The Effectiveness of FT-NIR Spectral Analysis for Identifying Bio-Based Finishes

STSM COST ACTION FP 1006
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Anna Rozanska - Warsaw University of Life Sciences

Anna Sandak - IVALSA Tree and Timber Institute


Palace of Versailles, the Hall of Mirrors, 1679
Jules Hardoiun-Mansart and Charles Le Brun (1647-1708)


Hermitage, St Peterzburg, 2 half of XVIIIw.

Usage properties of parquets -DURABILITY

the period of resistance (that is, the preservation of properties in a condition permitting the usage) to the factors causing wood decomposition

= MATERIAL + FINISHING

- **density**
- **hardness**
- **wood elasticity**
- **strength properties (compressive strength across fibres, shear strength and splitting strength)**
- **resistance to abrasion and scratches**
- **resistance to microbiological factors**

= SPECIES + SECTION

DESTRUCTIVE FACTORS

- **biological agents (fungi, bacteria, algae, lichens, insects and others)**
- **chemical (acids, bases, salts, aerosols)**
- **physical and chemical (light, radiation, high temperature, fire)**
- **physical and mechanical (low temperatures, changes in humidity, mechanical forces)**

= ENVIRONMENT MICROCLIMATE

Usage properties of parquets

Properties – building physics

- Technical and usage comfort (health protection, calmness, comfort, safety, social values)
- Microclimate of the interior (heat and moisture conditions of the air, environment and divisions); health and hygiene (air, noise, electrostatics, aesthetics)
- Surface properties (surface level and smoothness, dimensional stability, thightness and easthetics of the layout, durable colour)

Technical properties of wood as a constructive material

- Physical (resistance to humidity)
- Mechanical
- Surface
- Heat related
- Acoustic
- Resistance to biological corrosion
- Aesthetical

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Usage properties of parquets

Physical properties

- **porosity** (ability to insulate**)**
- **water absorption** (swelling**)**
- **moisture** (air-dry moisture content of wood is 15÷18%, standard 9±2%**)**
- **hygroscopy** (shrinking-swelling**)**
- **rate of moisture exchange**

Surface properties

- **macro and microscopic image**
- **colour, gloss**
- **roughness tests**
- **hardness tests**
- **wear resistance tests**
- **resistance to scratches**
- **density profile, wettability, surface energy**

Mechanical properties

- **weight by volume of wood**
- **compressive strength**
- **compressive strength across fibers**
- **shear strength**
- **splitting strength**
- **bending**
- **elasticity**

Chemical properties

- **extractive compounds with the use of chloroform – ethanol 93/7 (v/v),**
- **cellulose separated with the Kürschner-Hoffer method,**
- **holocellulose using $NaClO_2$,**
- **lignin in accordance with PN (Polish standard), solubility in 1% NaOH,**
- **cellulose degree of polymerization**

Aim of study

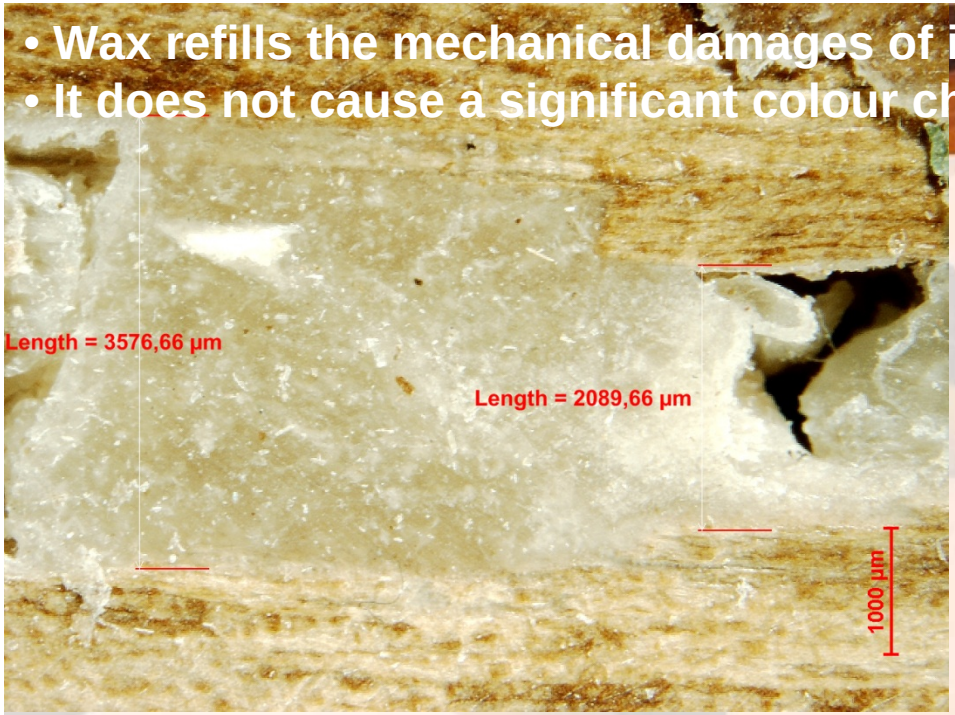
- The finishes used on floors had to create a hydrophobic layer on the surface, protect it against dirt, stains and discolorations, reduce its wear rate and be resistant to removal or scratches;
- They also needed to provide favourable roughness and gloss, with a minimum change in colour

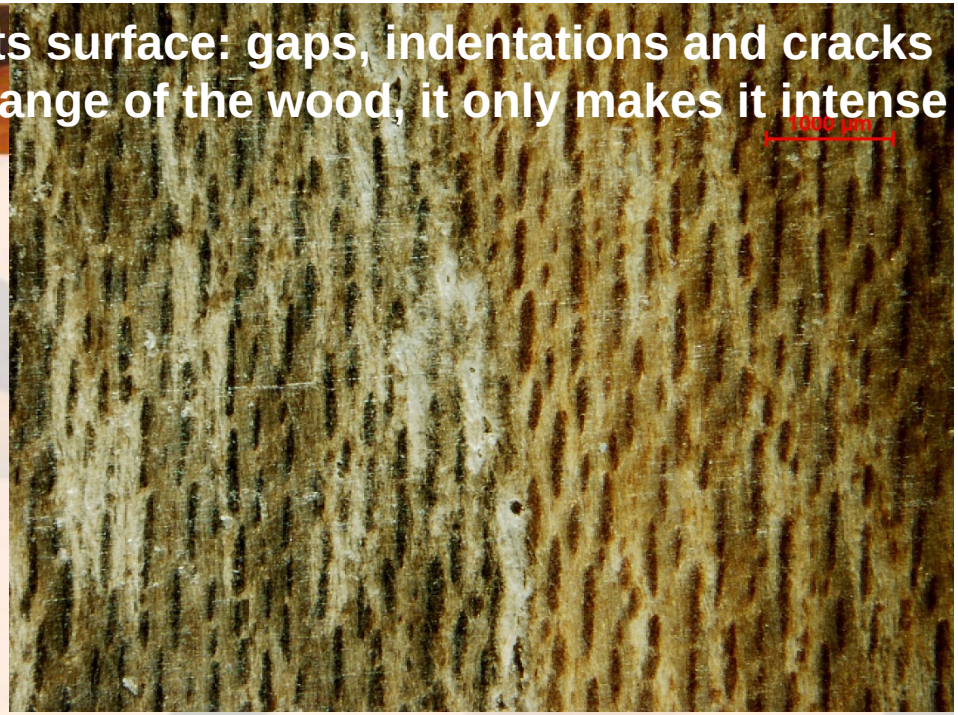
- Waxes and paraffin are resistant to moisture, reversible, resistant to organic solvents and non-toxic, but accumulate dust, are sensitive to hits and scratches and become darker in time

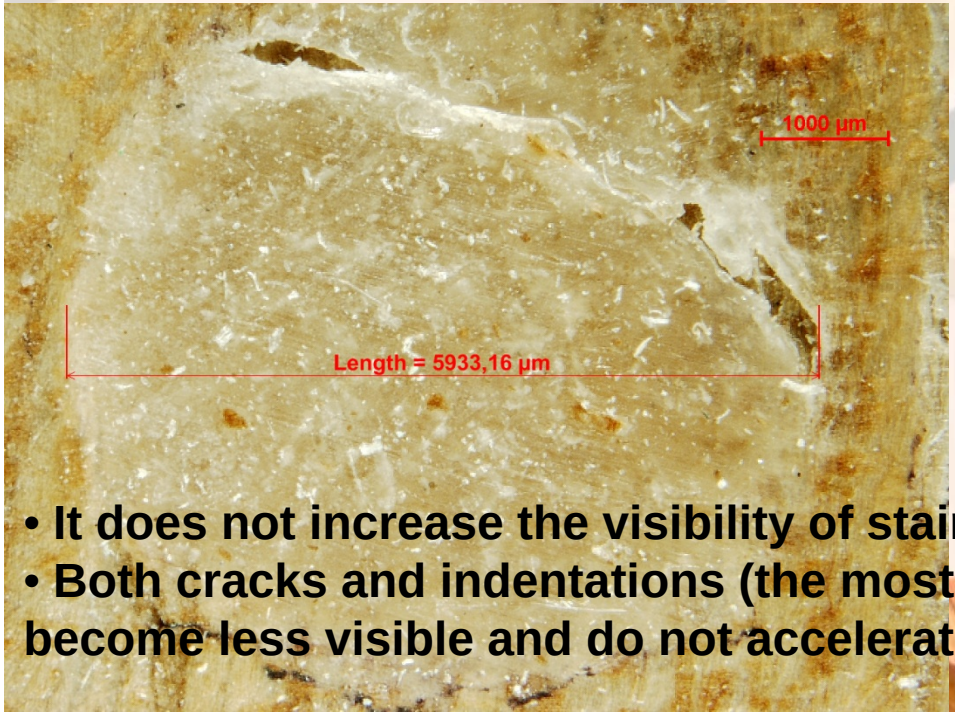
- Vegatable oils (linsed and tung oil and colophony) are hydrophobic, resistant to leaching, non-toxic and might be used as plasticizers

- FT-NIR spectroscopy was used for recognition of traditional finishing substances applied on contemporary and antique wooden parquets of 19th century manor houses located in South-Eastern Poland
- The other task was to create spectral database of substances commonly applied in 19th century
- Finally verification of effectiveness of FT-NIR as a tool supporting conservation decisions was evaluated

