NMR Spectroscopy in Cultural Heritage materials analysis

Apostolos Spyros

NMR Laboratory

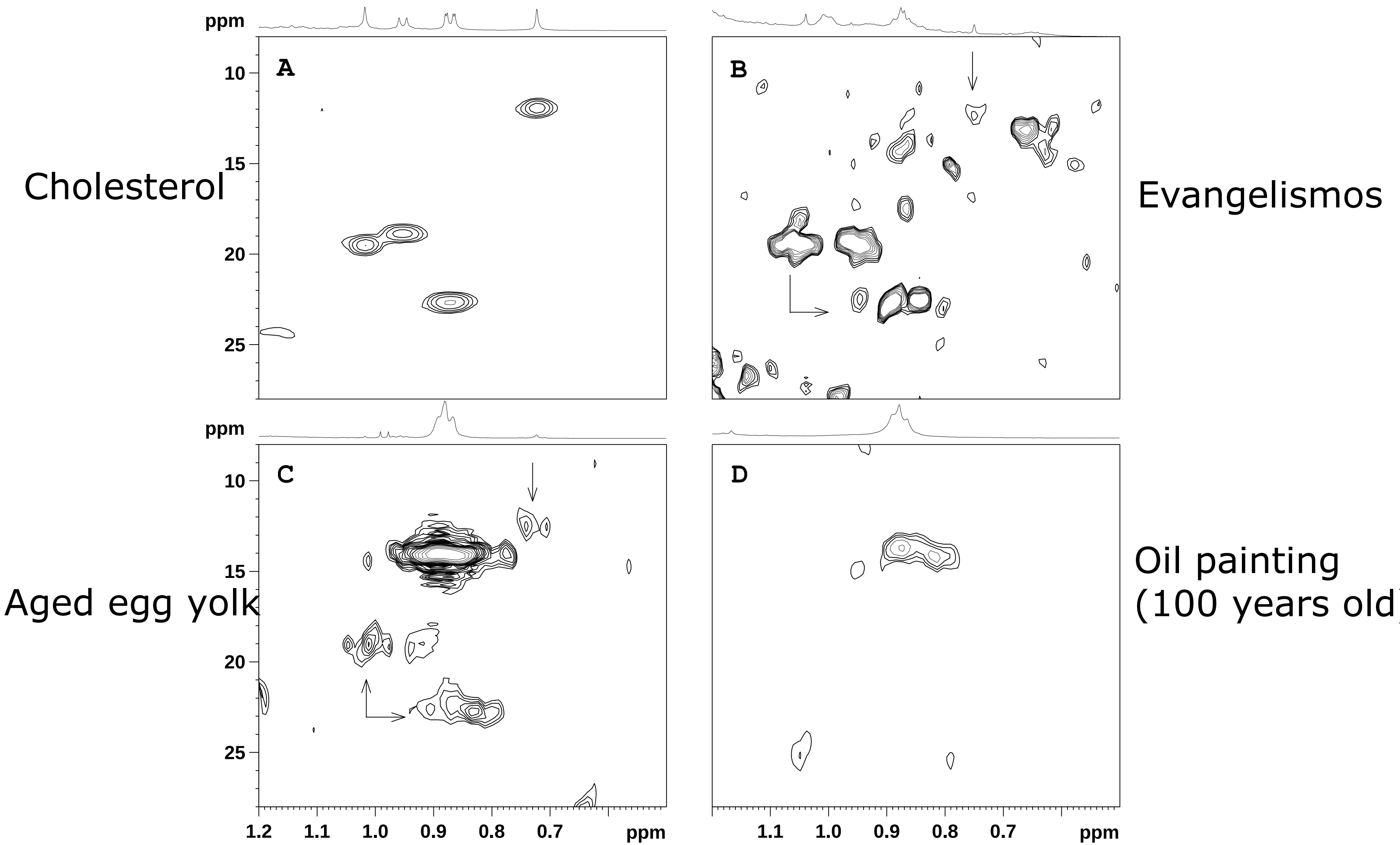
State of the art

- NMR spectroscopy seldom used for systematically for analysis in CH
- *Limitation*: quantity of sample
- *Advantage*: very powerful analytical capabilities for organic materials

