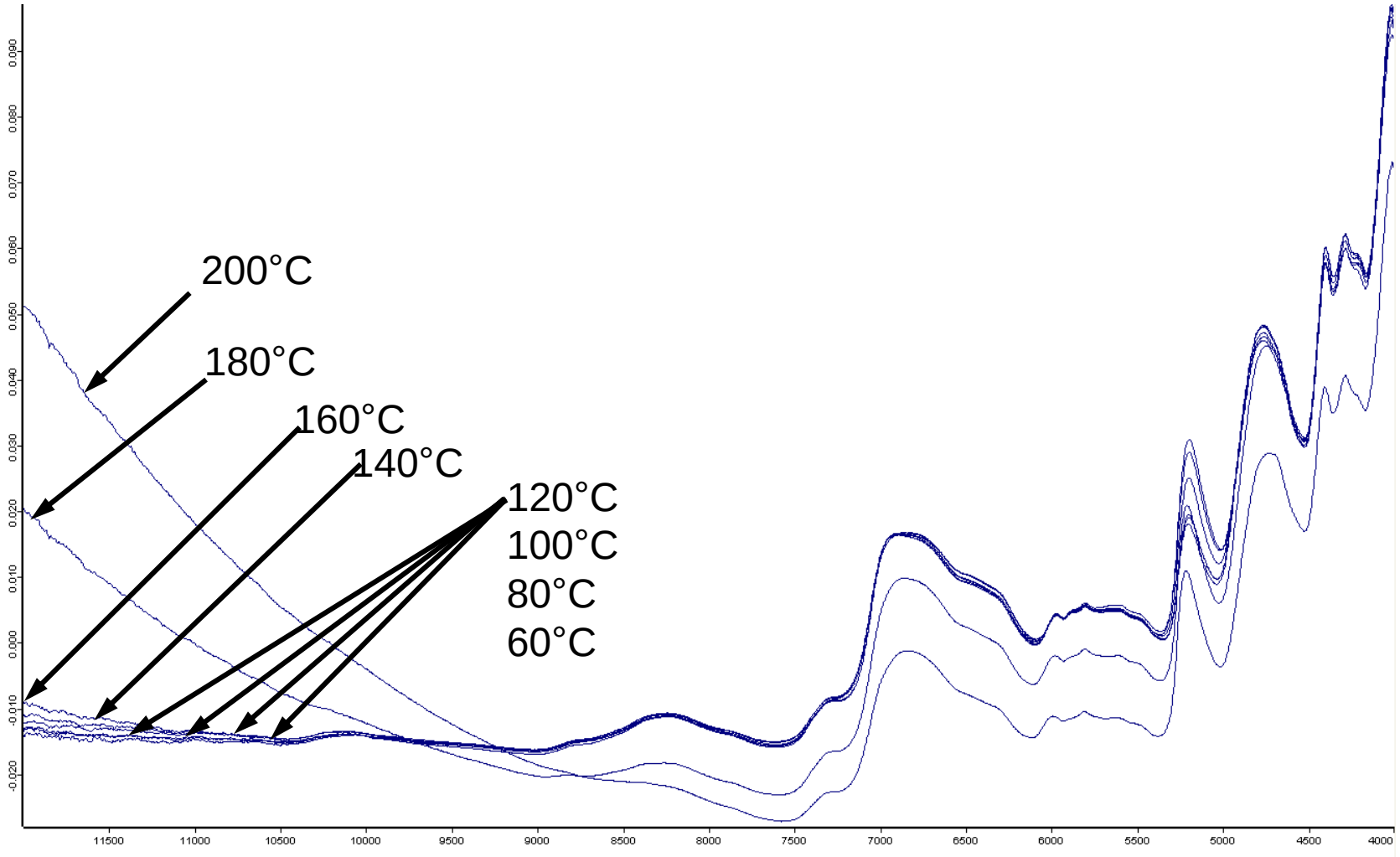
and also **wood**

Band assignment - wood

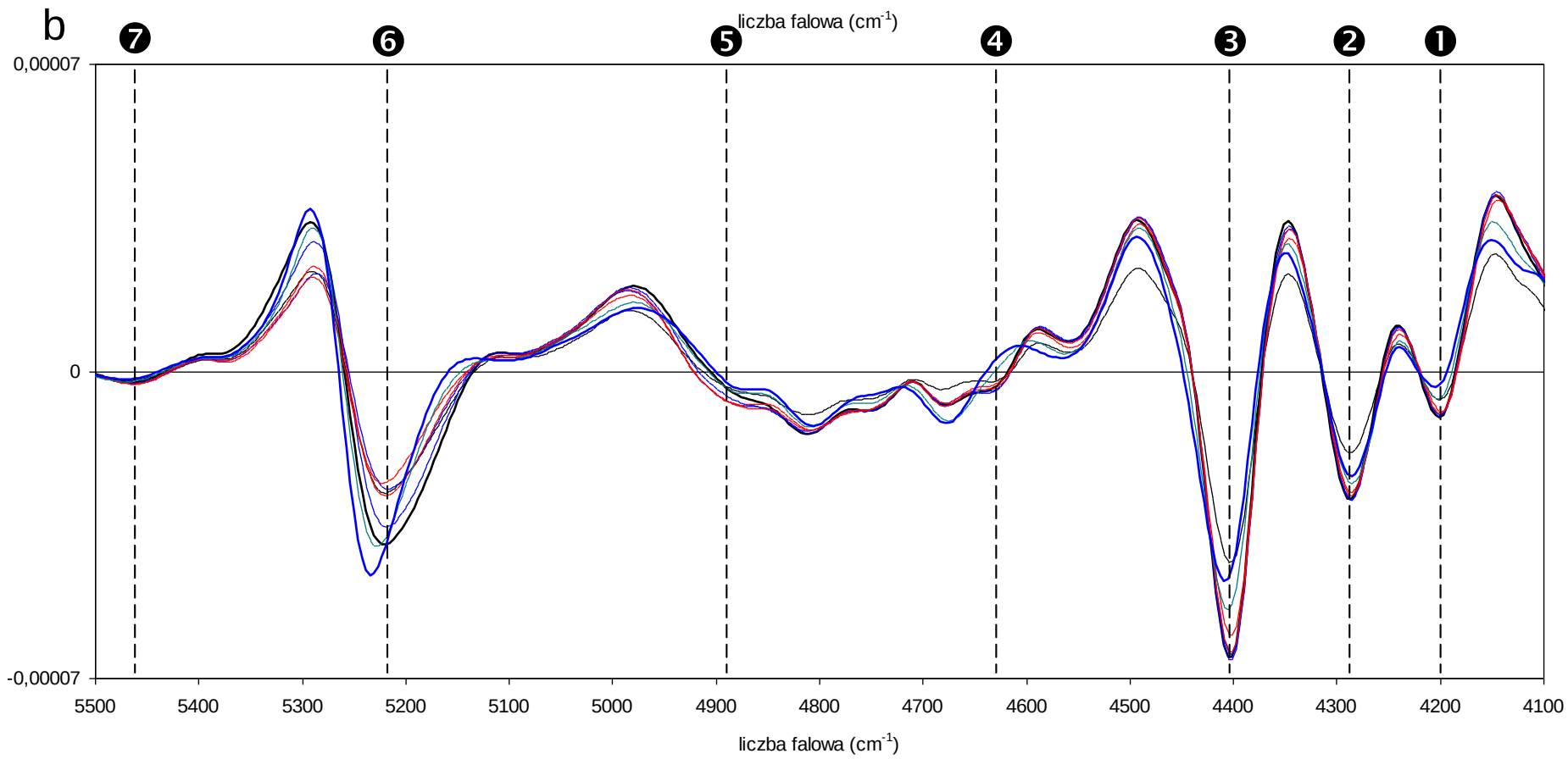
code	wavenumber (cm^{-1})	band assignment
1	4198	CH deformation in holocellulose
2	4280	CH stretching + CH deformation in semi- and crystalline region in cellulose
3	4404	CH_2 stretching + CH_2 deformation of cellulose
4	4620	OH stretching + CH deformation of cellulose
5	4890	OH stretching + CH deformation of cellulose
6	5219	OH stretching + OH deformation of water
7	5464	OH stretching + CH stretching semi- or crystalline regions of cellulose
8	5587	CH stretching semi- or crystalline regions of cellulose
9	5800	CH stretching in furanose/pyranose due to hemicelluloses
10	5883	CH stretching in aliphatic chains
11	5935	CH stretching of aromatic skeletal in lignin
12	5980	CH stretching of aromatic skeletal in lignin
13	6287	OH stretching in crystalline region in cellulose
14	6450	OH stretching in crystalline region in cellulose
15	6722	OH stretching in semi-crystalline region in cellulose
16	6785	OH stretching in semi-crystalline region of cellulose
17	7008	OH stretching in amorphous region in cellulose
18	7309	CH stretching in aliphatic chains
19	7418	CH stretching in aliphatic chains

around 100 bands assigned to wood components (Schwanninger et al. 2011)