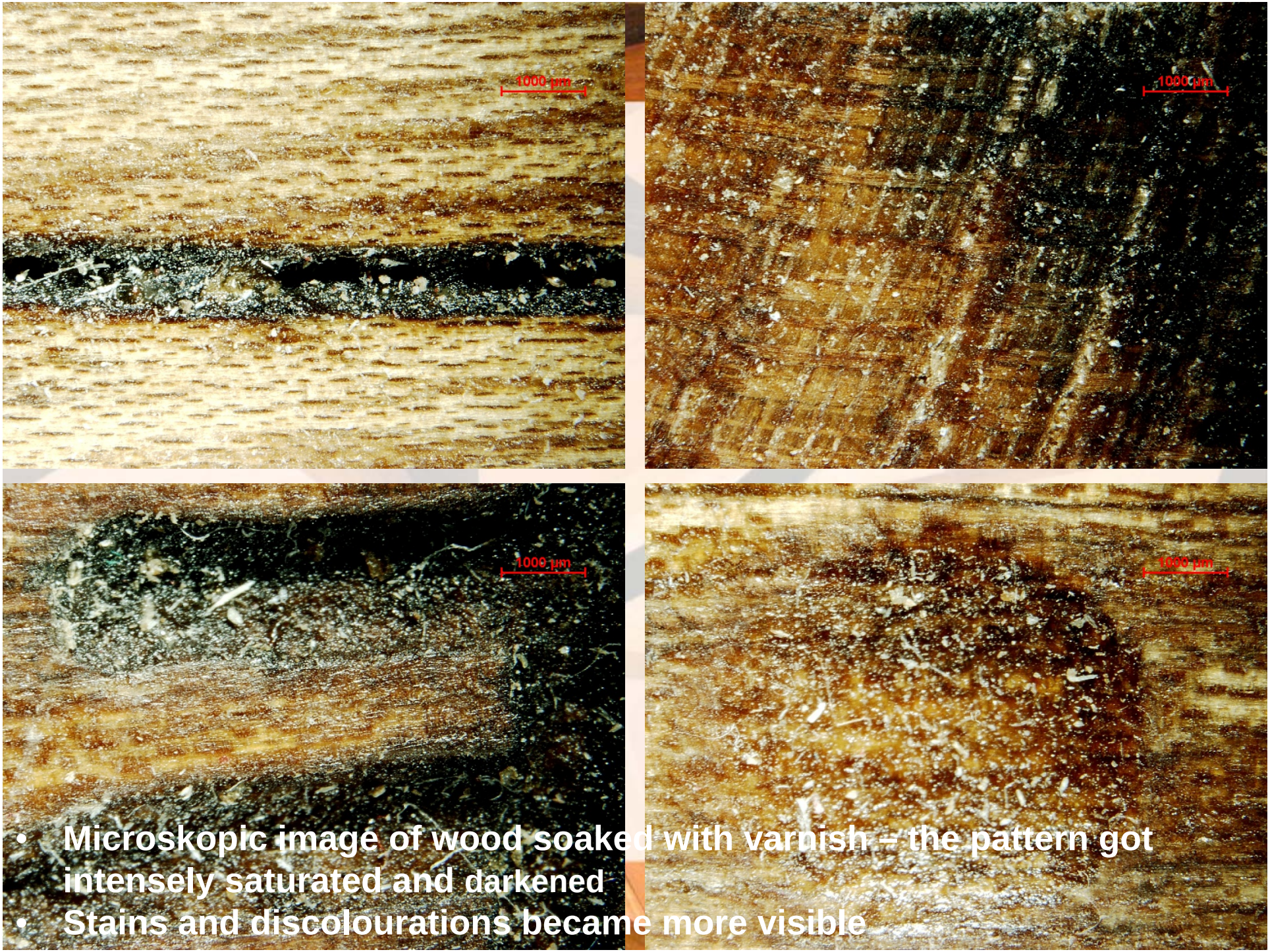
• Wax refills the mechanical damages of its surface: gaps, indentations and cracks
• It does not cause a significant colour change of the wood, it only makes it intense







• It does not increase the visibility of stains and wood discolourations.
• Both cracks and indentations (the most frequent damages of wooden surfaces) become less visible and do not accelerate wood degradation



- Microskopic image of wood soaked with varnish – the pattern got intensely saturated and darkened
- Stains and discolourations became more visible

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Portable and non-destructive method

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Materials and Methods

PROJECT WORKING PLAN

The project was carried out by two institutions (WULS-SGGW and IVALSA/CNR).

Research tasks were divided into five working packages:

1.Preparation of samples acquired from antique wooden parquets and reference samples made of contemporary wood;

2.Soaking contemporary wood samples with wax and varnish;

3.FT-NIR measurement of contemporary and antique samples;

4.Analysis of results by means of chemometric methods (development of models for contemporary wood and their verification);

5.Assessment of chemical substances used for surface finishing.

Materials and Methods

We studied the finishes using contemporary and antique wood samples of *Quercus* sp, *Ulmus* sp, *Fraximus excelsior* L. and *Pinus silvestris* L. (6 month after aplication).

Six parquets from 19th century manor houses located in Tarnowiec and Falejówka in South-Eastern Poland.

The antique parquet samples were taken from floors with differend kind of structure and from three points that differed as to the microclimate conditions.

Control samples of contemporary wood with similar parameters.

The parquets were made of local materials; therefore the control samples were taken from several local storage sites of construction materials.

Each sample was made from a different piece of wood.

The samples were acclimatized before the tests.

Materials and Methods

- **Bee wax obtained from a bee yard in honeycombs (wax bar + polishing)**

→ **more than 300 components:**
monoesters (~ 35%), hydrocarbons (~ 14%)
free acids (~ 12%)
diesters (~ 14%)
hydroxyl polyesters (~ 8%),
hydroxyl monoesters(~ 4%)
triesters (~ 3%)
acid polyesters (~ 2%)
acid monoesters(~ 1%) other unidentified components (~ 7%)

- **Varnish (98% linseed oil + 2% siccatives) applied hot**

→ **complex mixture of glycerol esters, mainly unsaturated fatty acids**

Materials and Methods

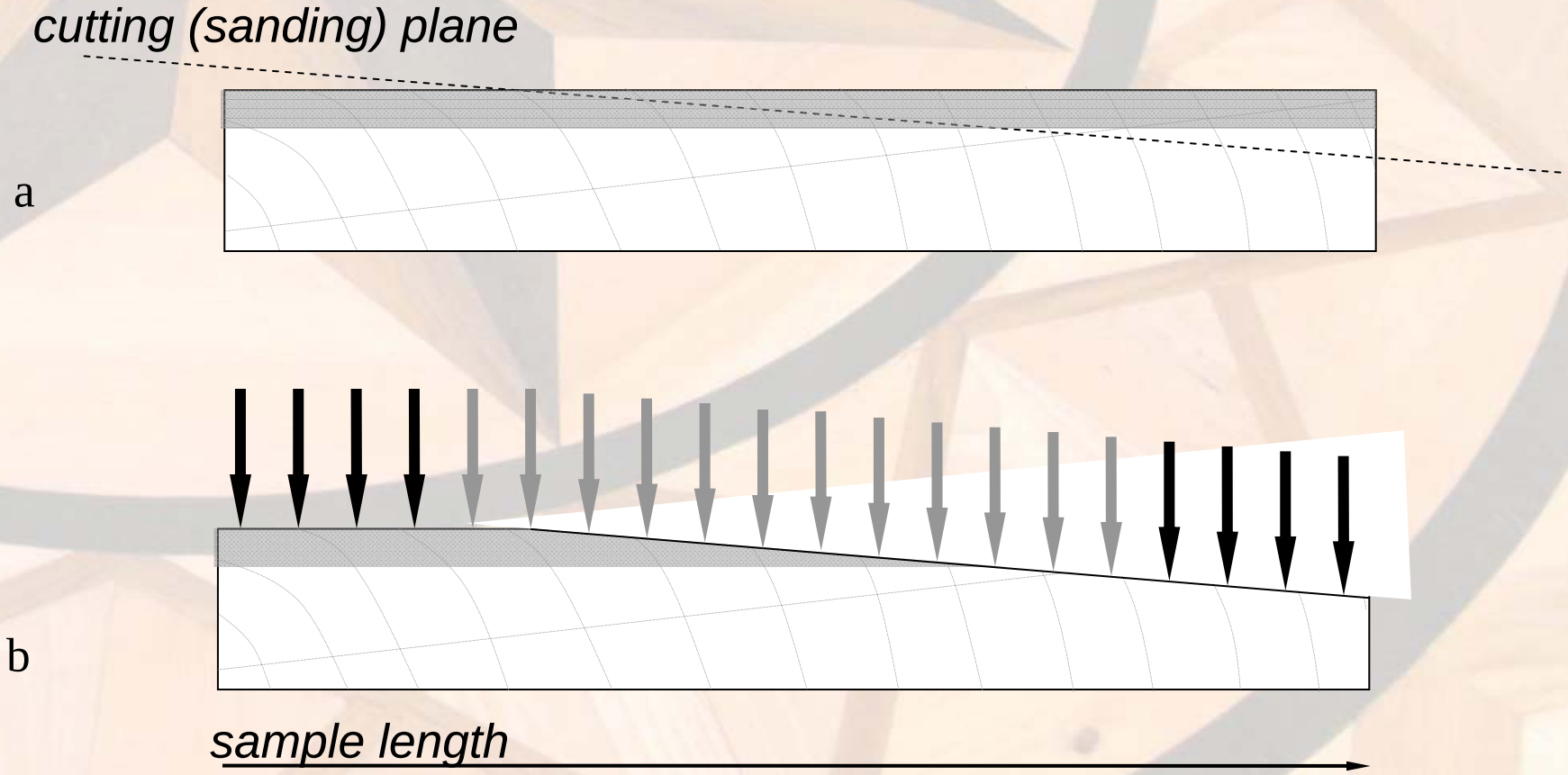
Experimental hardware

- **All the experimental samples were measured by using FT-NIR (Fourier Transform Near Infrared Spectrometer) VECTOR 22-N produced by Bruker Optics GmBH.**
- **The spectral range measured was between 4000cm^{-1} and 12000cm^{-1}.**
- **Each spectrum has been computed as an average of 32 successive measurements in order to minimize the measurement error.**

