*Łancut Castle parquet

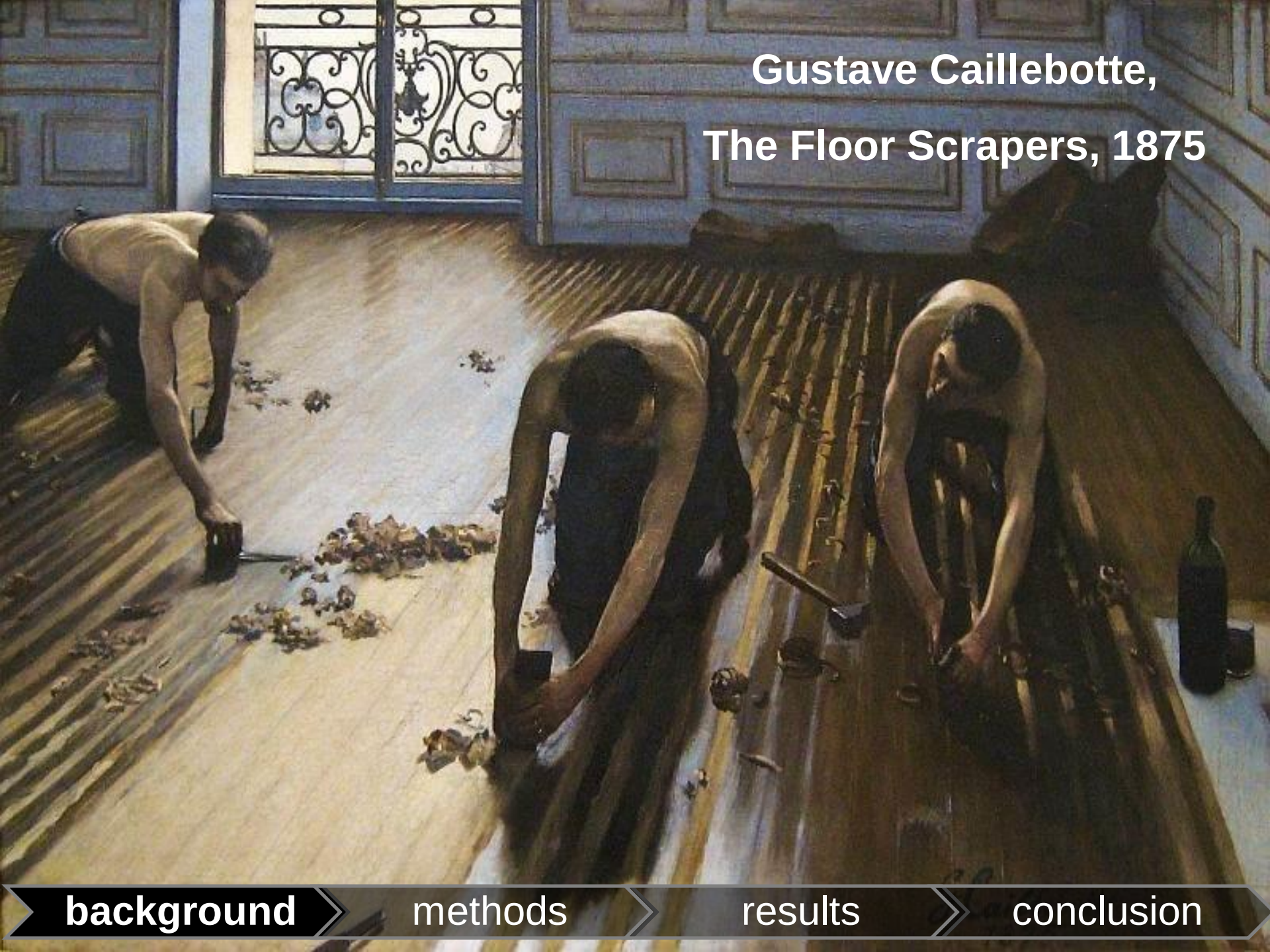
*Łancut Castle parquet

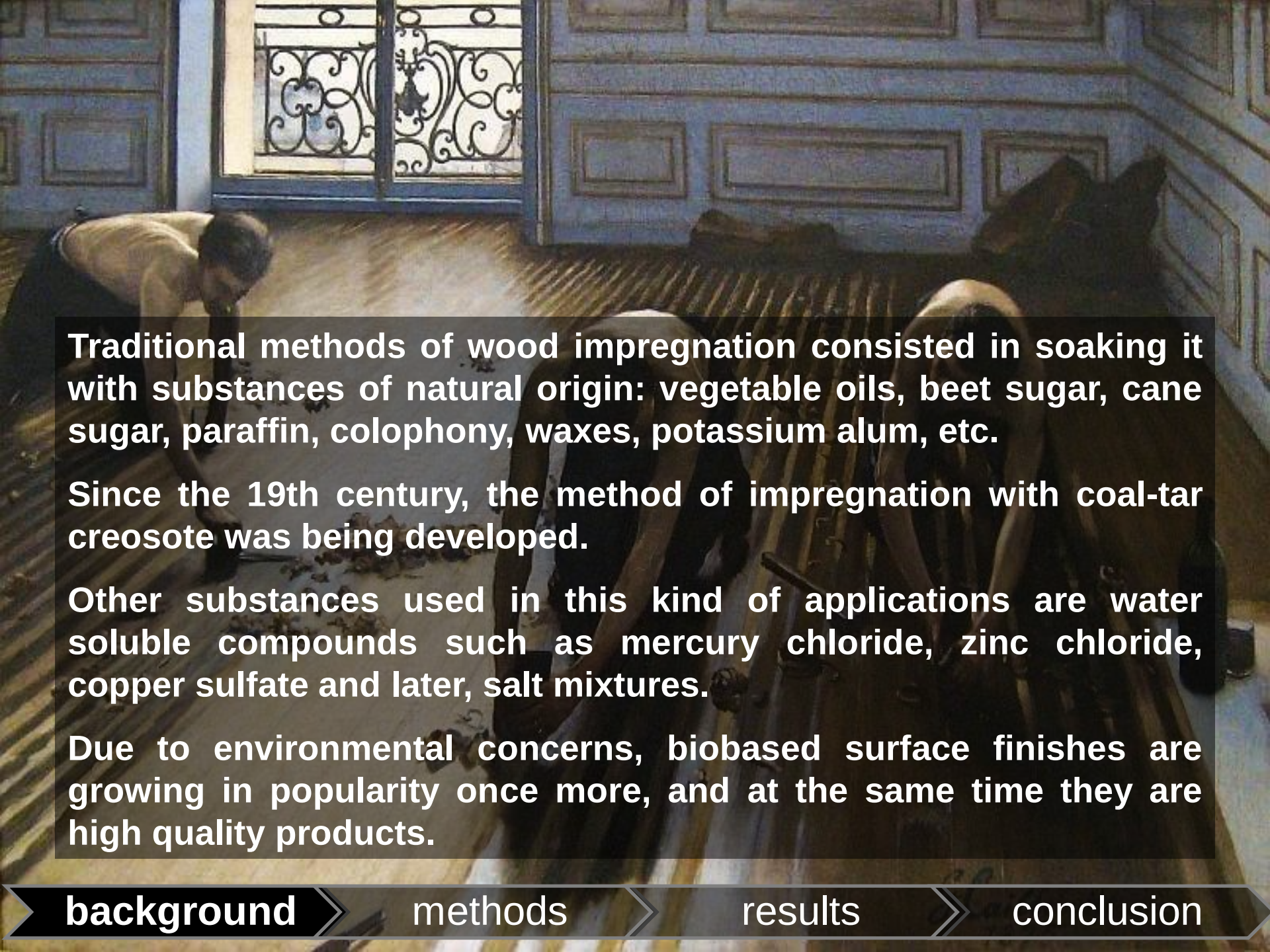
Identification Methods of Biobased Surface Finishes on Antique Wooden Parquets

PhD Anna Rozanska - Warsaw University of Life Sciences
PhD Anna Sandak - IVALSA Tree and Timber Institute