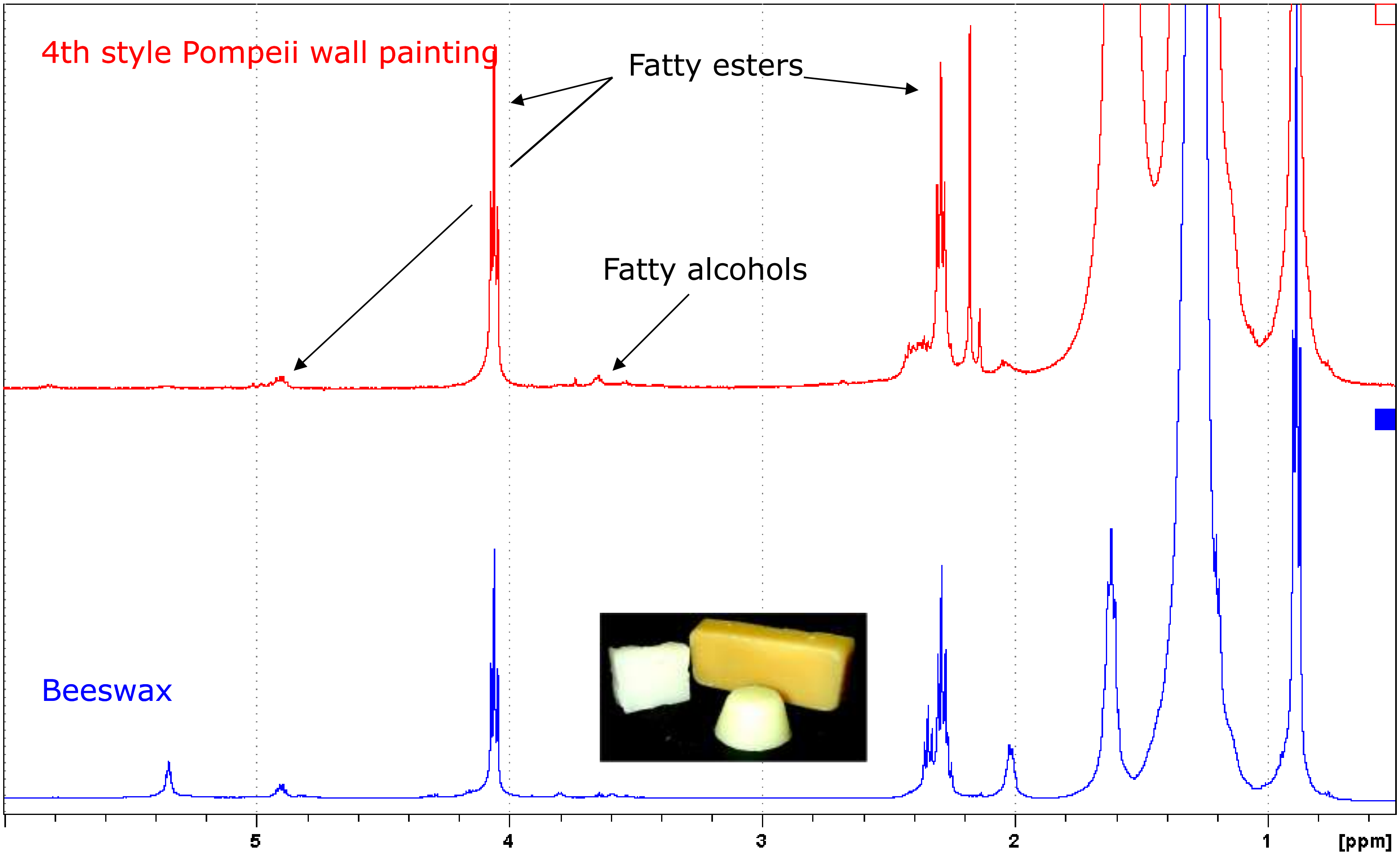
Cultural heritage materials analysis

- Oil and tempera binders
- Varnishes, Resins
- Paintings/Wall paintings
- Contemporary materials
- Modern Art
- Dyes
- Waxes
- Parchments