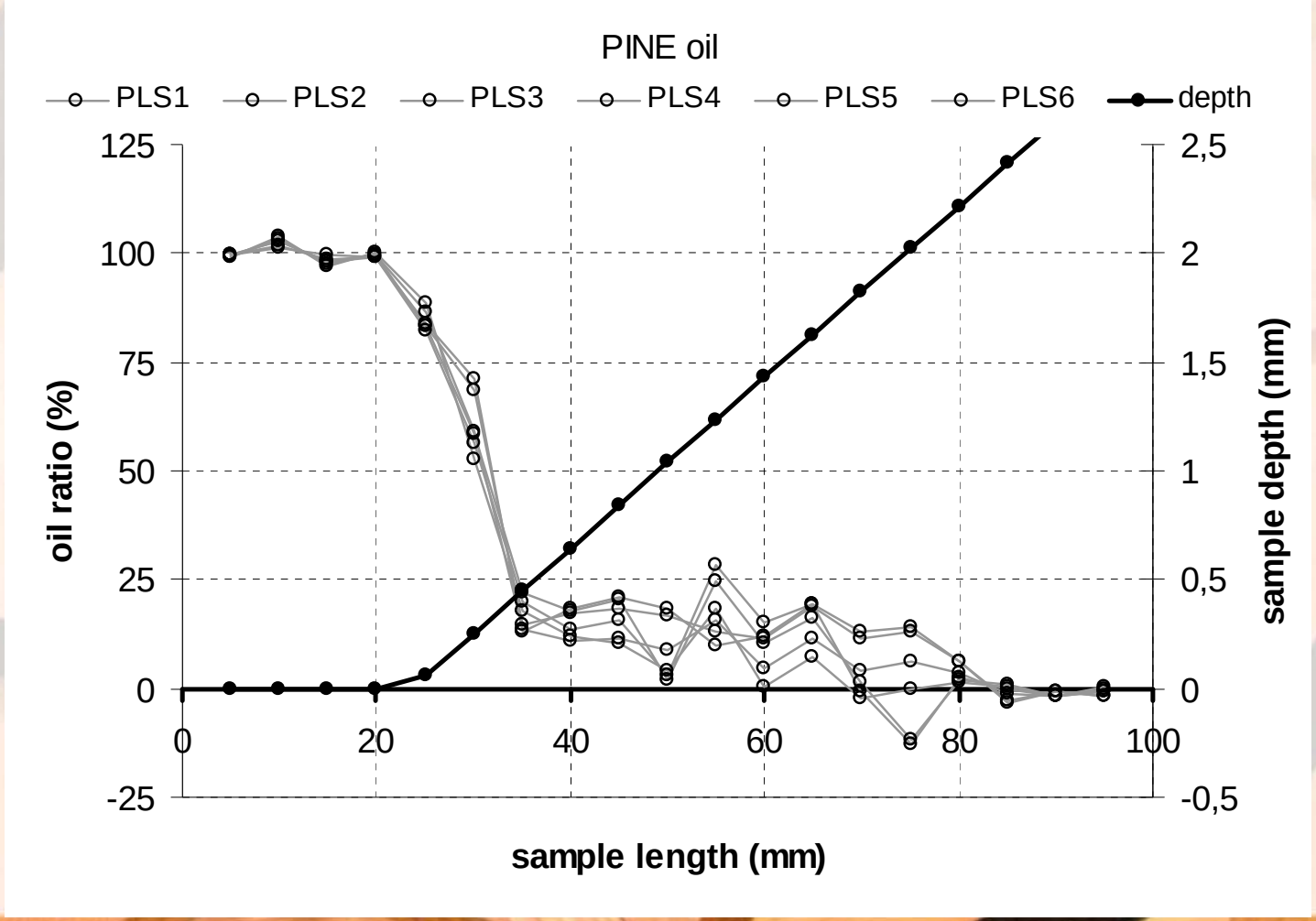
Scanning procedure

- **Five separate spectra have been measured on each wooden sample. The measurement location has been selected randomly; however any visible abnormalities of wood surface (knot or discoloration) were intentionally omitted.**
- **After capturing the spectrum a dedicated file has been created and measurement result has been saved on the hard disk for further post-processing as a *.OPS file**

The sample preparation; opening a gradient by sanding the surface -a, measurement position of the NIR probe –b (black arrows indicate measurements used for PLS calibrations, gray arrows indicate measurements used for oil/wax ratio estimation)



The depth of sample and predicted oil ratio along the sanded sample's length



Materials and Methods

Data analysis

- **OPUS 6.5 and National Instruments LabView 8.5 software packages have been used for signal processing and data analyzes.**

- **A typical NIR spectra preprocessing include computation of the second derivative. Derivatives were calculated simultaneous with the Savitzky-Golay algorithm.**

- **Spectra interpretation was performed according to review of Schwanninger et al. [2001].**

- **For mathematical evaluation of the results some methods as principal component analysis, partial least square, identity test, and cluster analysis were applied.**

band no.	wavenumber (cm-1)	wood component	functional group
1	4063	carbohydrates	CH, C-C
2	4195	lignin	not assigned
3	4202	holocellulose	OH
4	4235	cellulose	OH, CH, CH2
5	4268	cellulose	CH, CH2
6	4283	cellulose, hemicellulose	CH
7	4288	hemicellulose (xylan)	CH
8	4365	cellulose	CO, OH, CH2
9	4401	cellulose, hemicellulose	CH, CH2, OH, CO
10	4546	lignin	CH, C=O
11	4608	cellulose, hemicellulose	not assigned
12	4635	cellulose	OH, CH
13	4686	hemicellulose/lignin/extractives	CH, C=C, C=O
14	4739	cellulose	OH
15	4780	cellulose	OH, CH center of the range
16	4795	cellulose, hemicellulose (xylan)	OH, CH
17	4808	cellulose semicrystalline and crystalline	OH, CH
18	5051	water	OH
19	5198	water	OH center of the range
20	5236	hemicellulose	C=O
21	5245	hemicellulose	C=O
22	5464	cellulose semicrystalline and crystalline	OH, CO
23	5495	cellulose	OH, CO
24	5522	lignin	not assigned
25	5593	cellulose semicrystalline and crystalline	CH
26	5618	cellulose	CH2
27	5666	not assigned	CH, CH2
28	5692	not assigned	CH2
29	5776	cellulose	CH
30	5795	lignin	CH
31	5800	hemicellulose (furanose/pyranose)	CH
32	5816	cellulose/hemicellulose/lignin	CH
33	5865	hemicellulose	CH
34	5872	cellulose	CH
35	5900	not assigned	CH
36	5935	lignin	CH
37	5950	hemicellulose	CH
38	5963	lignin	CH
39	5995	extractives	CH
40	6003	hemicellulose	CH
41	6126	cellulose	OH
42	6188	not assigned	CH
43	6286	cellulose crystalline	OH
44	6334	cellulose	OH
45	6450	cellulose crystalline	OH
46	6472	cellulose	OH
47	6520	cellulose	OH
48	6622	cellulose	OH
49	6660	cellulose	OH
50	6700	hemicellulose (glucomannan)	OH
51	6715	cellulose semicrystalline	OH
52	6740	cellulose	OH
53	6757	cellulose	OH
54	6770	cellulose	OH
55	6790	cellulose semicrystalline	OH
56	6800	hemicellulose (glucomannan)	OH
57	6874	lignin	OH
58	6944	lignin	CH
59	6974	not assigned	OH
60	7003	amorphus cellulose/water	OH
61	7092	lig/extr	OH
62	7215	not assigned	OH, CH
63	7300	hemicellulose/all	CH
64	7315	cellulose	CH begining
65	7321	cellulose	CH end
66	7353	all	CH
67	7410	hemicellulose/all	CH
68	8160	cellulose	CH begining
69	8250	cellulose	CH end
70	8654	hemicellulose	CH
71	8749	lignin	CH

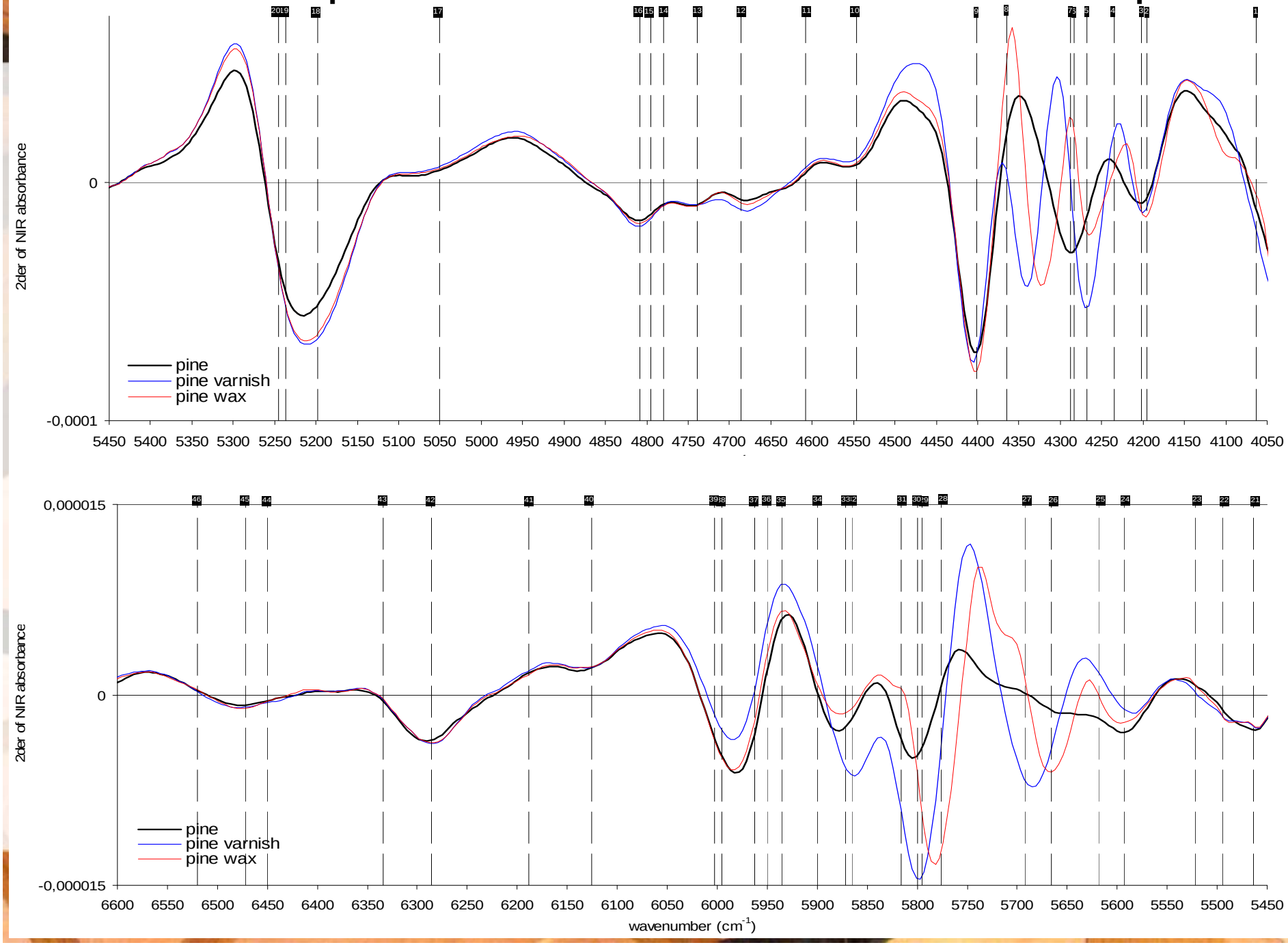
Band assignment of FT-NIR spectra [Schwanninger et al. 2001]