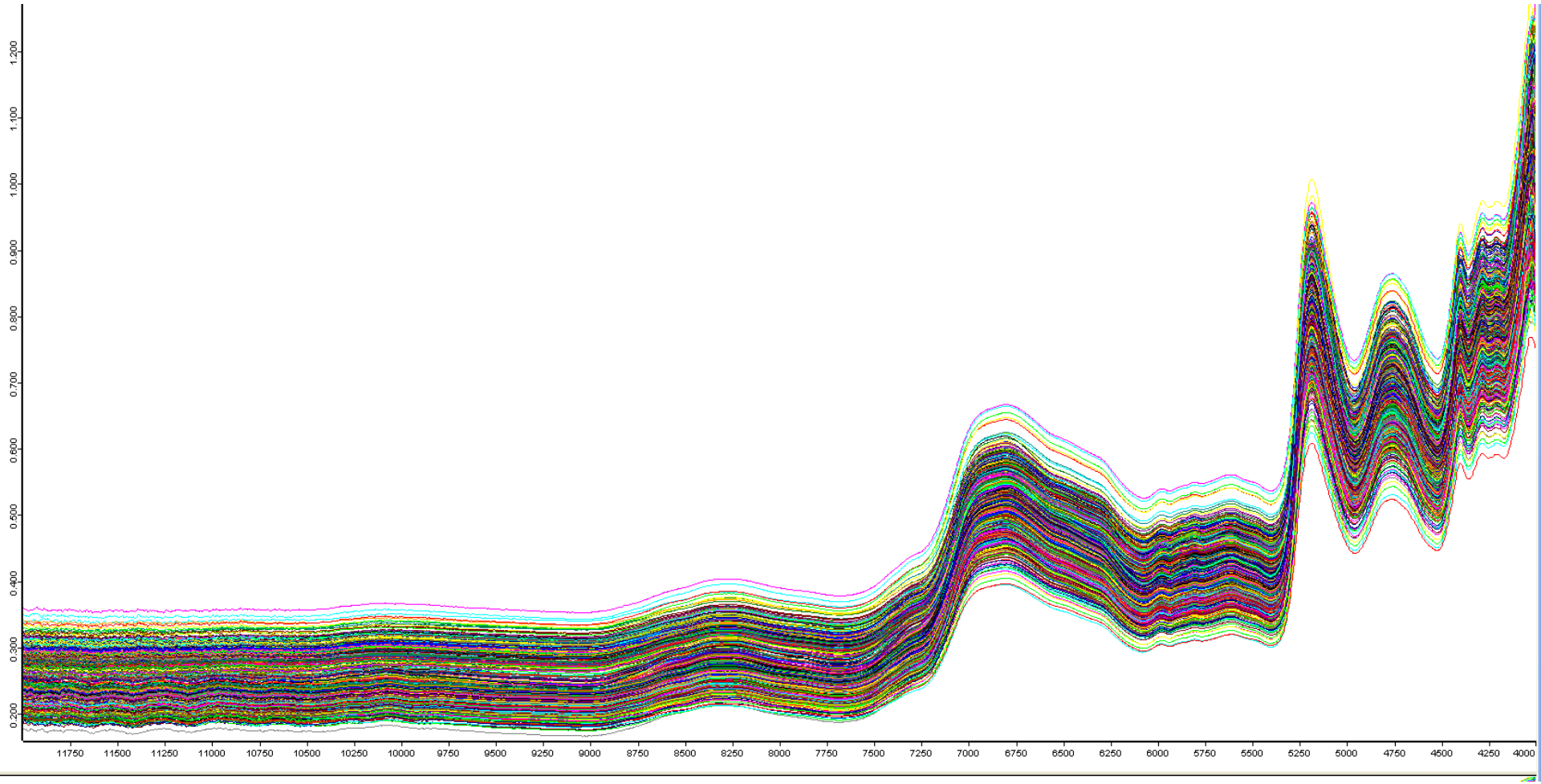
Raw spectra


200°C
180°C
160°C
140°C
120°C
100°C
80°C
60°C
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
-0.010
-0.020
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000

Second derivative



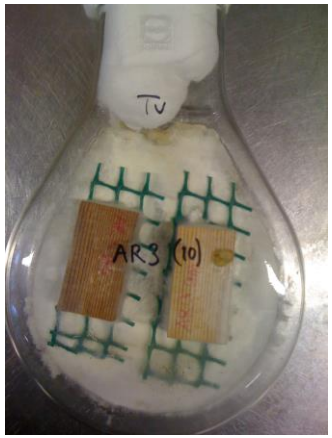
When we have more spectra to be analyzed...