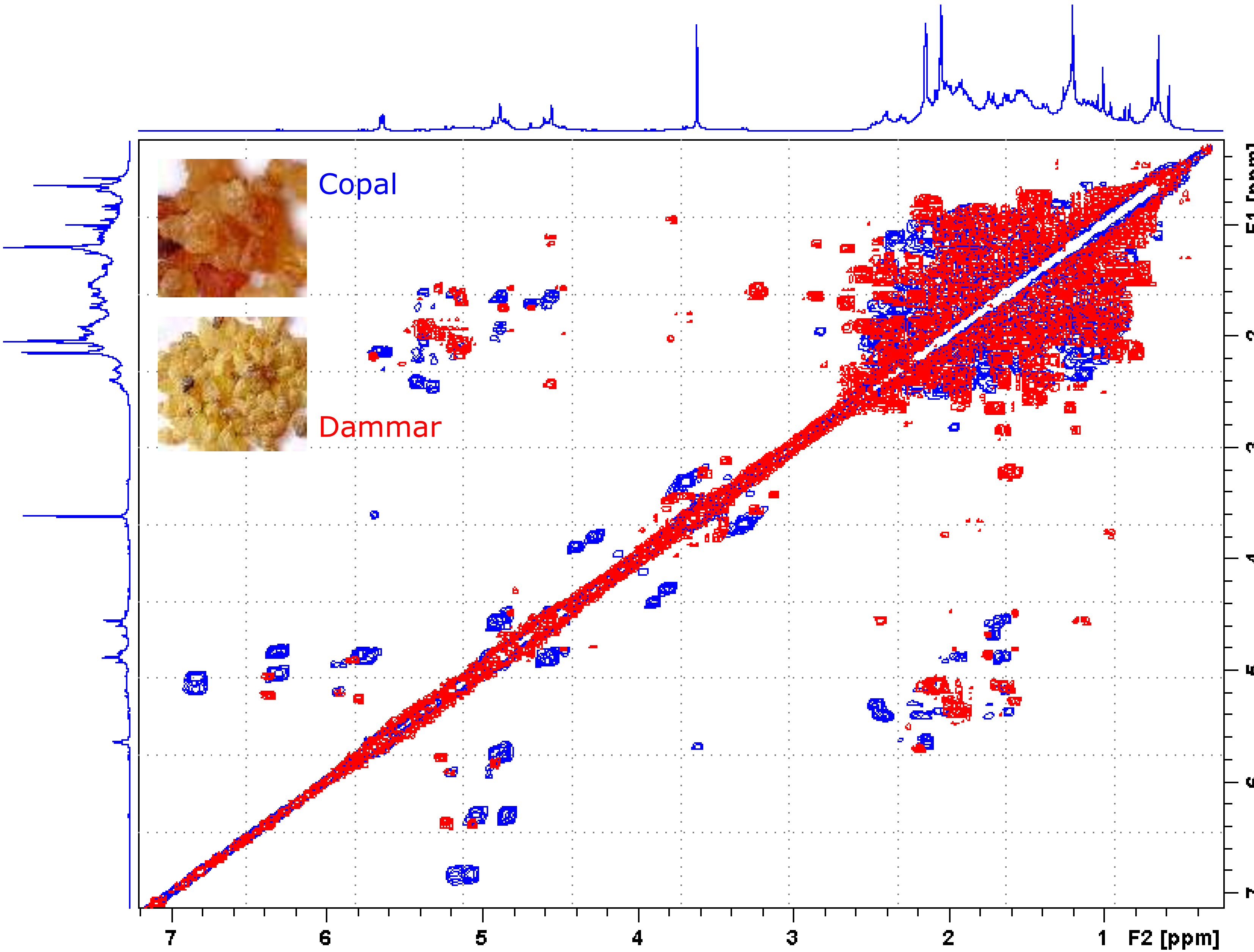
Egg yolk in a 19th cent. Byzantine icon
^{1}H-^{13}C 2D HMQC NMR



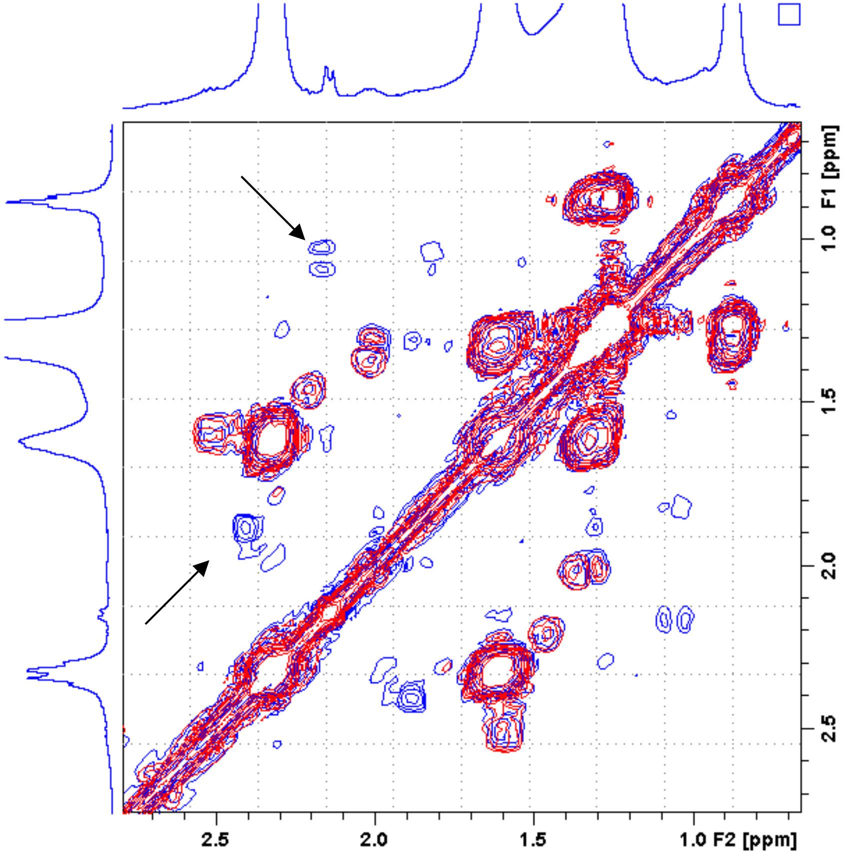
Beeswax identification in Pompei wall paintings