Results

1.Analysis of contemporary wood (spectral data base of surfce of four investigated species)

2.Analysis of antiques flooring

Second derivative spectra of natural and finished with wax and varnish pine wood



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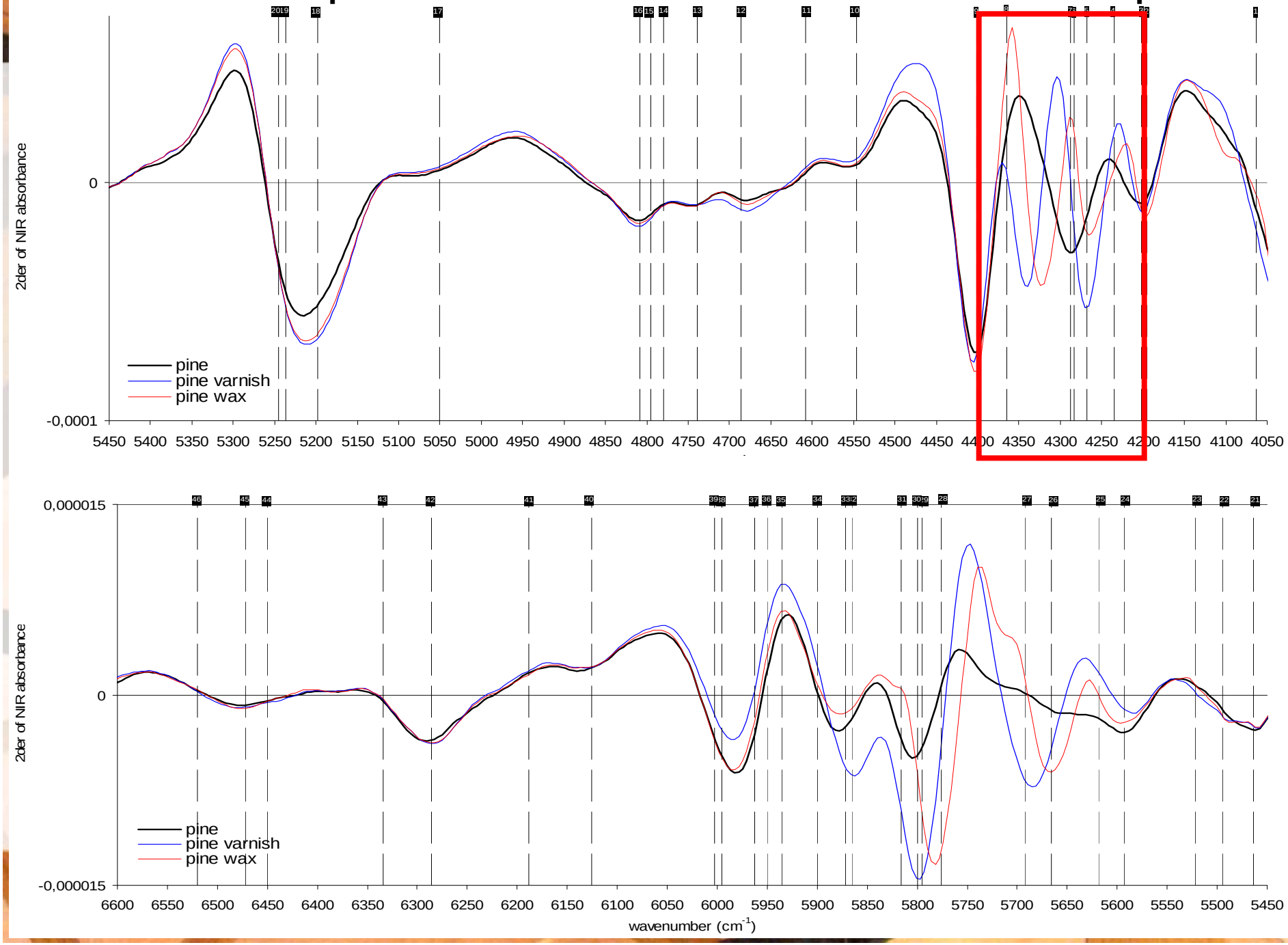

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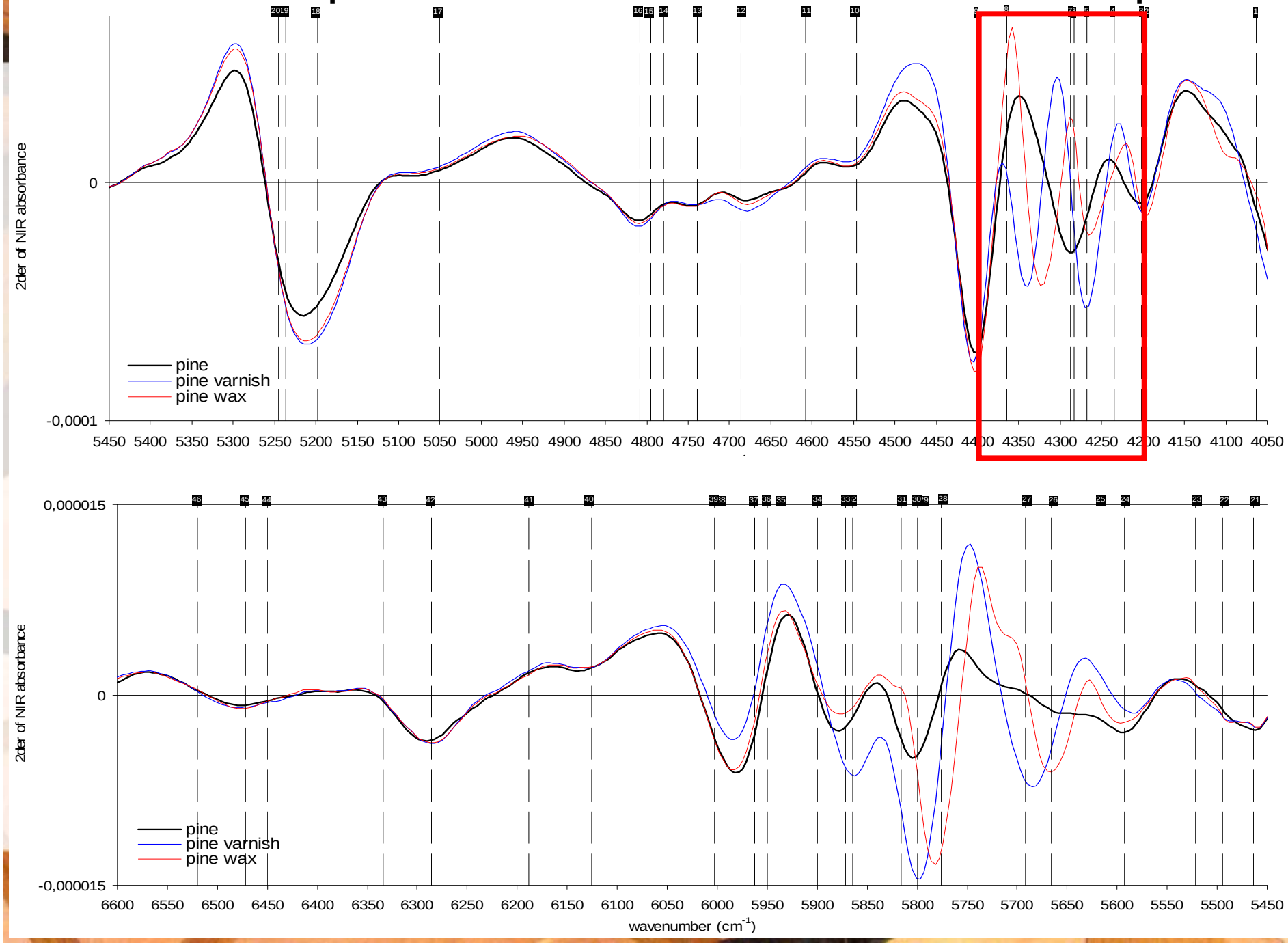

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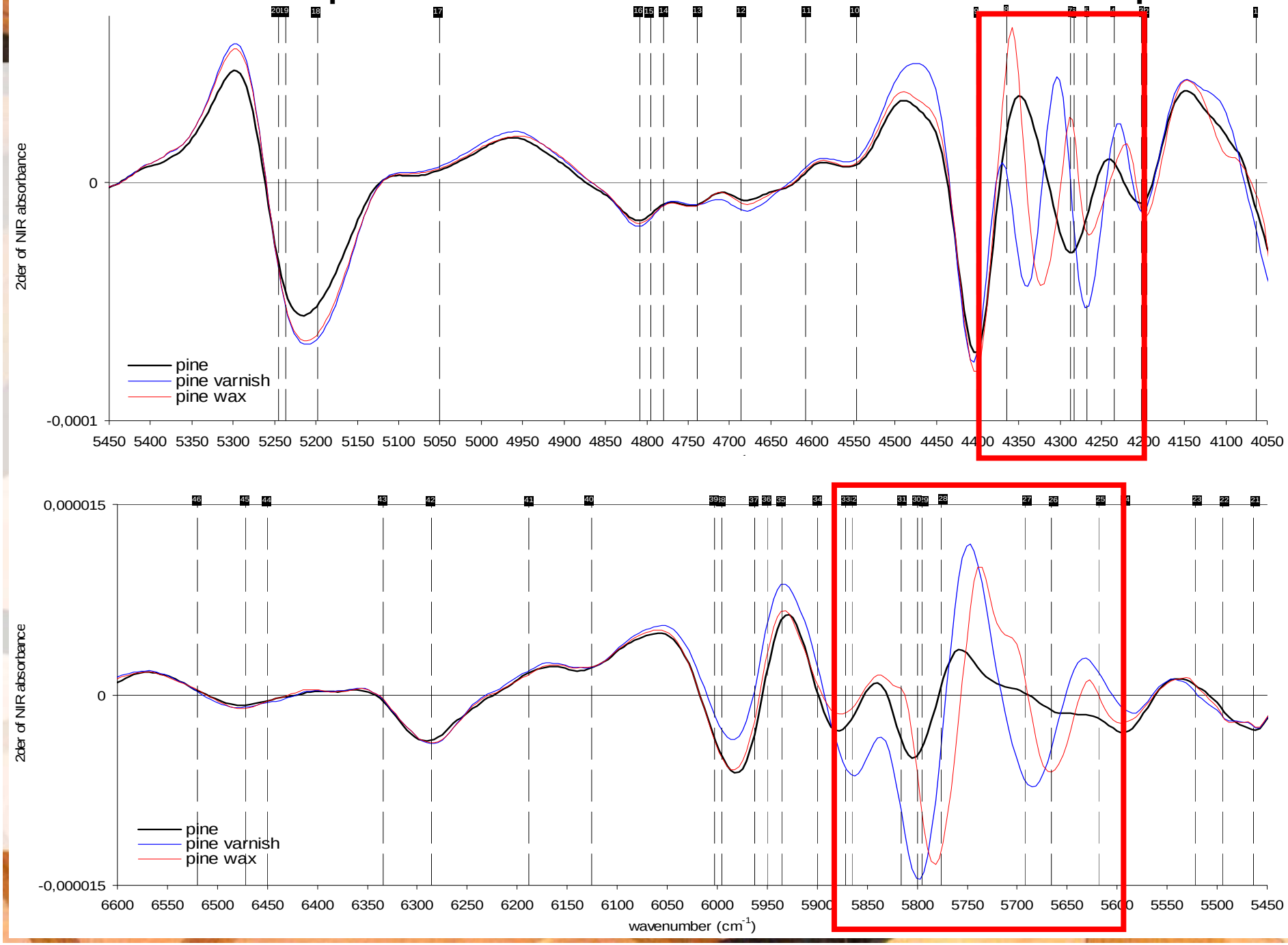