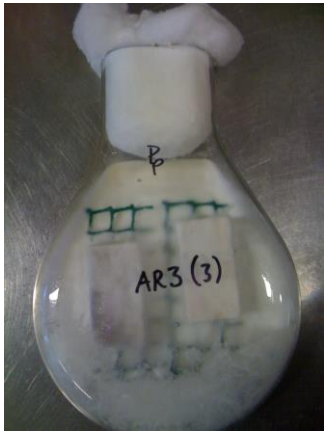
Portable spectrophotometers

Wood decay

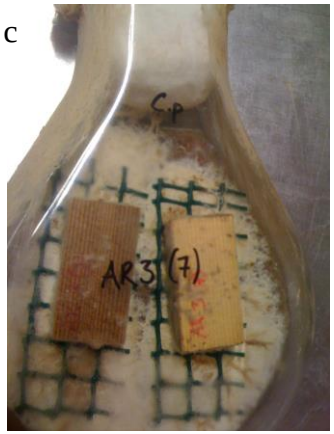
a



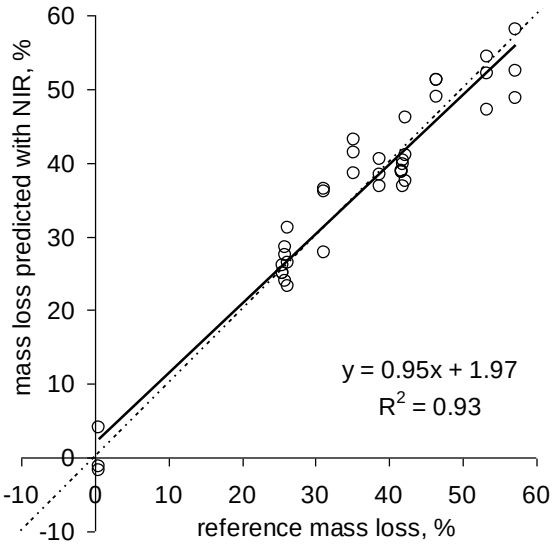
b

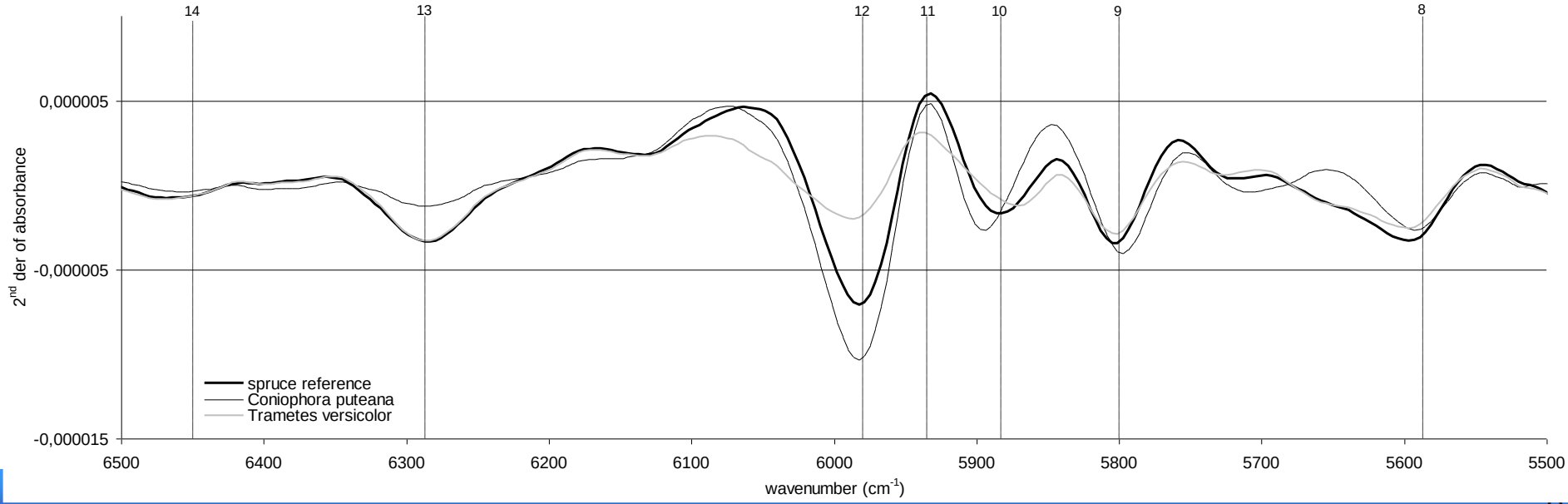


c

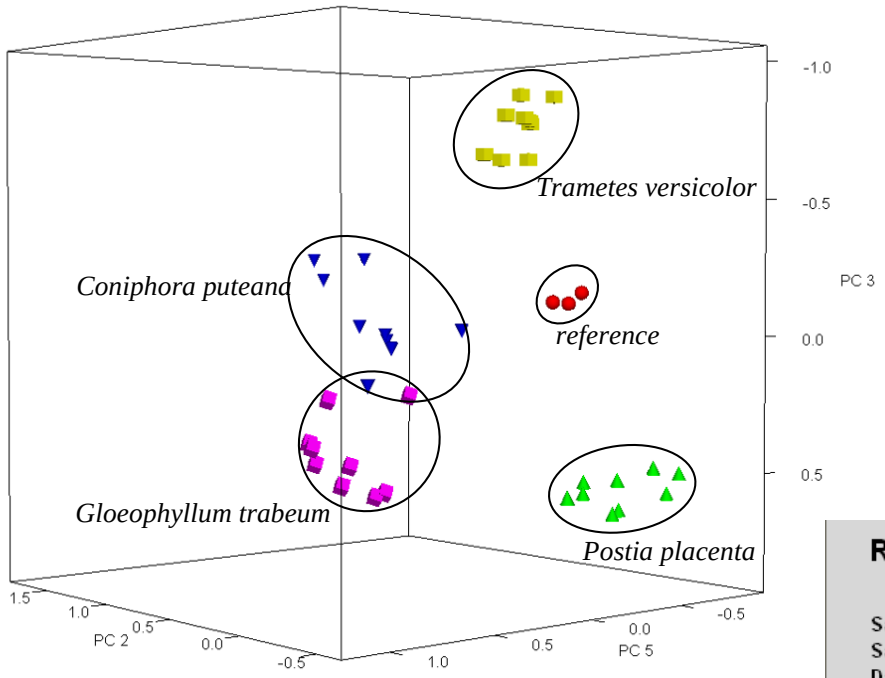


Trametes versicolor *Postia placenta* *Coniophora puteana*