CNR-IVALSA
TREES AND TIMBER INSTITUTE


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


Gustave Caillebotte,
The Floor Scrapers, 1875

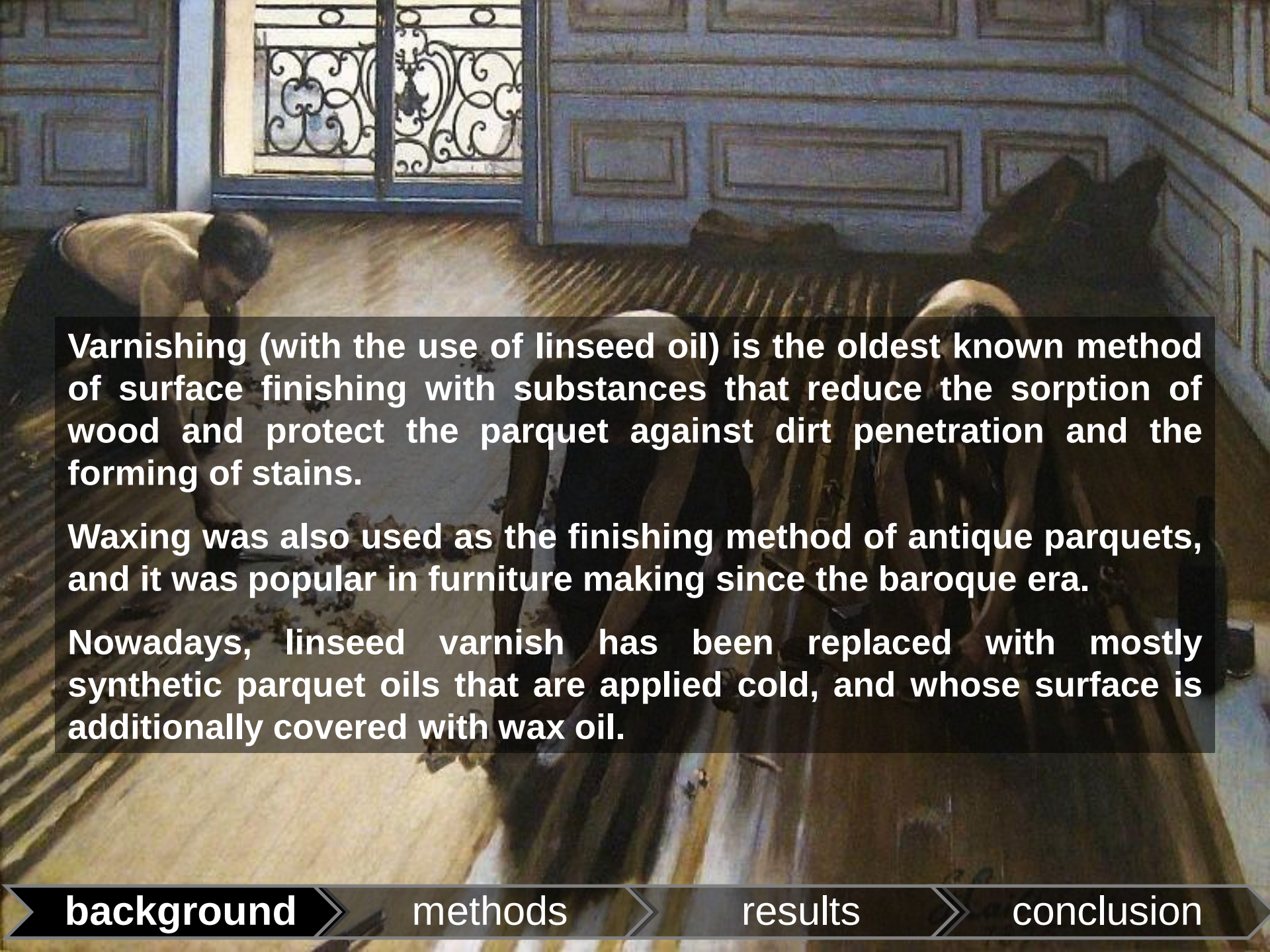


Traditional methods of wood impregnation consisted in soaking it with substances of natural origin: vegetable oils, beet sugar, cane sugar, paraffin, colophony, waxes, potassium alum, etc.

Since the 19th century, the method of impregnation with coal-tar creosote was being developed.

Other substances used in this kind of applications are water soluble compounds such as mercury chloride, zinc chloride, copper sulfate and later, salt mixtures.

Due to environmental concerns, biobased surface finishes are growing in popularity once more, and at the same time they are high quality products.



Varnishing (with the use of linseed oil) is the oldest known method of surface finishing with substances that reduce the sorption of wood and protect the parquet against dirt penetration and the forming of stains.

Waxing was also used as the finishing method of antique parquets, and it was popular in furniture making since the baroque era.

Nowadays, linseed varnish has been replaced with mostly synthetic parquet oils that are applied cold, and whose surface is additionally covered with wax oil.

AIM OF STUDY

The research was aimed at specifying different finish coatings / proprerties used as traditional means of wooden floor surface finishing

Correct identification of surface finishes used in a given antique parquet is crucial for the planned conservation works, because the kind of surface finish has a major influence on its visual and resistance properties

The following parameters were calculated: density profile, contact angle and surface energy

FT-NIR spectroscopy and XRF spectrofluorimetry was used for recognition of traditional finishing substances applied on antique wooden parquets

The other task was to create spectral database of substances commonly applied in 19th century

Finally verification of effectiveness of FT-NIR and XRF as a tools supporting conservation decisions was evaluated

MATERIALS

We studied wood samples of *Quercus* sp, *Ulmus* sp, *Fraximus excelsior* L. and *Pinus silvestris* L.

4 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 samples were acclimatized before the tests

METHODS

Contact angles were determined for different test liquides (diiodomethane and water)

The samples were examined with FT-NIR for the presence of wax and linseed varnish on the sample surface

With X-ray spectrofluorimetry (XRF), the surface of antique wood was tested for the presence of chosen elements (microbiological factors)

The qualitative and quantitative element content was carried out for elements whose content in wood was high, such as potassium or calcium, as well as elements whose content was lower - even trace quantities of several ppm*: chlorine (Cl), iodine (I), scandium (Sc), tin (Sn), iron (Fe), zinc (Zn), magnesium (Mg), copper (Cu)

***(*parts per million* = µmg·g–1 [Fukumoto et al. 1999, Ferrero et al. 1999]**

The reference distribution of elements on the surface of samples was calculated for contemporary oak, elm, ash and pine; without finish as well as finished

METHODS FT-NIR

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

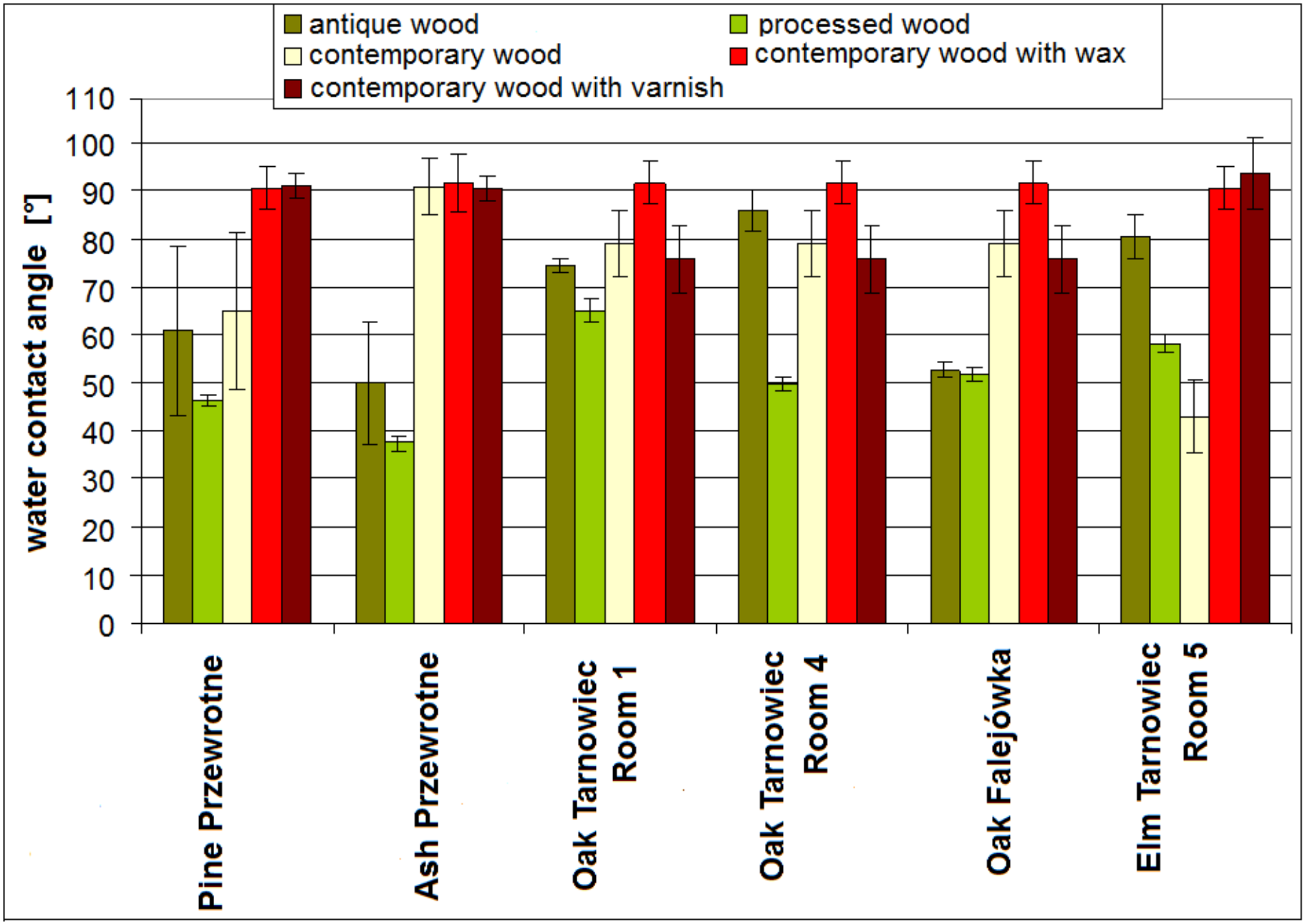
Five separate spectra have been measured on each wooden sample