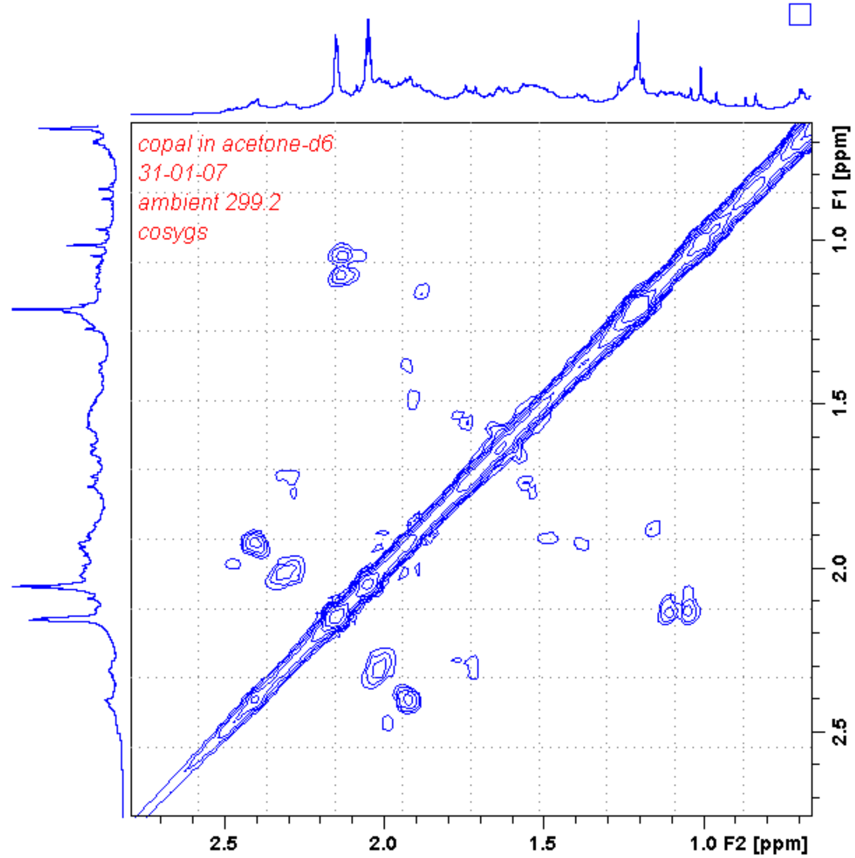
Terpenoid resins differentiation



Identification of resins in aged varnishes
Solid state HR-MAS NMR



Blue: Aged varnish spectrum
Red: Aged linseed oil spectrum



Fresh copal spectrum

Contemporary Works of Art

Oulu City Art Museum, Finland

The last milk platform,
Jan-Eric Andersson, 1992

The Cocotte with two dogs,
Karry Tykkylainen, 1987

Case studies

1. Paint samples from clock faces on Government Palace in Helsinki
2. Dyes and dyed wool fibres
3. Oil colours from the workshop of artist Remo Brindisi

1. Paint samples from clock faces

The west façade of the Government Palace in Helsinki.

Clock face VN1 before restoration.

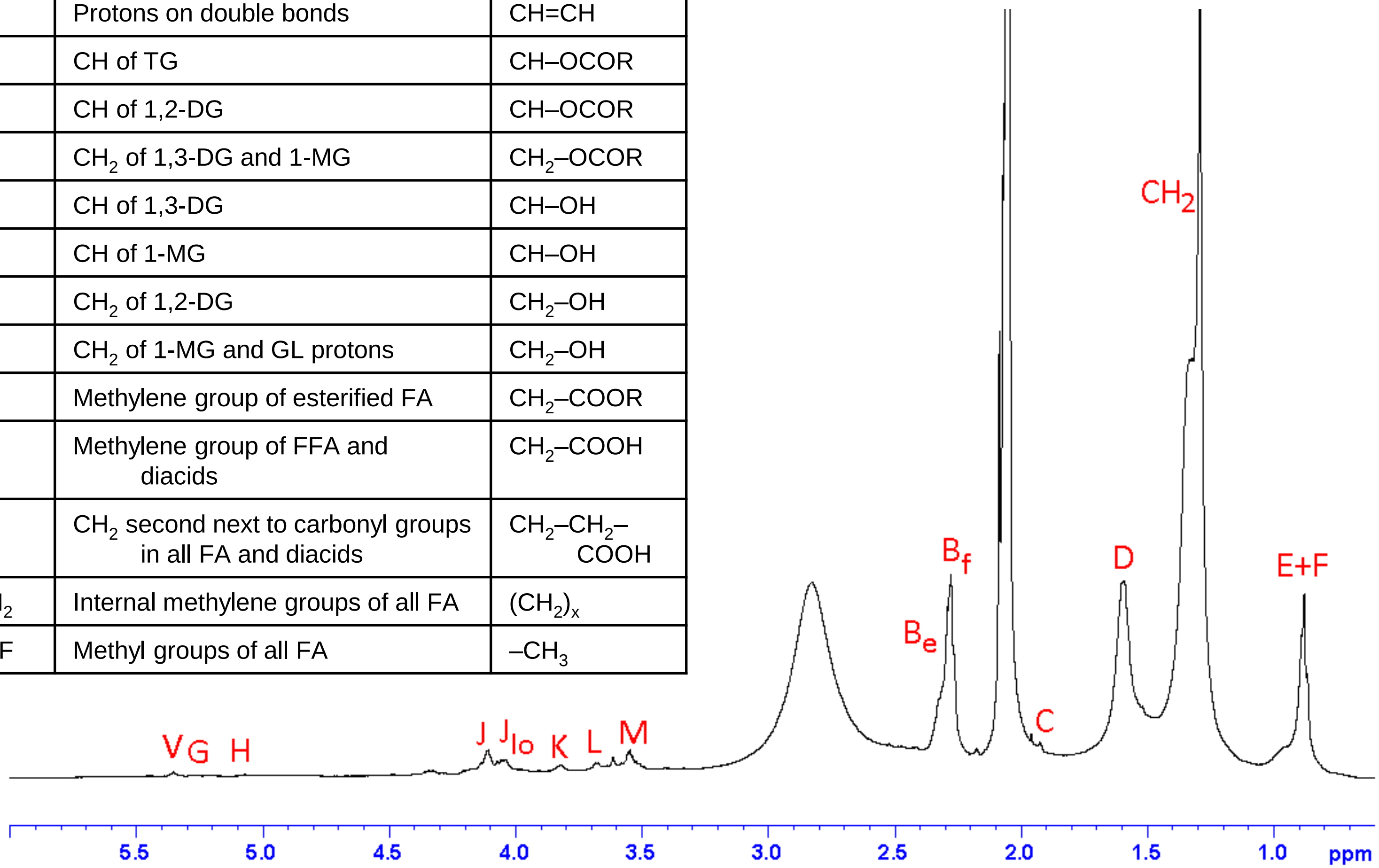
Cross section of a sample from VN1. Notice the thick black layer.