Decay type identification



Result of IDENT evaluation:

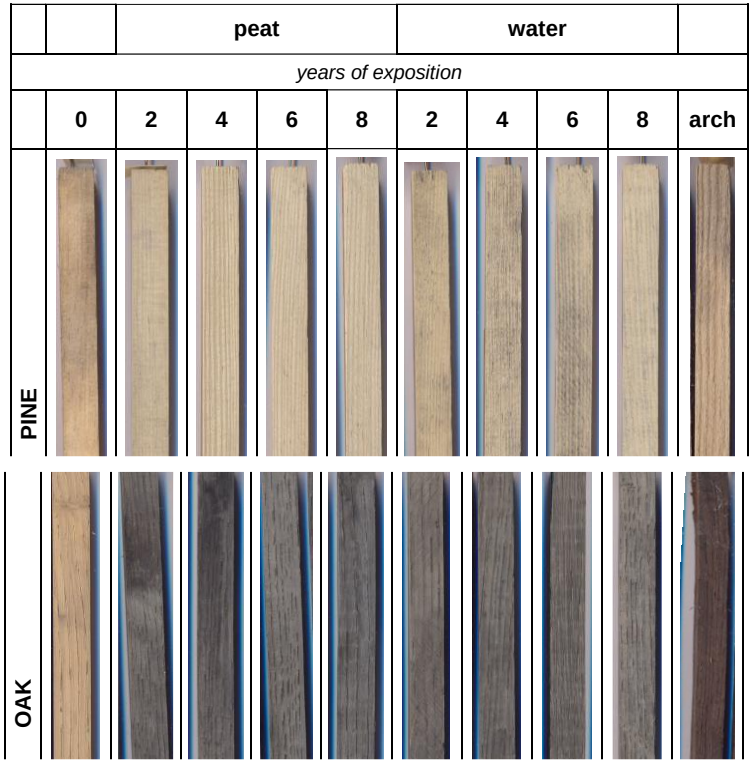
Sample name: wood | Av. of 3
Sample: D:\TENNO\Av.right degraded inside.0
Date and time (measurement): 2011/06/06 12:21:35 (GMT+2)
Method file: D:\Nasco wood\analysis\all fungi general classification.faa