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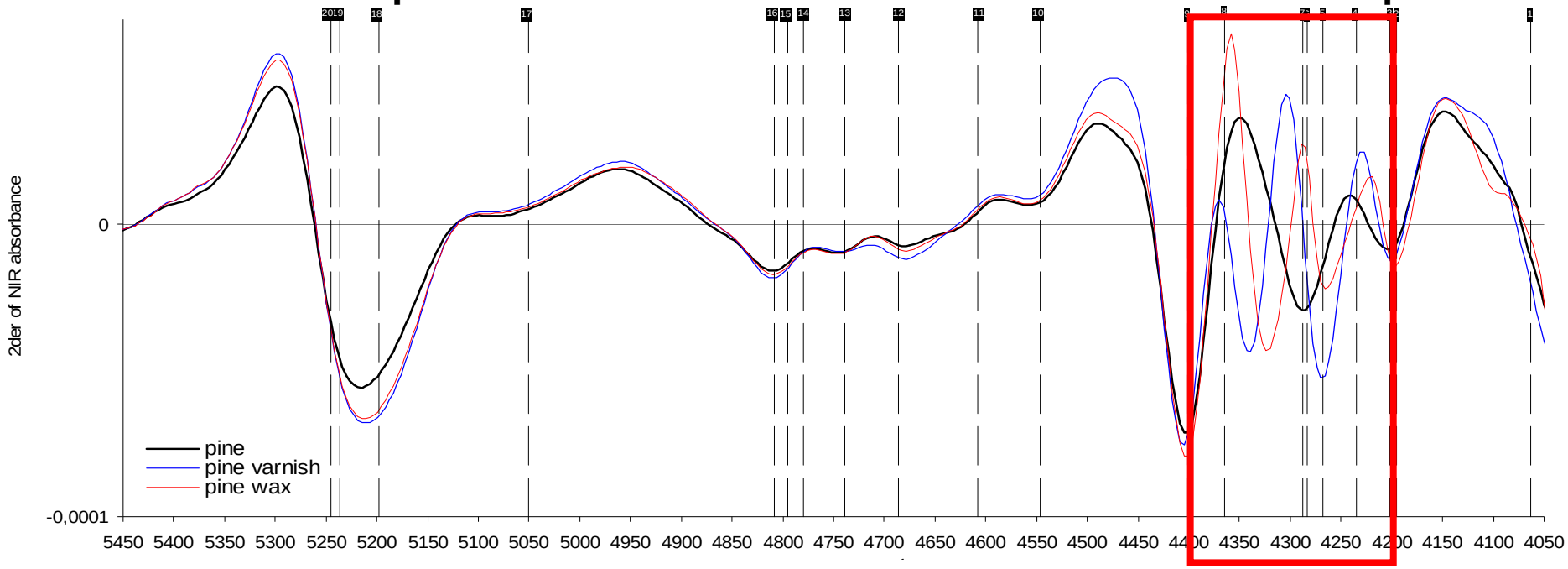
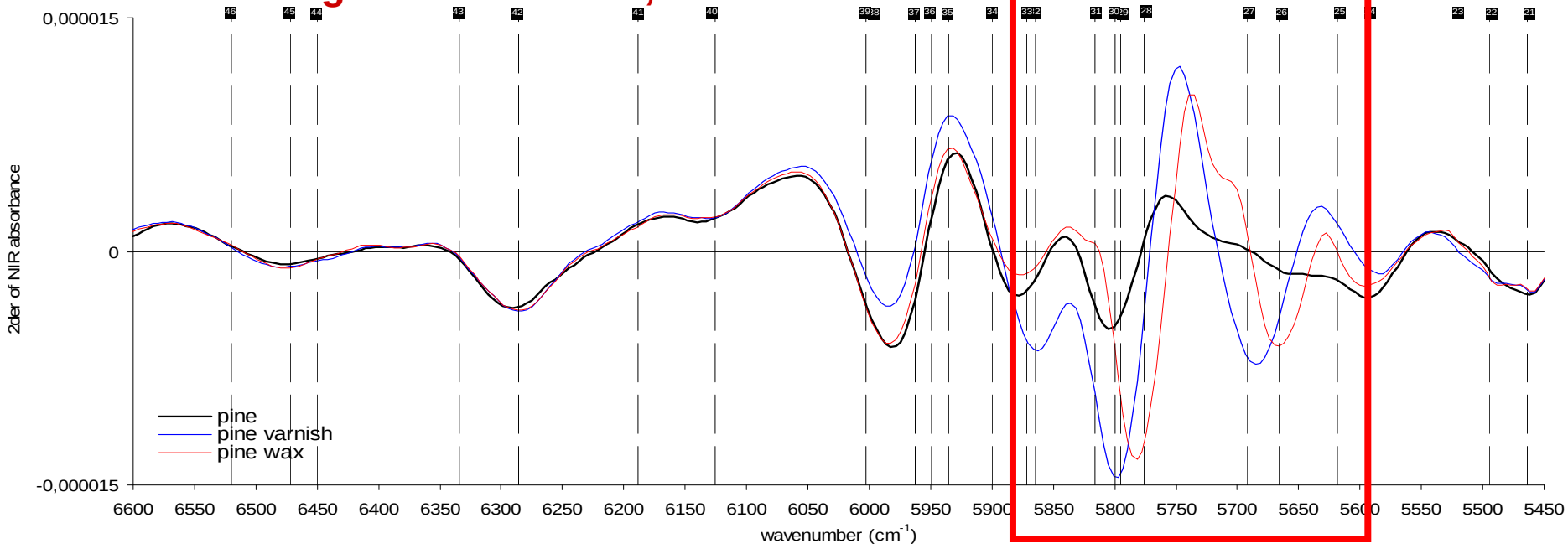
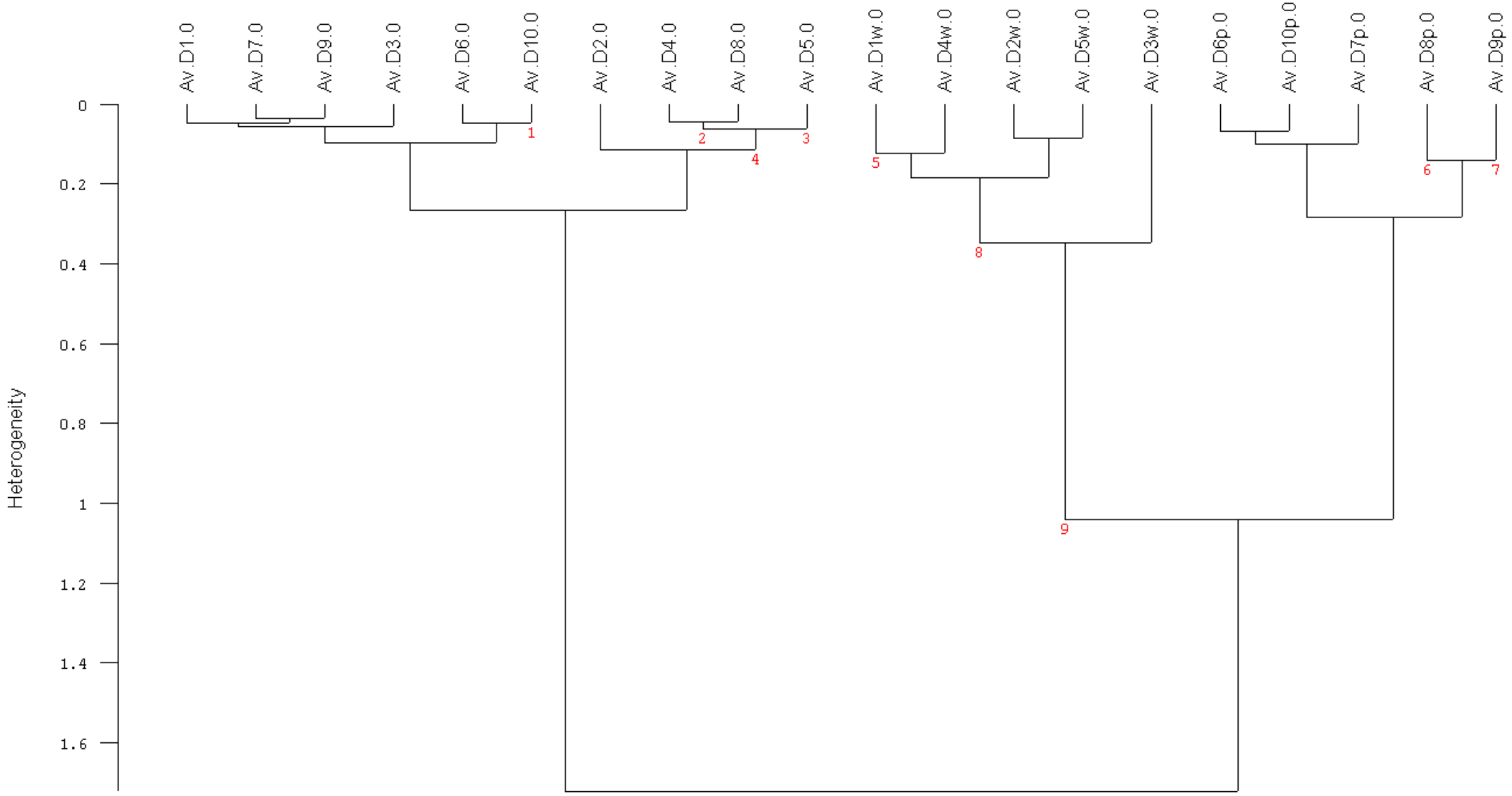