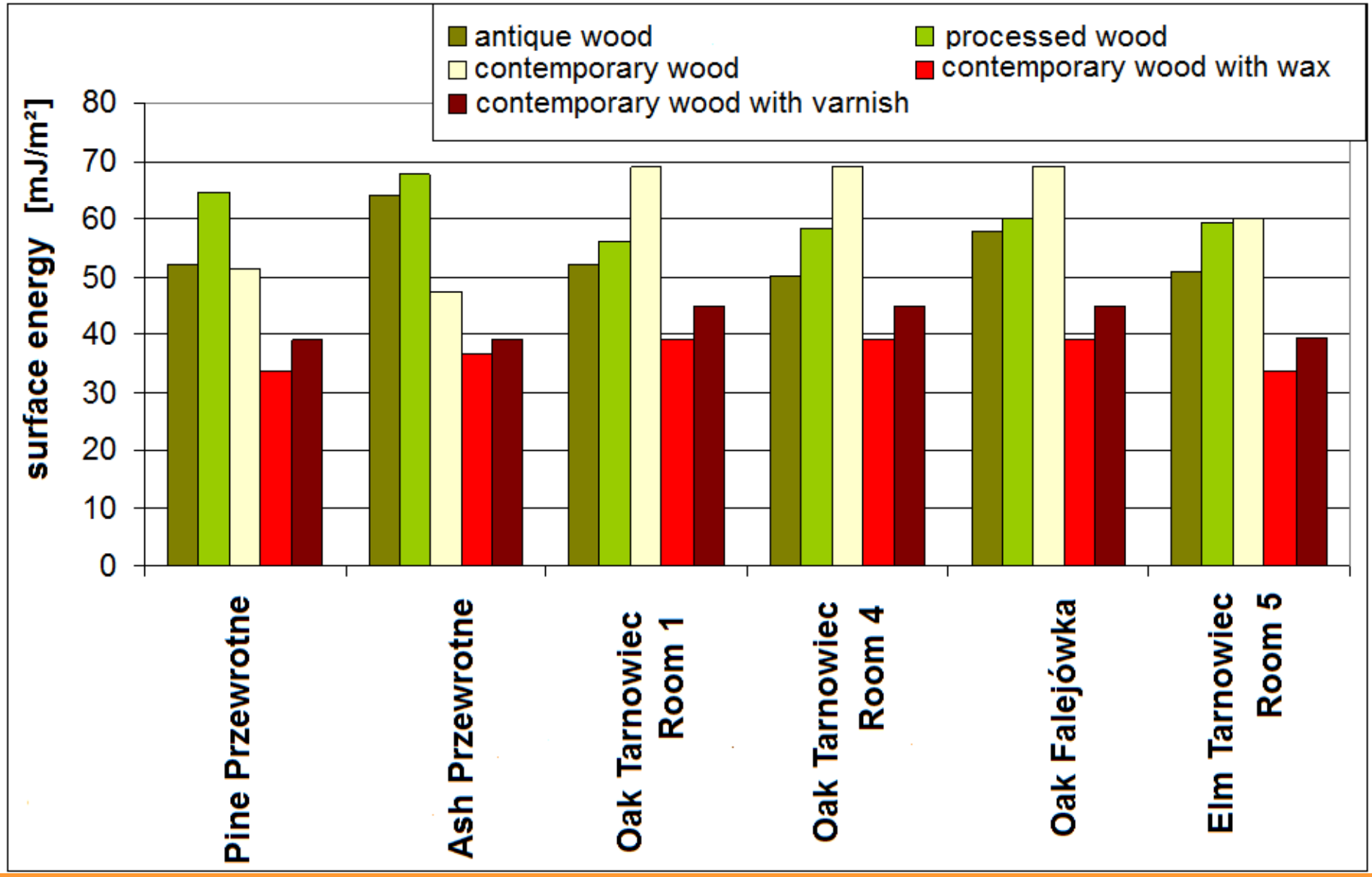
Measurement result has been saved on the hard disk for further post-processing as a *.OPS file.

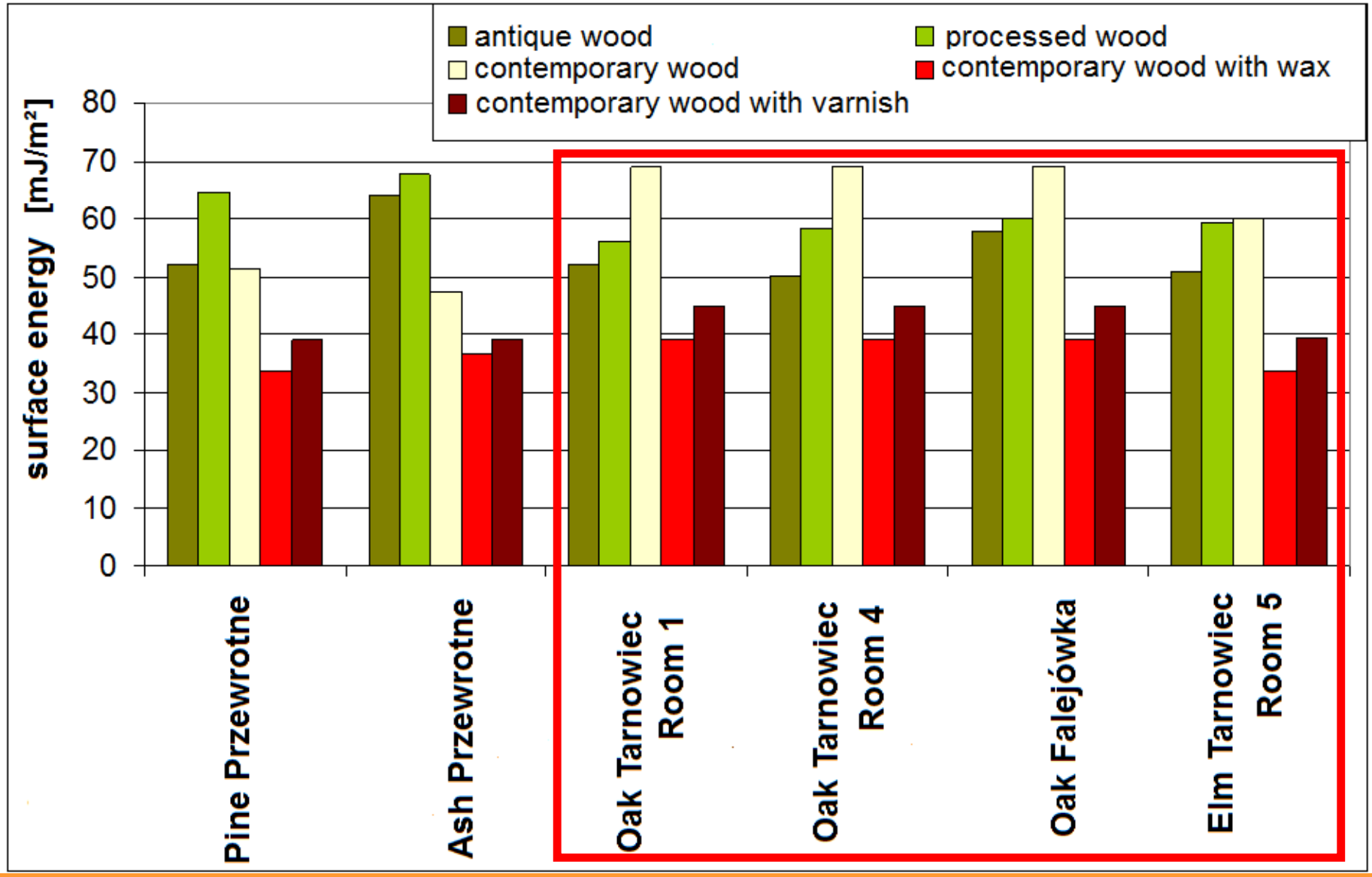
Data analysis: OPUS 6.5 and National Instruments LabView 8.5 software packages, derivatives calculated simultaneous with the Savitzky-Golay algorithm