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

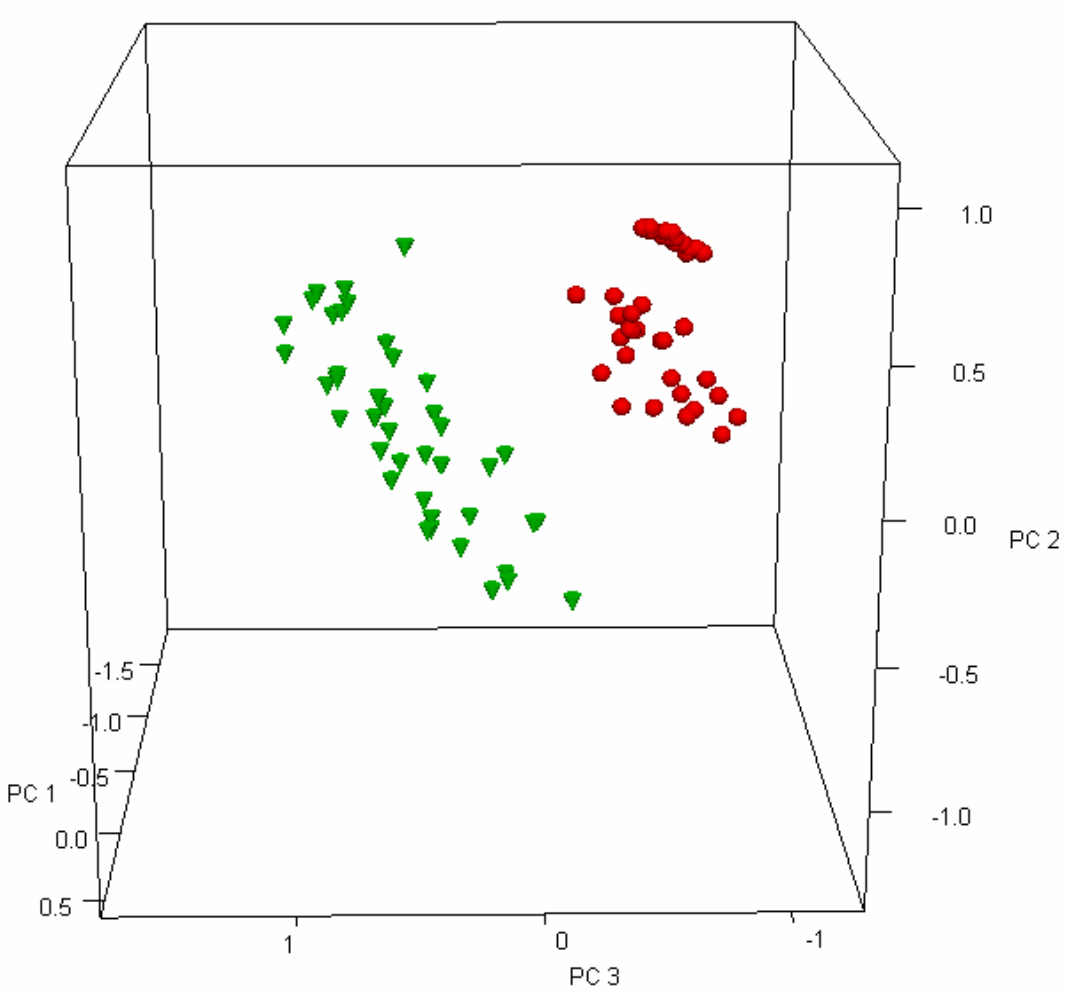
Short term waterlogging



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

nr	band assessment			pine		oak	
	wave number (cm^{-1})	wood component	functional group	peat	water	peat	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	◯	◯	◯	○