in regions 4200-4400 ; 5600-5850cm^{-1}



Cluster analysis of natural, wax and varnish soaked oak



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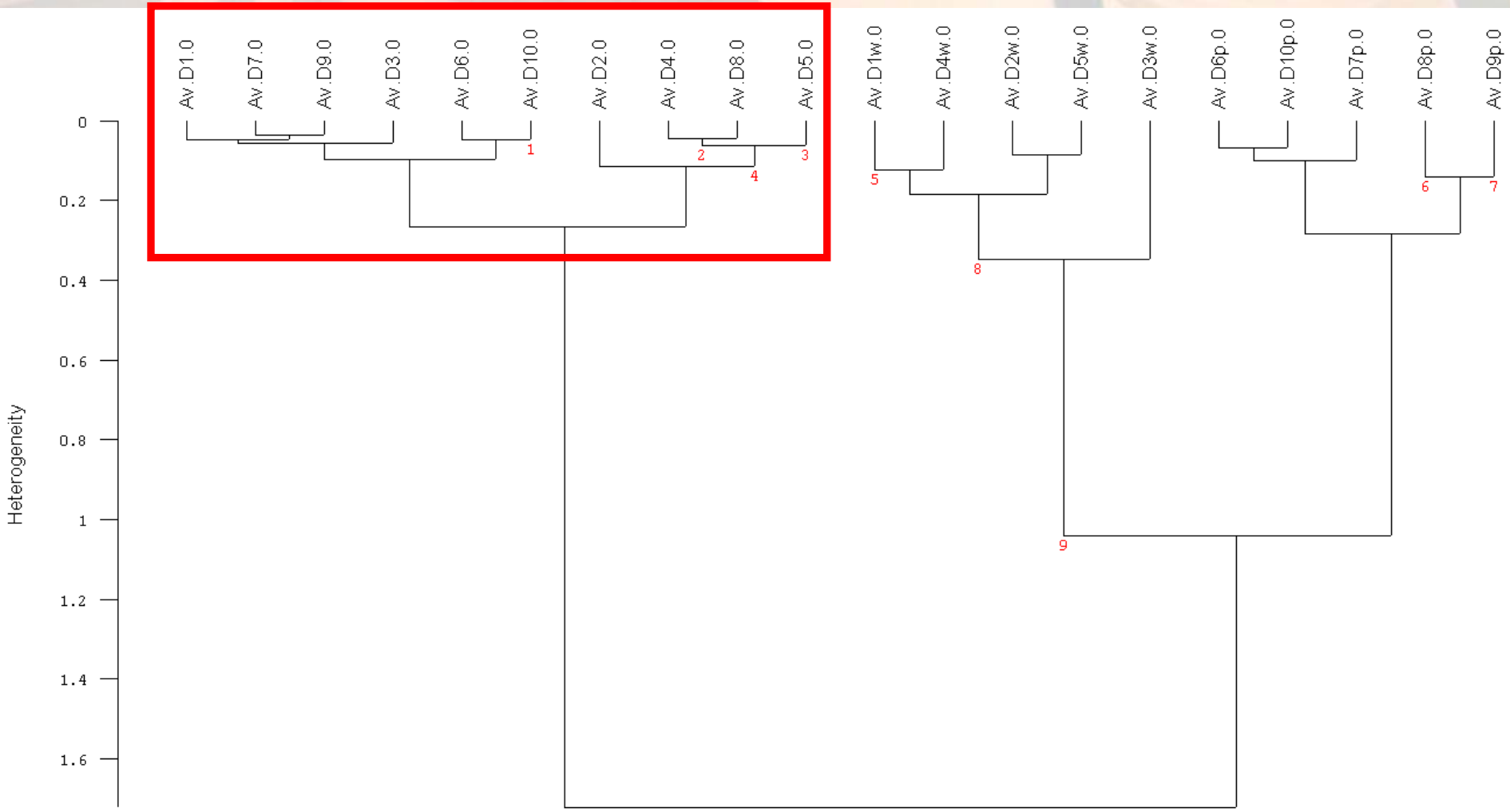

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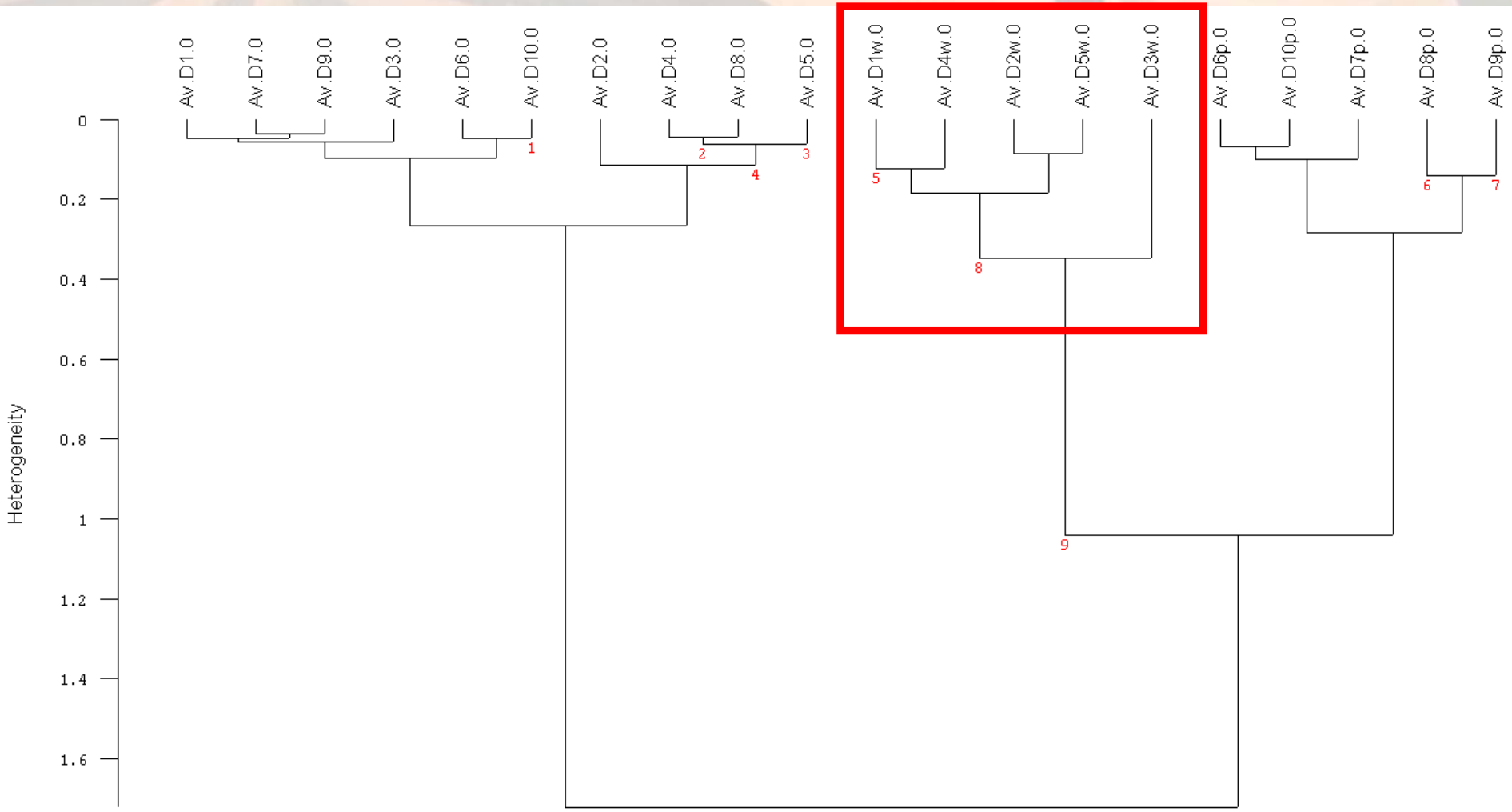