1. Paint samples from clock faces

- Objectives:
  - Characterization of binding medium.
  - Assessment of the extent of degradation.
- Sample preparation:
  - Paint chip in 700 μl of acetone-d_6
  - 40 minutes sonication

1. Paint samples from clock faces

Peak	Assignment	Group
V	Protons on double bonds	CH=CH
G	CH of TG	CH–OCOR
H	CH of 1,2-DG	CH–OCOR
J	CH_2 of 1,3-DG and 1-MG	CH_2–OCOR
J_{lo}	CH of 1,3-DG	CH–OH
K	CH of 1-MG	CH–OH
L	CH_2 of 1,2-DG	CH_2–OH
M	CH_2 of 1-MG and GL protons	CH_2–OH
B_e	Methylene group of esterified FA	CH_2–COOR
B_f	Methylene group of FFA and diacids	CH_2–COOH
D	CH_2 second next to carbonyl groups in all FA and diacids	CH_2–CH_2–COOH
CH_2	Internal methylene groups of all FA	$(CH_2)_x$
E+F	Methyl groups of all FA	$–CH_3$



^{1}H NMR spectrum of VN2-8 in acetone-d_6. Letters indicate peaks characteristic of the species in the oil binder.

1. Paint samples from clock faces

Markers

B_f/B	Free to total carboxyl groups	B_f/B (=B_f+B_e)
Di/FA	Diacids to fatty acids	(3B-1)/8F
TG/FA	Triglycerides to fatty acids	9G/F
Iodine value IV	Degree of unsaturation	V/F
%FFA	Free fatty acids molar percentage	(2DG+4MG+6GL)/ 6(TG+DG+MG+GL)

+ glycerides analysis

1. Paint samples from clock faces

Glycerides analysis (molar %)

Sample	TG	1,2-DG	1,3-DG	MG	GL
VN1-1 (black)	**3,2**	5,9	32,1	24,4	**34,3**
VN2-8 (black)	**5,2**	6,3	32,0	24,3	**32,1**
Fresh linseed oil	**95,4**	2,7	1,9	0	**0**
Linseed oil 5 years	**30,9**	19,6	20,9	28,7	**-**

TG=triglycerides
1,2-DG and 1,3-DG=diglycerides
MG=monoglycerides
GL= glycerol.