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

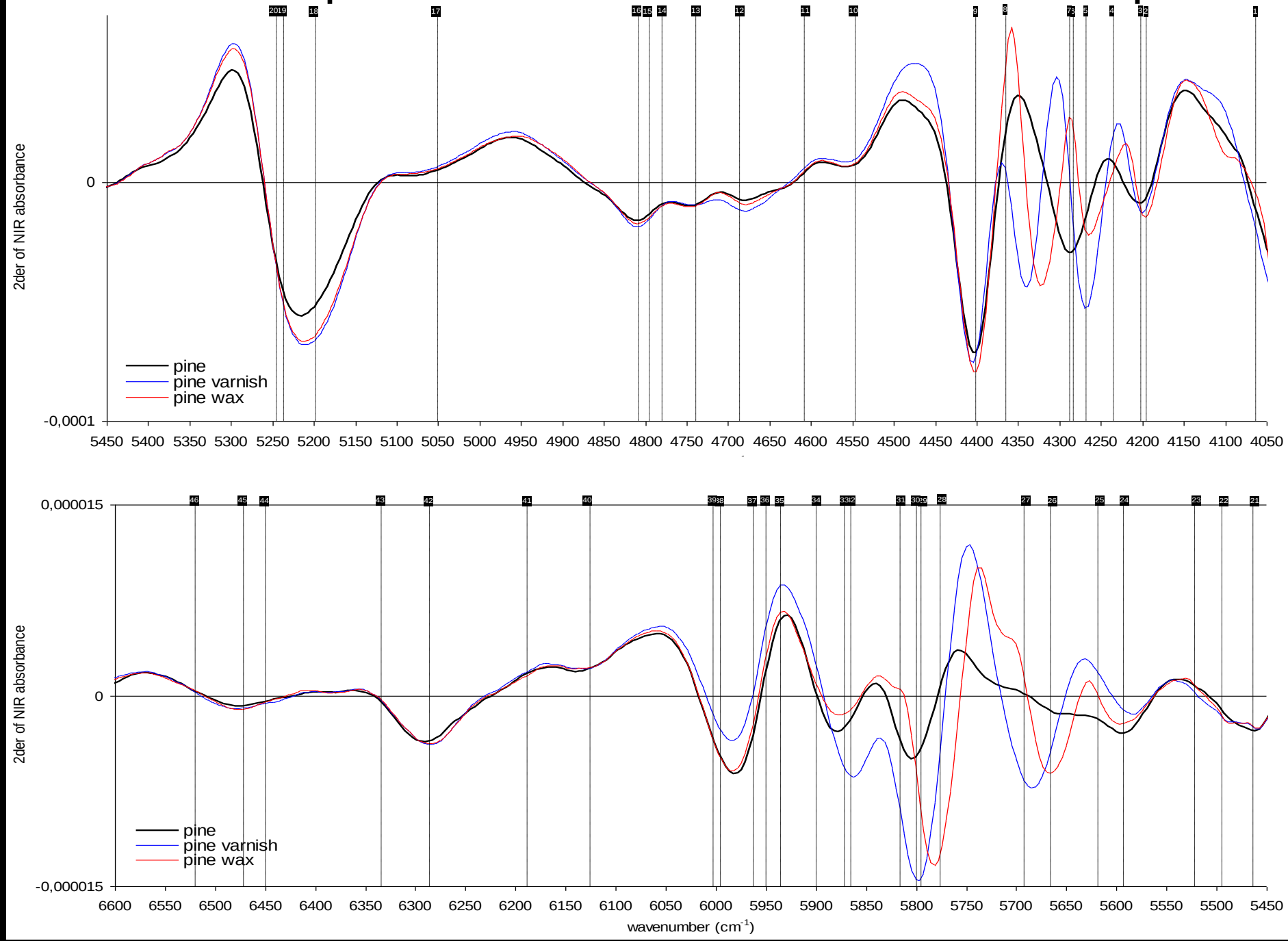
For mathematical evaluation of the results some methods as principal component analysis, partial least square, identity test, and cluster analysis were applied.


antique wood
processed wood
contemporary wood
contemporary wood with wax
contemporary wood with varnish
water contact angle [°]
110
100
90
80
70
60
50
40
30
20
10
0
Pine Przewrotne
Ash Przewrotne
Oak Tarnowiec Room 1
Oak Tarnowiec Room 4
Oak Falejówka
Elm Tarnowiec Room 5

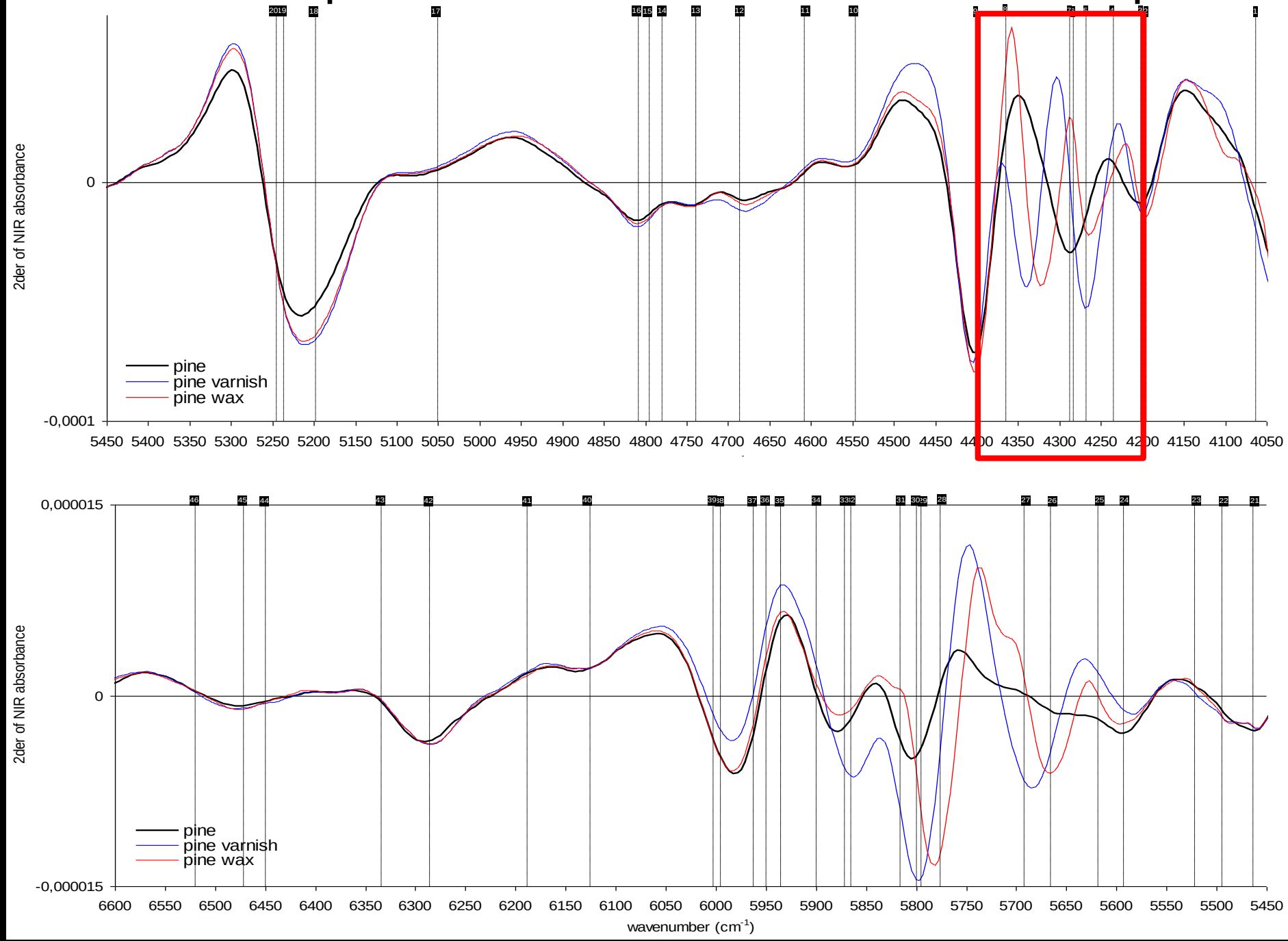

antique wood
processed wood
contemporary wood
contemporary wood with wax
contemporary wood with varnish
surface energy [mJ/m²]
80
70
60
50
40
30
20
10
0
Pine Przewrotne
Ash Przewrotne
Oak Tarnowiec Room 1
Oak Tarnowiec Room 4
Oak Falejówka
Elm Tarnowiec Room 5


antique wood
processed wood
contemporary wood
contemporary wood with wax
contemporary wood with varnish
surface energy [mJ/m²]
80
70
60
50
40
30
20
10
0
Pine Przewrotne
Ash Przewrotne
Oak Tarnowiec Room 1
Oak Tarnowiec Room 4
Oak Falejówka
Elm Tarnowiec Room 5