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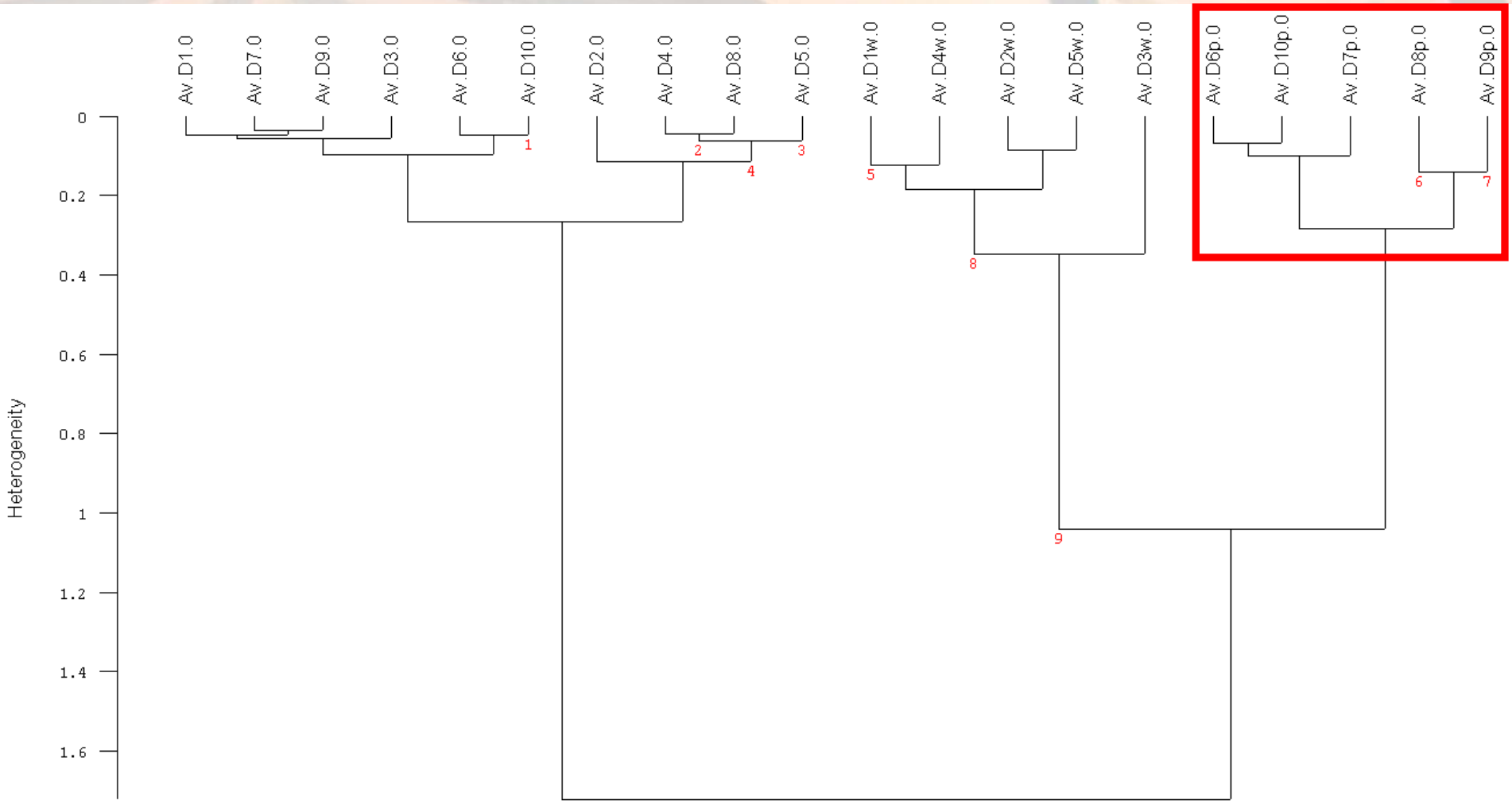
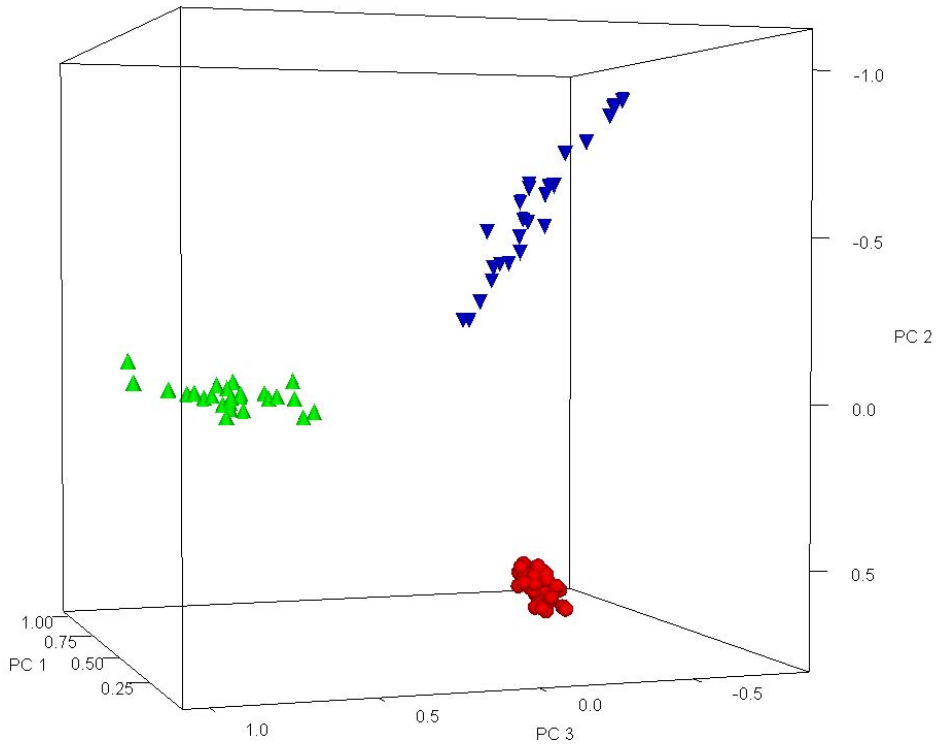
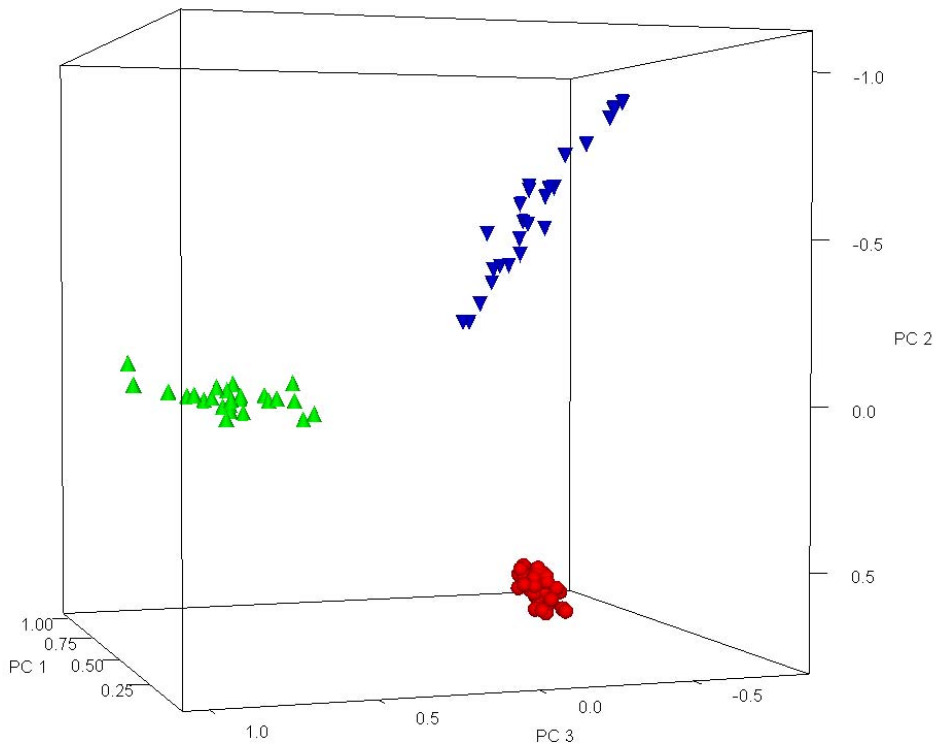




elm

		ID	Group1	Group2	IP-Level	S	Threshold1	Threshold2	D
1	-	1	elm natural	elm wax	IP1: New	2.052096	0.160371	0.528745	1.414132
2			"	elm varnish	IP1: New	2.479130	"	0.130153	0.720248
3	-	2	elm varnish	elm wax	IP1: New	1.053098	0.130153	0.528745	0.693884
4			"	elm natural	IP1: New	2.479130	"	0.160371	0.720248
5	-	3	elm wax	elm varnish	IP1: New	1.053098	0.528745	0.130153	0.693884
6			"	elm natural	IP1: New	2.052096	"	0.160371	1.414131

Principal Component Analysis of elm samples (a) and results of selectivity coefficient calculated for samples with various finishing (b). Note: red – natural wood, blue – wood with wax, green wood with varnish.



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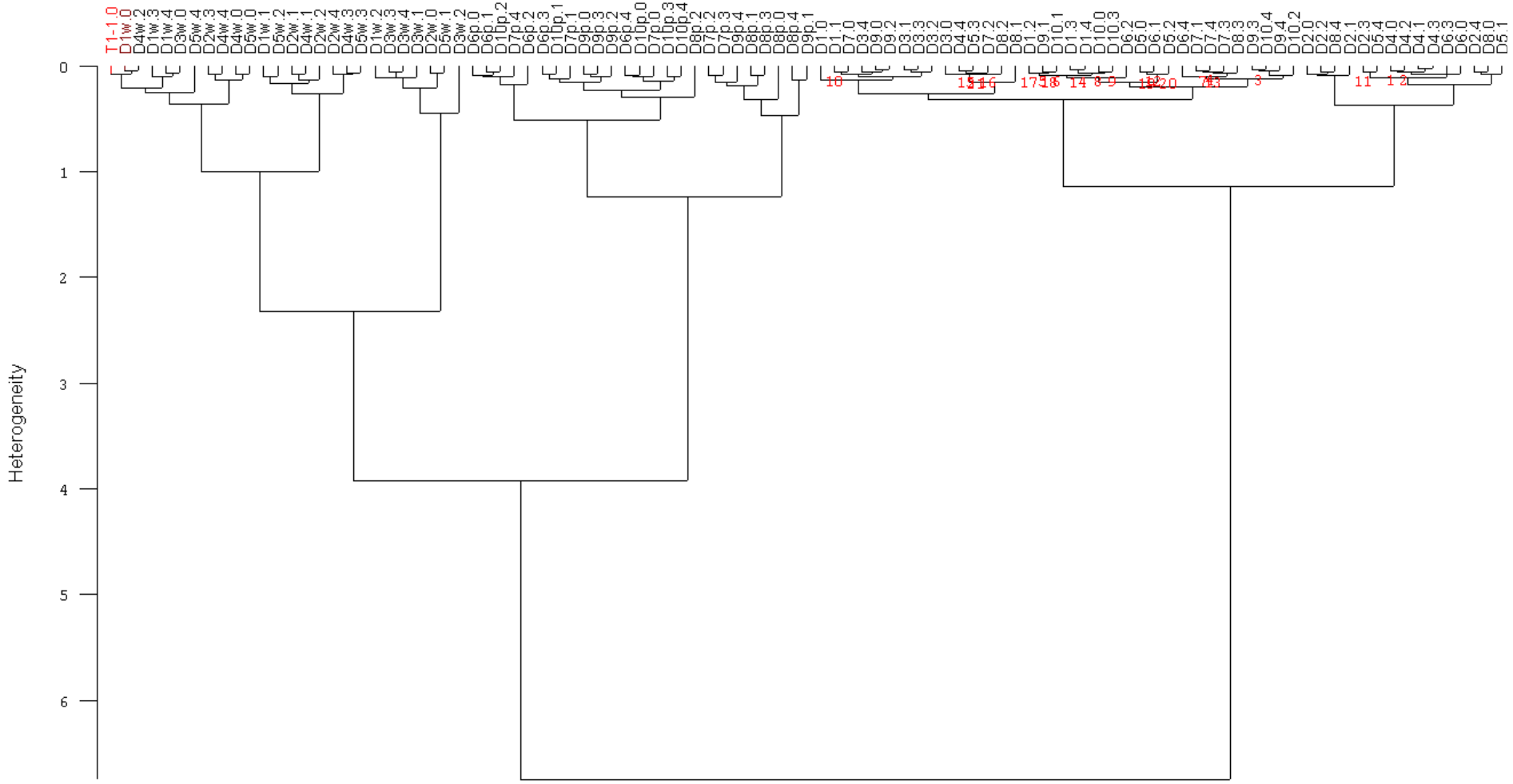
Cluster analysis test of oak samples from Falejowka manor house