1. Paint samples from clock faces

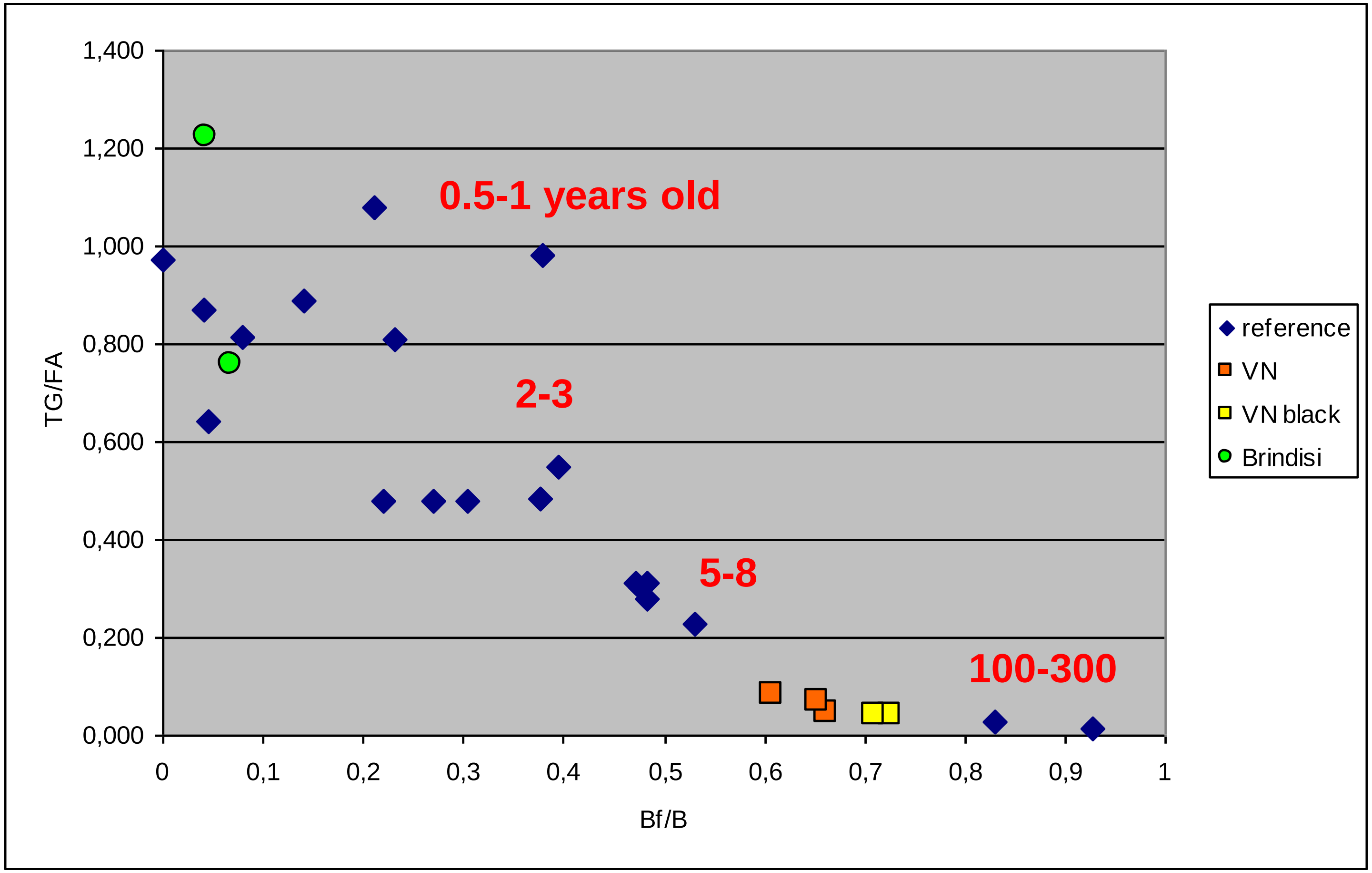
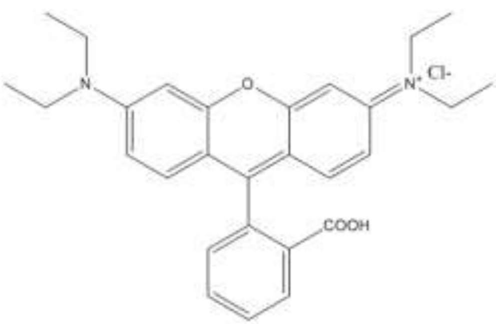


Diagram of TG/FA versus B_f/B.