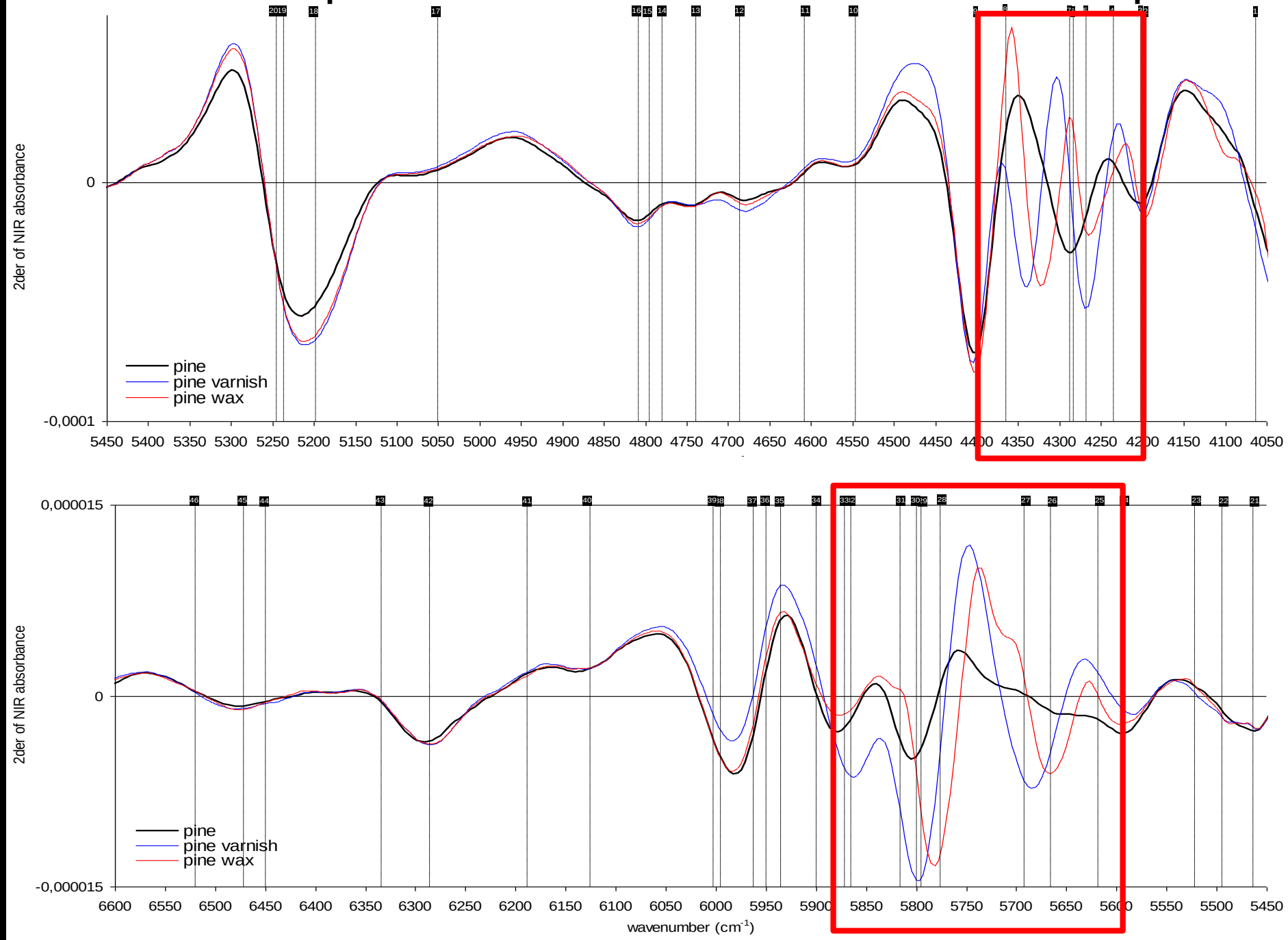
Second derivative spectra of natural and finished with wax and varnish pine wood



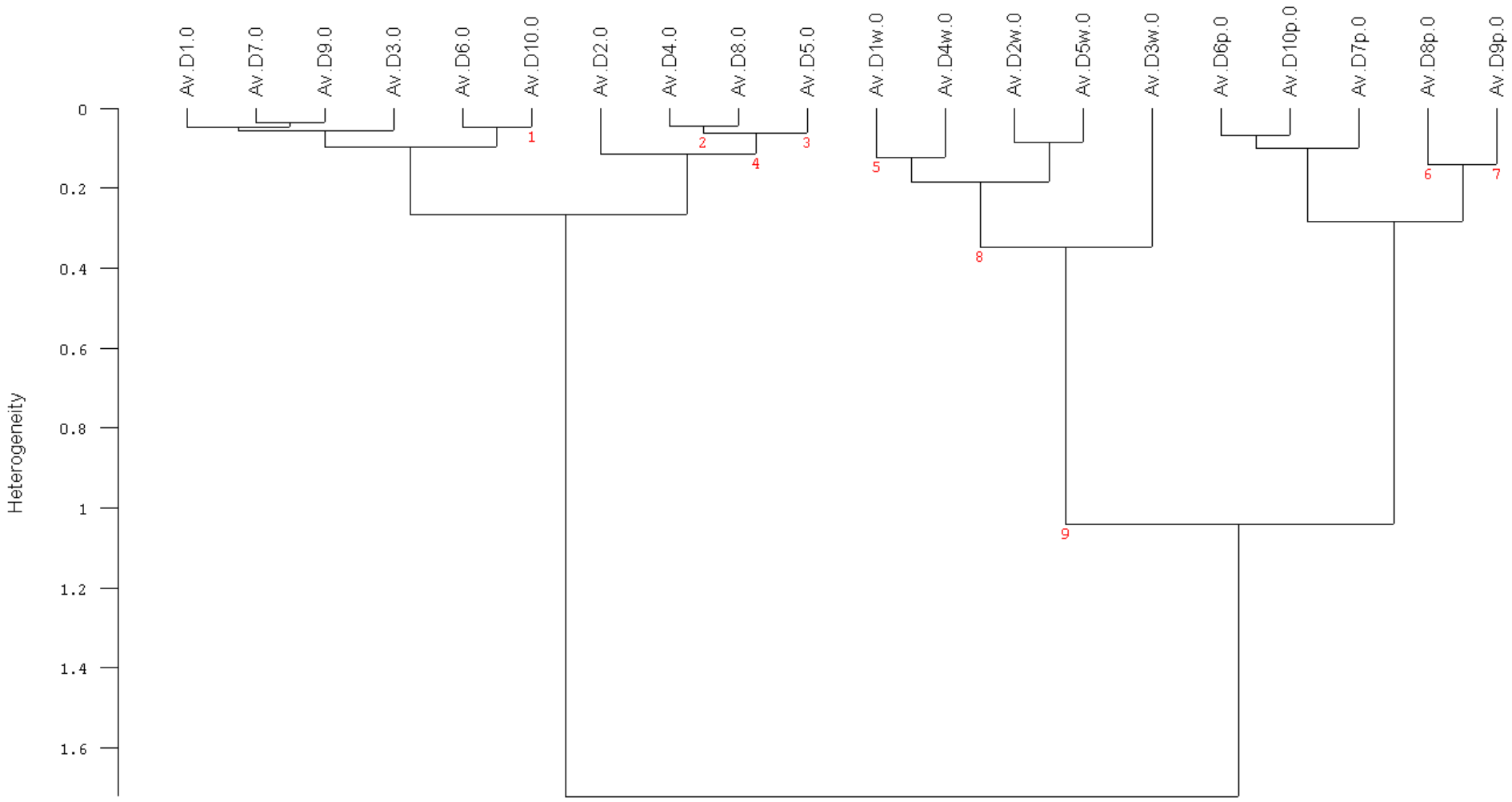
Second derivative spectra of natural and finished with wax and varnish pine wood