Identity test – coating recognition



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

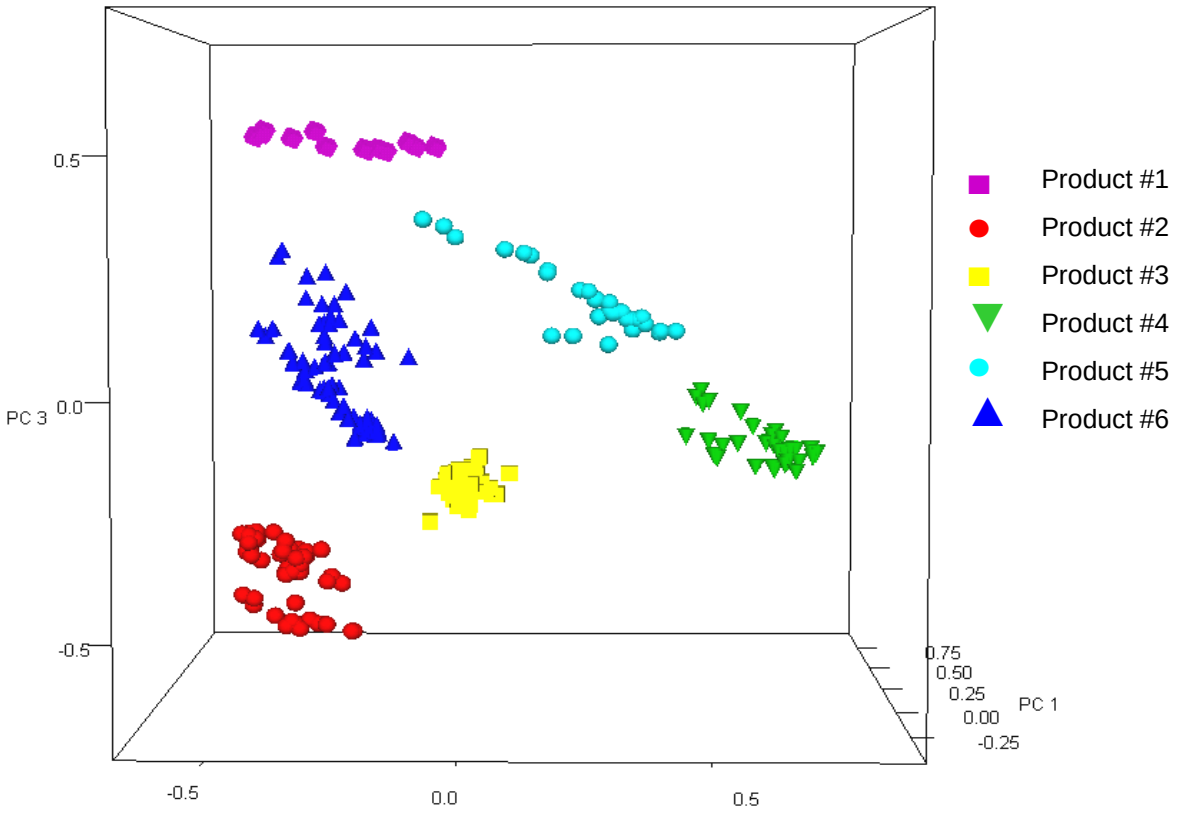
Organic solvent based products: #11, #12, #42

Preprocessing: 2 derivative + vector normalization, 9 smoothing points

Method: factorization

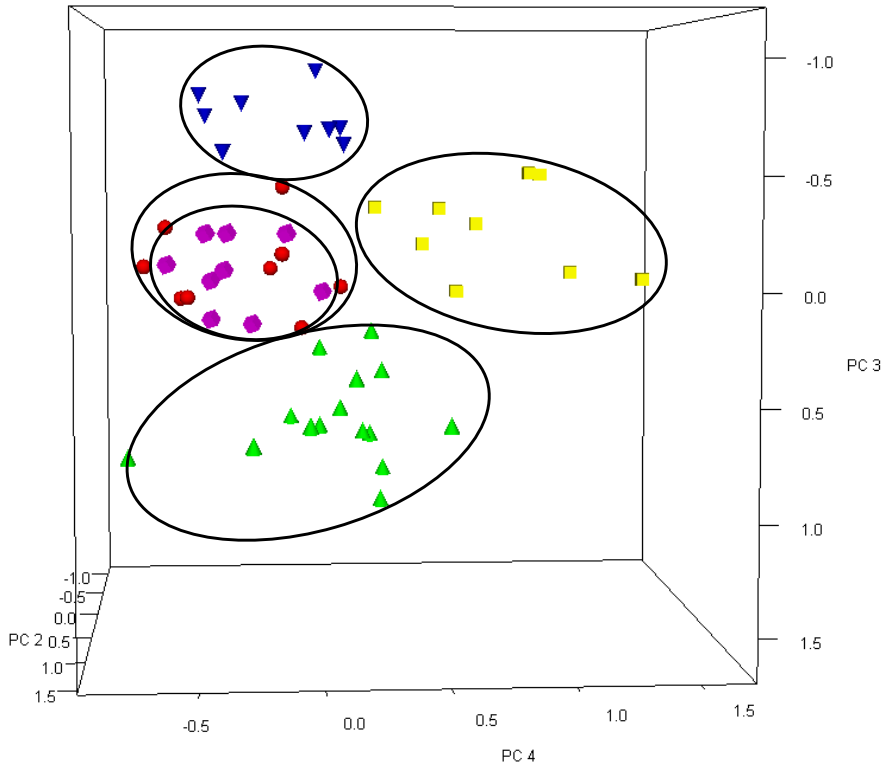
Regions (cm^{-1}): 4135-4350, 5365-5520, 5800-6000, 6290-6480, 7000-7200