Results of identification of investigated samples by means of CA test, IT and QC

Sample code	Cluster analysis test	Identity test	Quick compare (similarity [%])		
			natural	varnish	Wax
Oak F	natural	natural	99.79	83.02	99.86
Oak T1-1	natural	natural	99.66	85.81	99.89
Oak T1-2	natural	natural	98.47	88.84	99.88
Oak T1-3	natural	natural	95.40	90.21	99.98
Oak T4-1	natural	natural	99.62	84.59	99.91
Oak T4-2	natural	natural	99.59	82.44	99.87
Oak T4-3	natural	natural	99.58	83.32	99.92
Elm T5-1	natural	natural	99.13	77.48	91.56
Elm T5-2	wax	natural	97.75	78.94	92.58
Elm T5-3	wax	natural	98.03	77.86	92.22

Results of identity test for Falejowka floor samples

Result of IDENT evaluation:

Sample name: Falejowka
Sample: D:\Ania Rozanska feb 2013\Srednie antyczne\F.0
Date and time (measurement): 2012/03/21 16:21:43 (GMT+1)
Method file: D:\Ania Rozanska feb 2013\analizy\dab waski band.faa

Hit no.	Sample name	Hit qual.	Threshold	Group
1	wood	0.02982	0.12728	oak natural
2	wood	0.26225	0.17233	oak varnish
3	wood	1.06052	0.93197	oak wax

IDENTIFIED AS oak natural

OK

Results of identification of investigated samples by means of CA test, IT and QC

Sample code	Cluster analysis test	Identity test	Quick compare (similarity [%])		
			natural	varnish	Wax
Oak F	natural	natural	99.79	83.02	99.86
Oak T1-1	natural	natural	99.66	85.81	99.89
Oak T1-2	natural	natural	98.47	88.84	99.88
Oak T1-3	natural	natural	95.40	90.21	99.98
		natural	99.62	84.59	99.91
		natural	99.59	82.44	99.87
		natural	99.58	83.32	99.92
		natural	99.13	77.48	91.56
		natural	97.75	78.94	92.58
		natural	98.03	77.86	92.22

Result of IDENT evaluation:

Falejowka

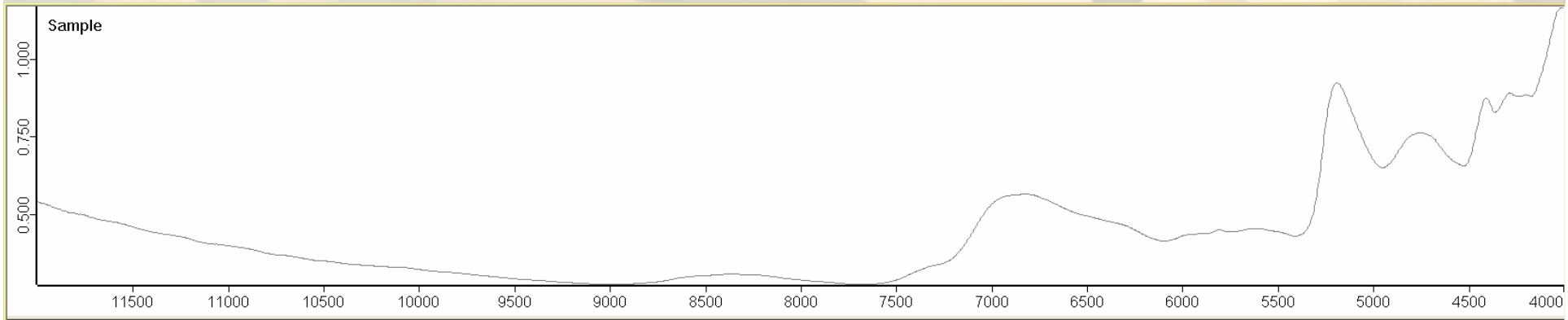
Sample name:
Sample: D:\Ania Rozanska feb 2013\Srednie antyczne\F.0
Date and time (measurement): 2012/03/21 16:21:43 (GMT+1)
Method file: D:\Ania Rozanska feb 2013\analizy\dab waski band.faa

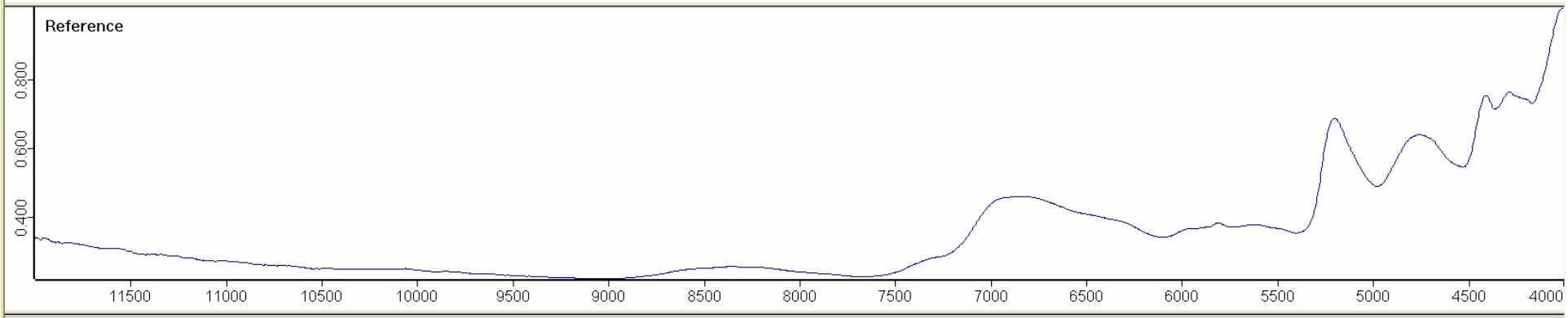
Hit no.	Sample name	Hit qual.	Threshold	Group
1	wood	0.02982	0.12728	oak natural
2	wood	0.26225	0.17233	oak varnish
3	wood	1.06052	0.93197	oak wax

IDENTIFIED AS oak natural

OK

Results of Quick compare test between sample from Tarnowiec manor house (room 5, external corner of the room) and natural elm wood



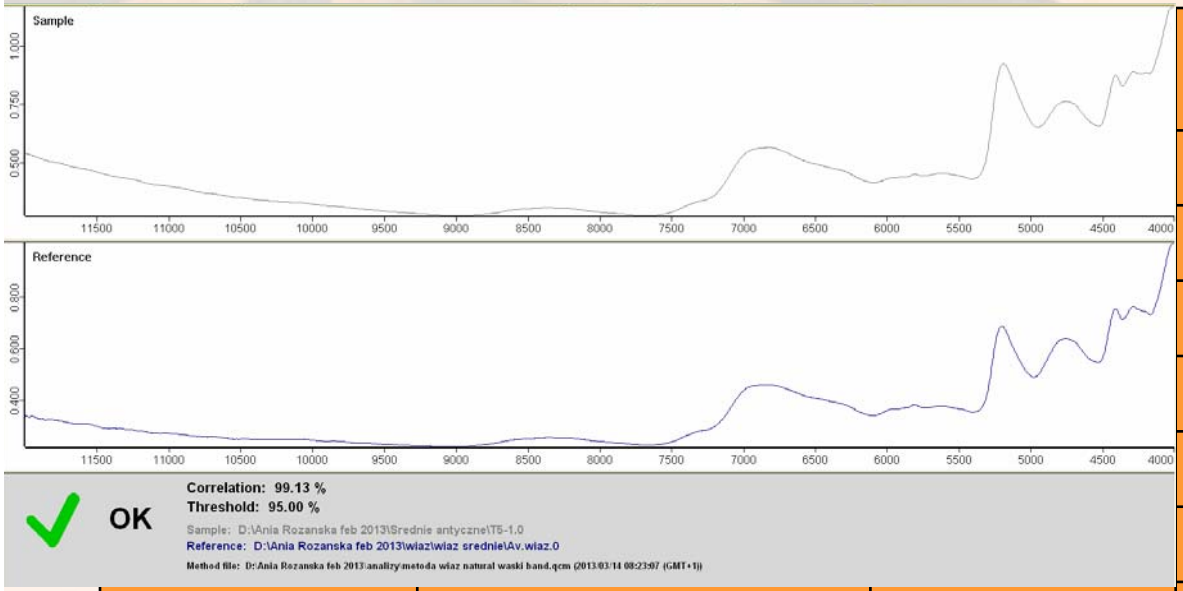


OK

Correlation: 99.13 %
Threshold: 95.00 %

Sample: D:\Ania Rozanska feb 2013\Srednie antyczne\T5-1.0
Reference: D:\Ania Rozanska feb 2013\wiaz\wiaz srednie\Av.wiaz.0
Method file: D:\Ania Rozanska feb 2013\analizy\metoda wiaz natural waski band.qcm (2013/03/14 08:23:07 (GMT+1))

Results of identification of investigated samples by means of CA test, IT and QC



			Quick compare (similarity [%])		
			natural	varnish	Wax
			99.79	83.02	99.86
			99.66	85.81	99.89
			98.47	88.84	99.88
			95.40	90.21	99.98
			99.62	84.59	99.91
Oak T4-2	natural	natural	99.59	82.44	99.87
Oak T4-3	natural	natural	99.58	83.32	99.92
Elm T5-1	natural	natural	99.13	77.48	91.56
Elm T5-2	wax	natural	97.75	78.94	92.58
Elm T5-3	wax	natural	98.03	77.86	92.22

CONCLUSION

- FT-NIR spectroscopy is a technique allowing fast and non-destructive measurement of wooden samples.
- In this research highlighted differences between different natural surfaces finishing methods.
- Each algorithm used for data evaluation has different mathematical background, therefore highlighted specific properties of spectra.
- Evaluation of antique floor is problematic:
  - aging of samples
  - natural weathering
  - grated or rinsed
  - finishing once with wax and then with varnish
  - way of preparation of historic samples - manual grinding in order to remove dirt and gain flatness.

The next step of this research is repetition of FT-NIR measurement of antique samples without surface preparation and validation previously developed models.

Thank you for your attention!

annamaria.rozanska@gmail.com

anna.sandak@ivalsa.cnr.it