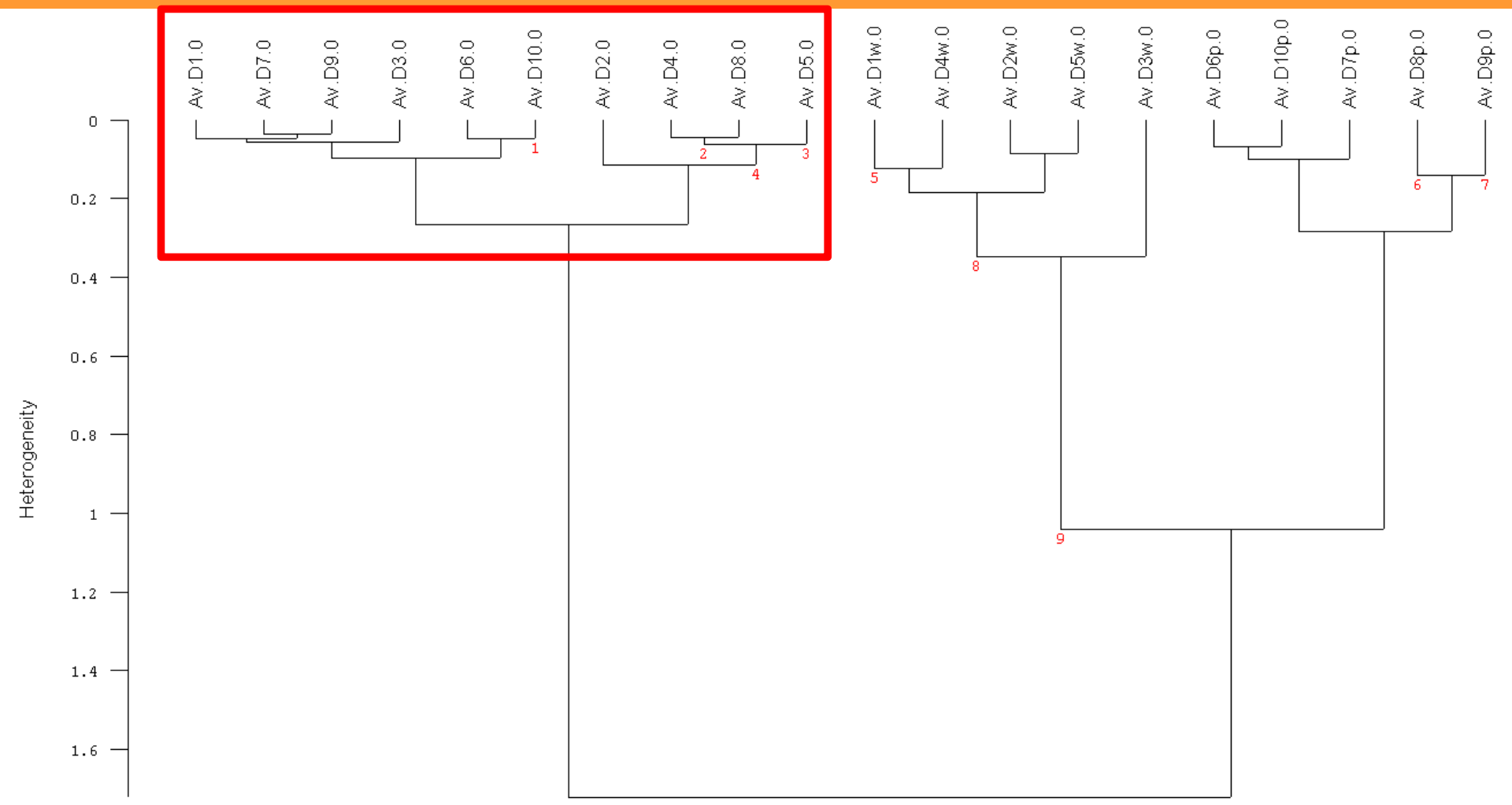
Second derivative spectra of natural and finished with wax and varnish pine wood



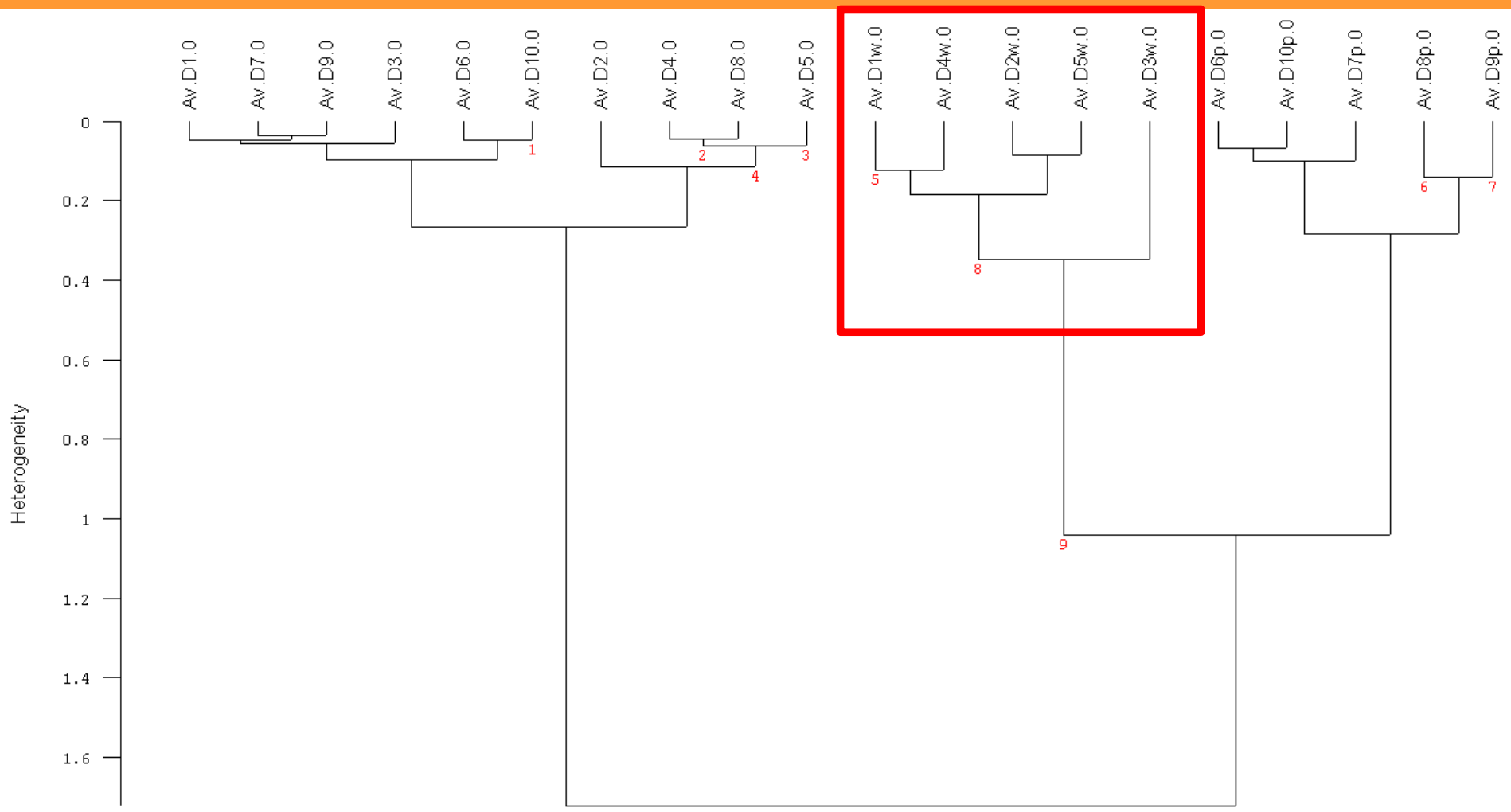
Cluster analysis of natural, wax and varnish soaked oak