Identification of coatings



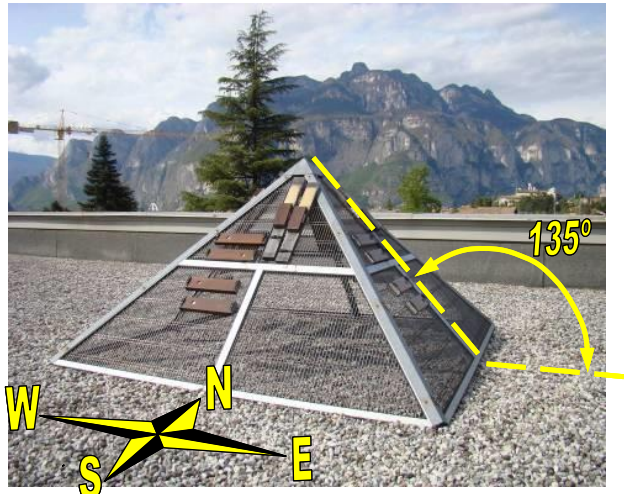
band: 4200-10000cm^{-1}, 2 derivative, 5 smoothing points, vector normalization, 2 factors

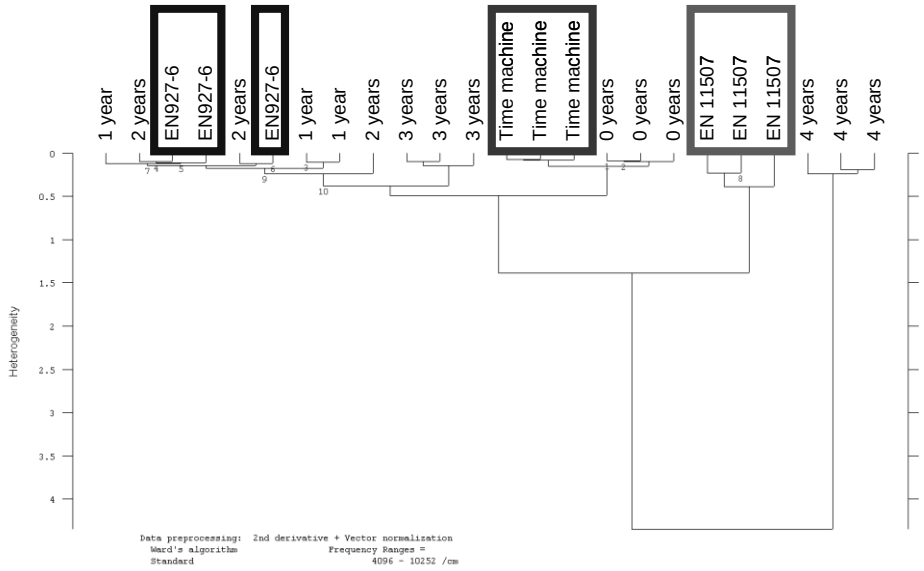
Principal Component Analysis

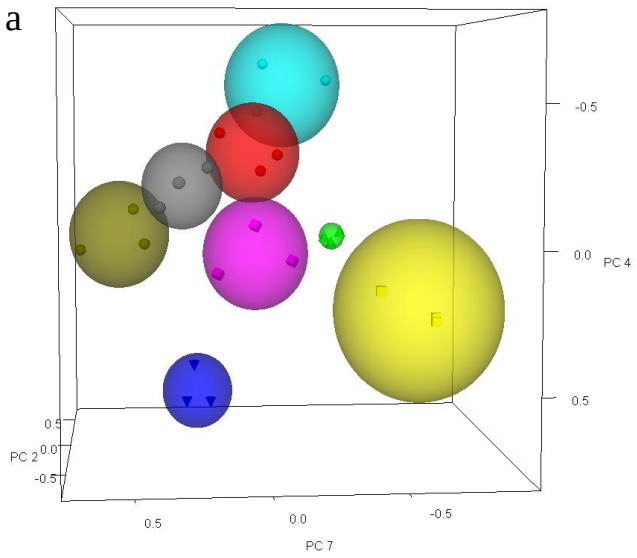


PCA of samples exposed for >20 days against: South West North East Reference

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

Thanks!

Comments/critics/problms?

God made the bulk;
surfaces were invented by the devil.

Wolfgang Pauli (1900 - 1958)
Nobel for physics in 1945