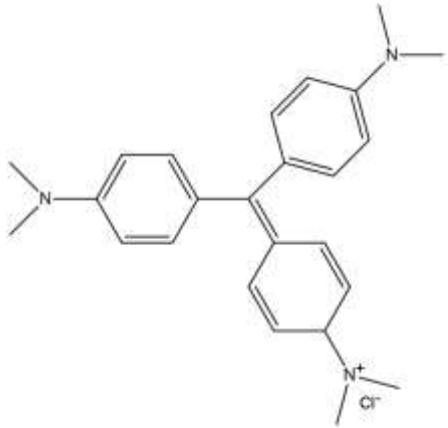
2. Standards of pure dyes and dyed wool

Basic dyes

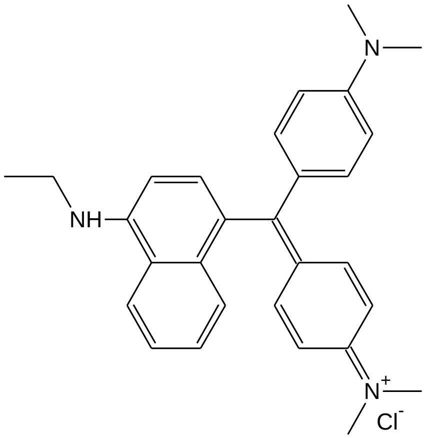
Rhodamine B



Crystal Violet

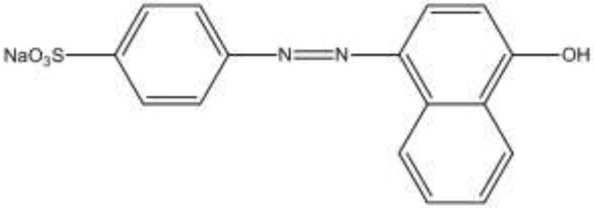


Victoria Blue R

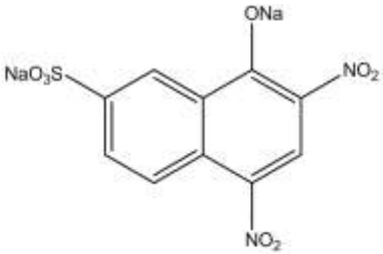


Acid dyes

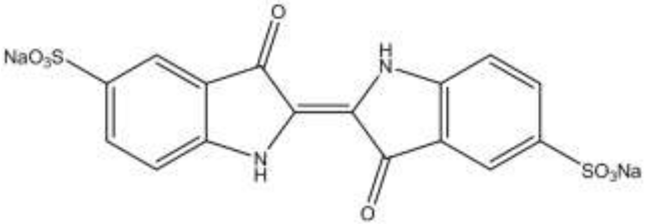
Orange I



Naphthol Yellow S



Indigo Carmine



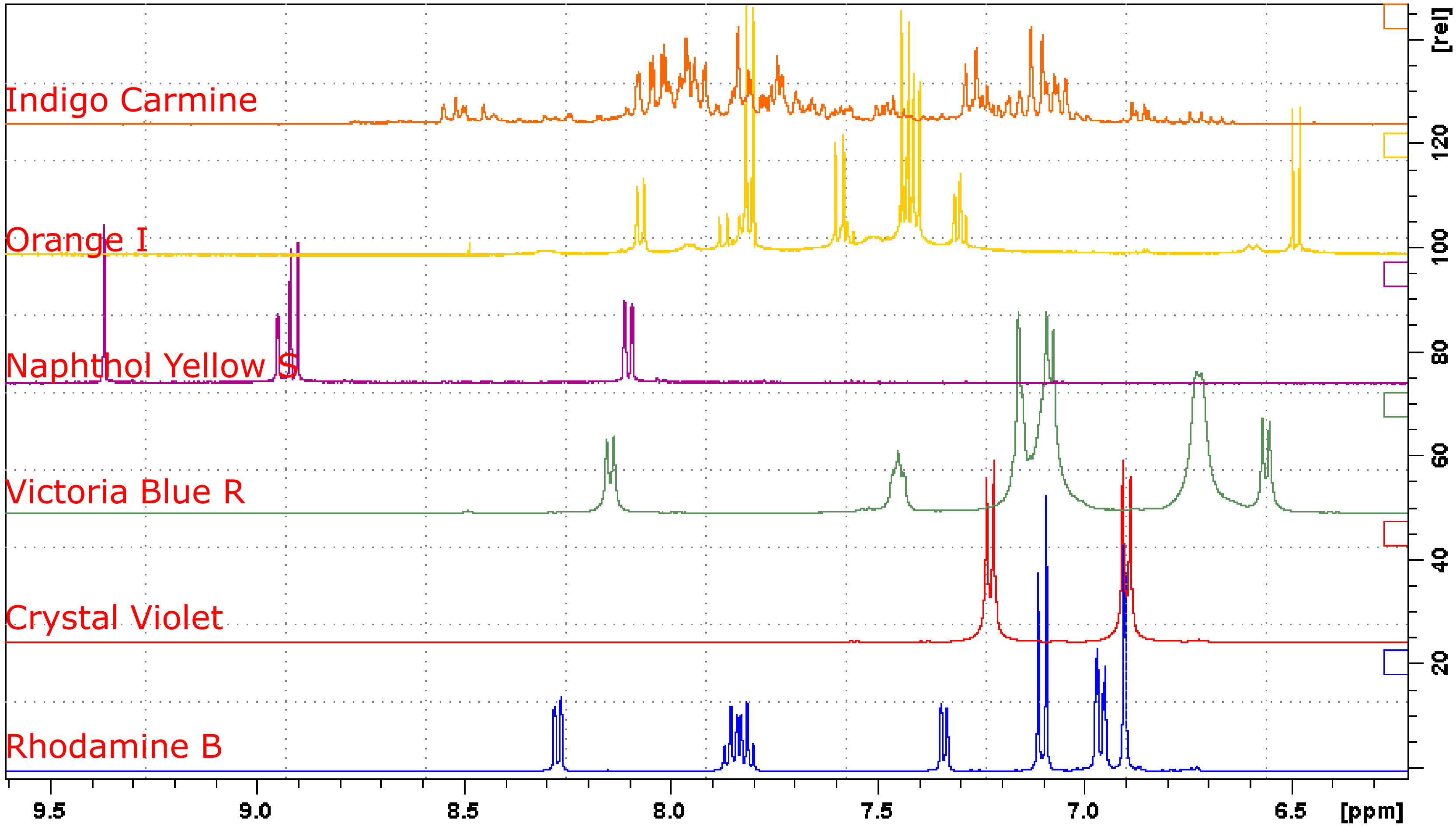
2. Standards of pure dyes and dyed wool