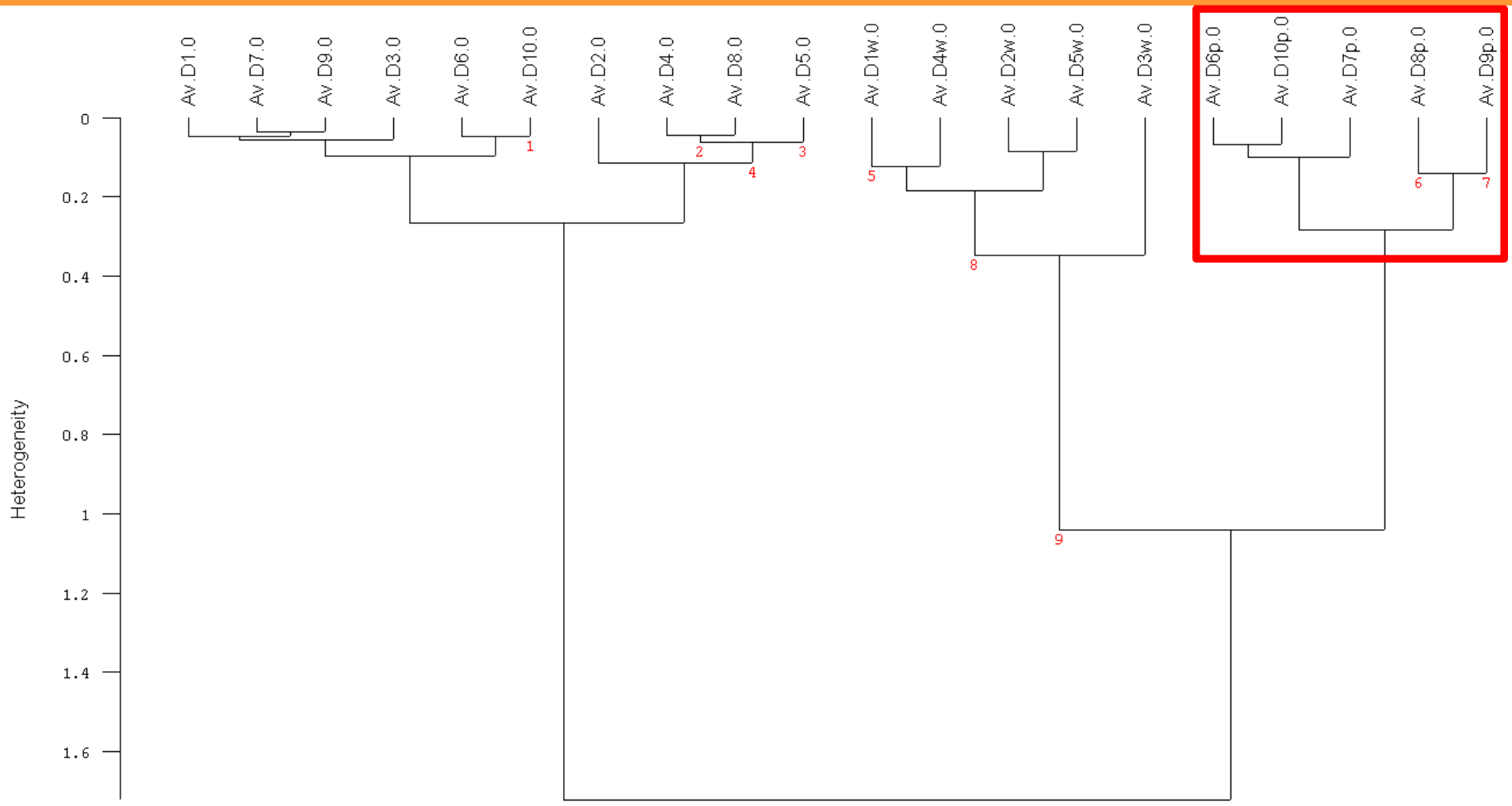
Cluster analysis of natural, wax and varnish soaked oak

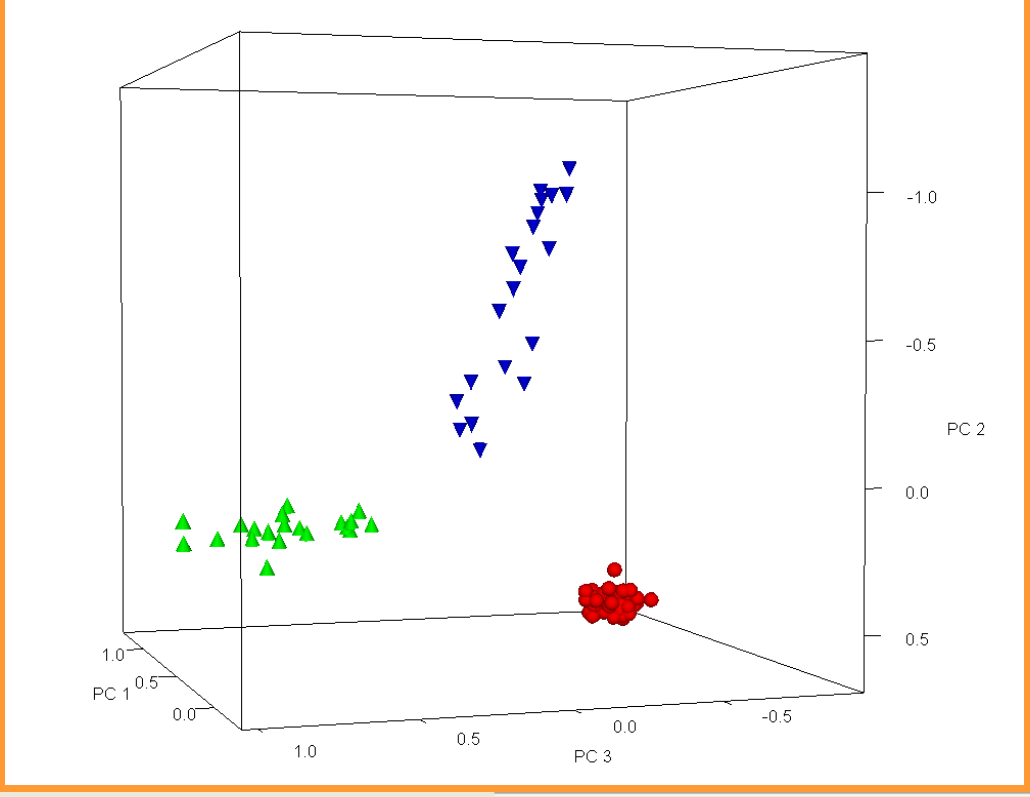


Cluster analysis of natural, wax and varnish soaked oak



Cluster analysis of natural, wax and varnish soaked oak

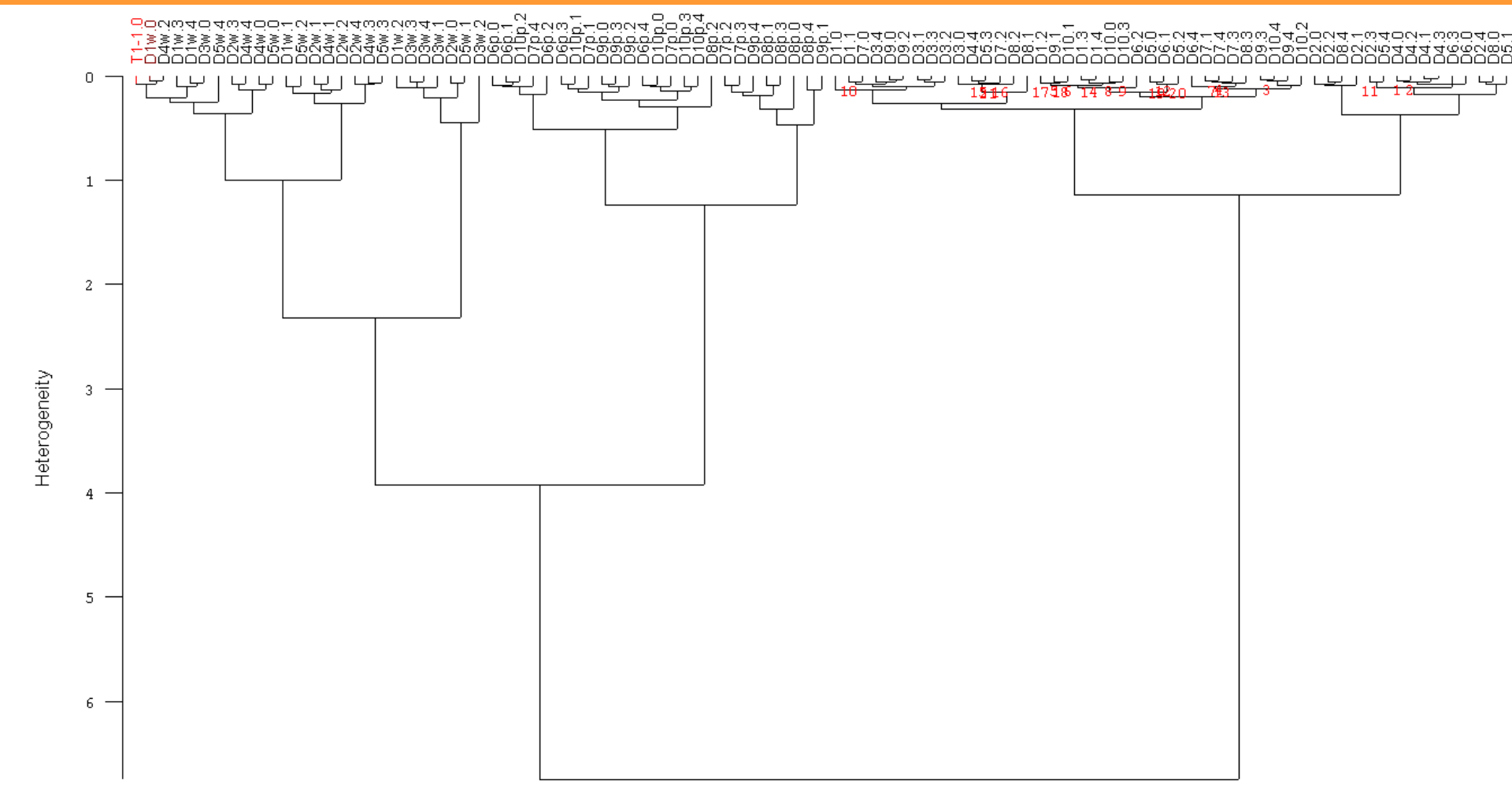




		ID	Group1	Group2	IP-Level	S	Threshold1	Threshold2	D
1	-	1	dab nat	dab pok	IP1: New	1.087769	0.192758	0.125568	0.346266
2			"	dab wosk	IP1: New	1.333953	"	0.827042	1.360367
3	-	2	dab pok	dab wosk	IP1: New	1.064549	0.125568	0.827042	1.014101
4			"	dab nat	IP1: New	1.087769	"	0.192758	0.346266
5	-	3	dab wosk	dab pok	IP1: New	1.064549	0.827042	0.125568	1.014101
6			"	dab nat	IP1: New	1.333953	"	0.192758	1.360367

Principal Component Analysis of oak samples and results of selectivity coefficient calculated for samples with various finishing (red – natural wood, blue – wood with wax, green wood with varnish)

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

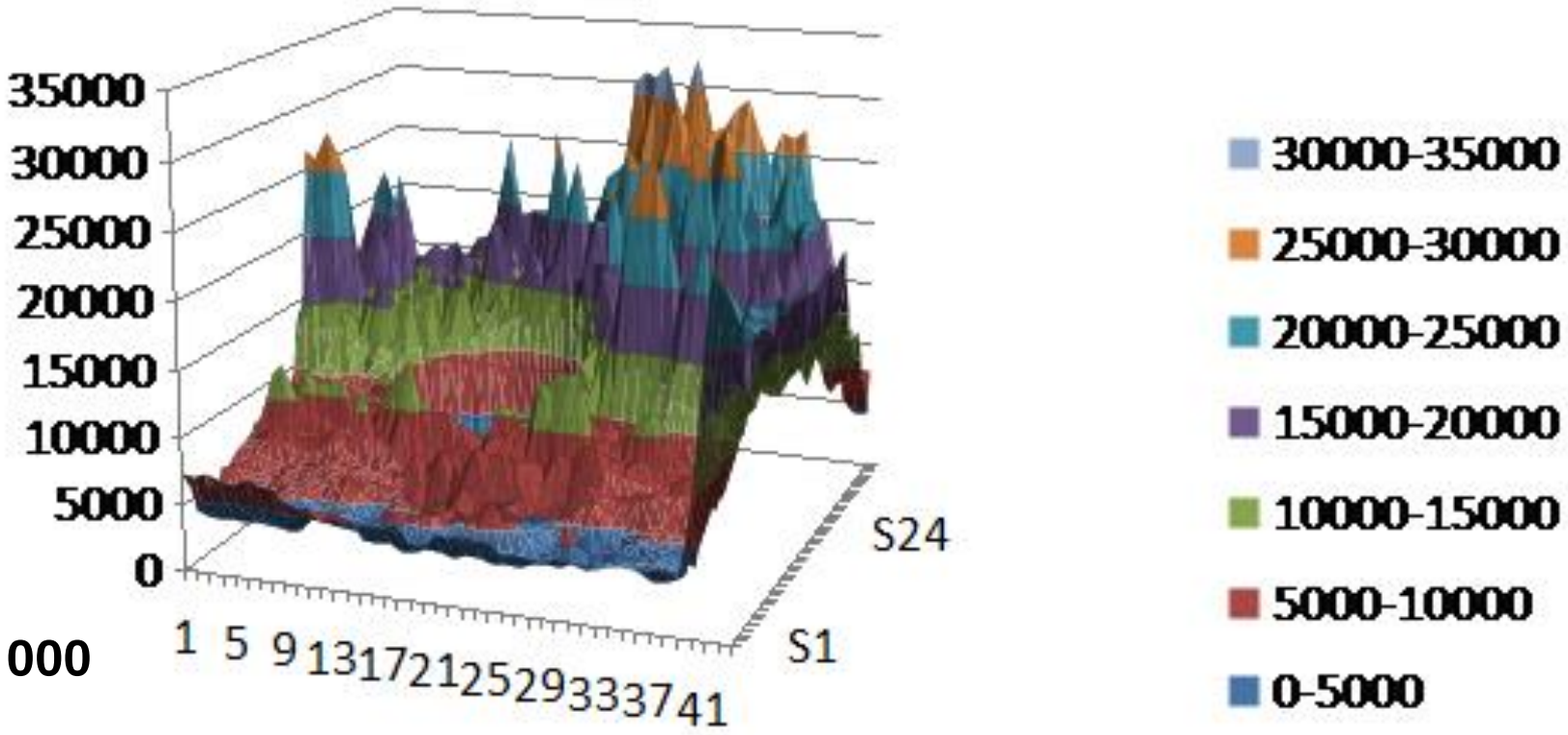
Results of identification of investigated samples by means of CA test, IT and QC

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 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

PRESENCE OF CHOSEN ELEMENTS

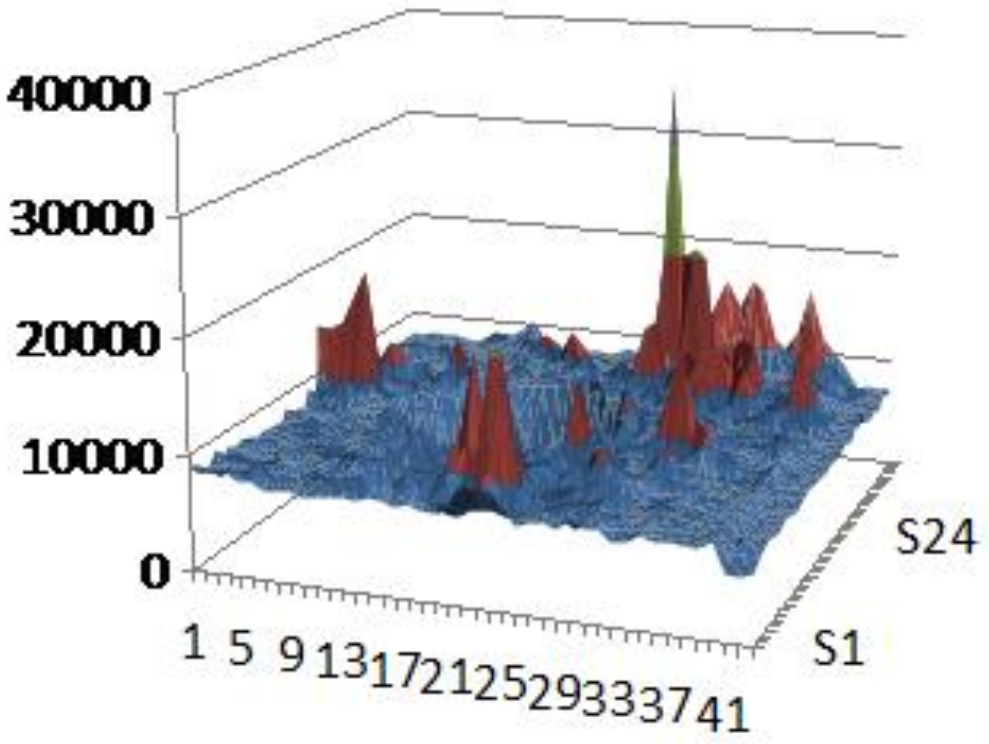


Ca: 30 000

Reference distribution

Oak	**3090,**	**2480,**	**3244**
Elm	**6702,**	**6034,**	**5961**

PRESENCE OF CHOSEN ELEMENTS



Fe

CONCLUSION

FT-NIR spectroscopy and XRF spectrofluorimetry is a technique allowing fast and non-destructive measurement of wooden samples

FT-NIR and XRF highlighted differences between different surfaces finishing methods

Even if algorithm work well for classification of wax / oil of contemporary wood, evaluation of antique floor is problematic

The impossibility of unambiguously classification of the historic wood finishes with the FT-NIR

Each algorithm used for FT-NIR data evaluation has different mathematical background, therefore highlighted specific properties of spectra

REFLECTION

The primary surface finishes might be grated or rinsed

Natural weathering

The floors were finished once with wax and then with varnish

Way of preparation of historic samples - manual grinding surface of the samples after cutting them from sheets of elements in order to remove dirt and gain flatness might lead to removal of natural substances used for their conservation

The next step of this research is repetition of FT-NIR measurement of antique samples without any surface preparation and validation previously developed models (STSM ?)