- Objective:
  - → Characterization of the dyes in both pure dyes and dyed wool
  - → Develop rapid analytical tools able to distinguish them

2. Standards of pure dyes and dyed wool

- Sample preparation
  - Dye extraction from wool (sonication method)
  - Solubilization of pure dyes

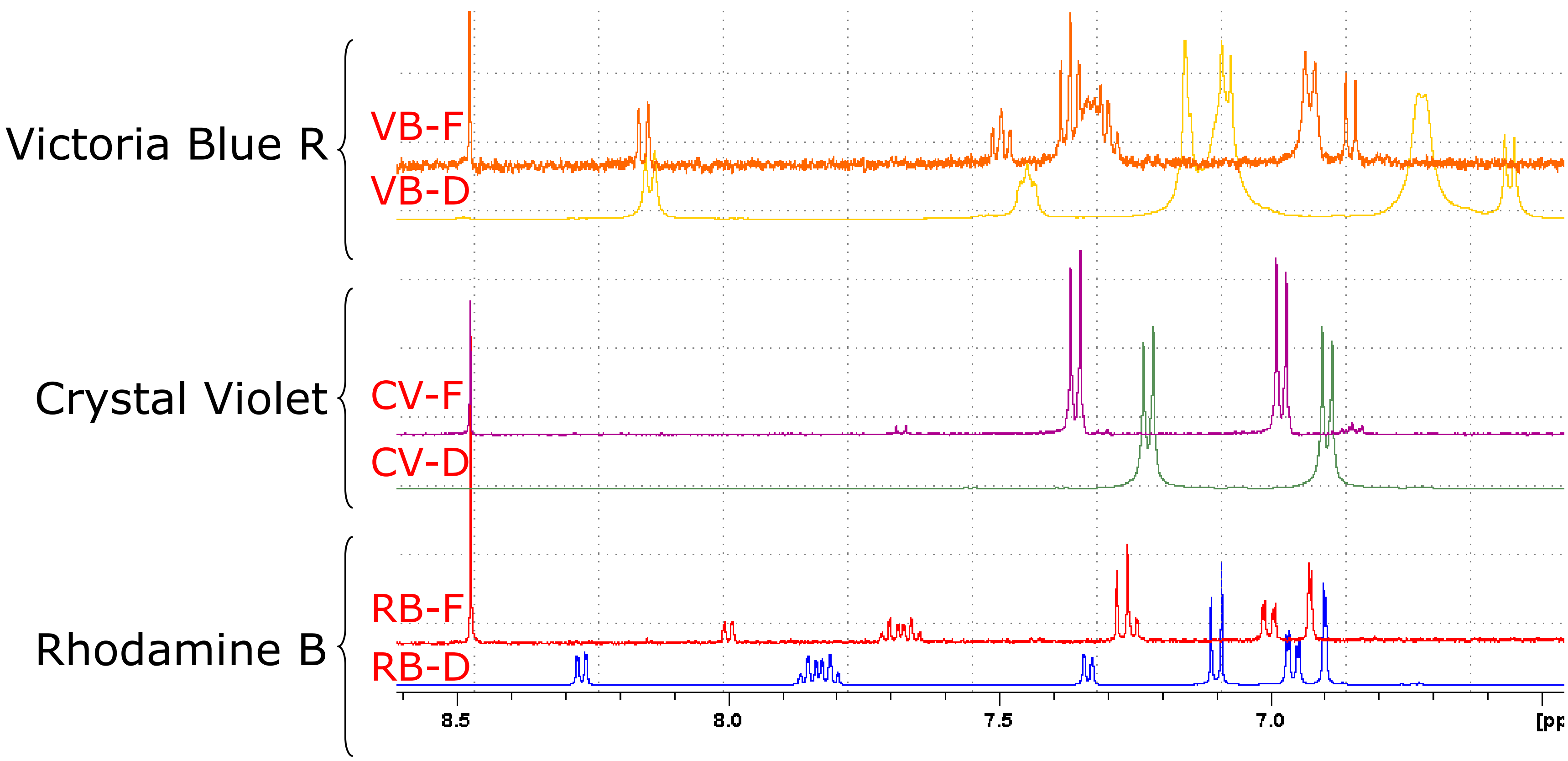
2. Standards of pure dyes and dyed wool



Chemical shifts of pure dyes in aromatic region of ^{1}H NMR spectra.

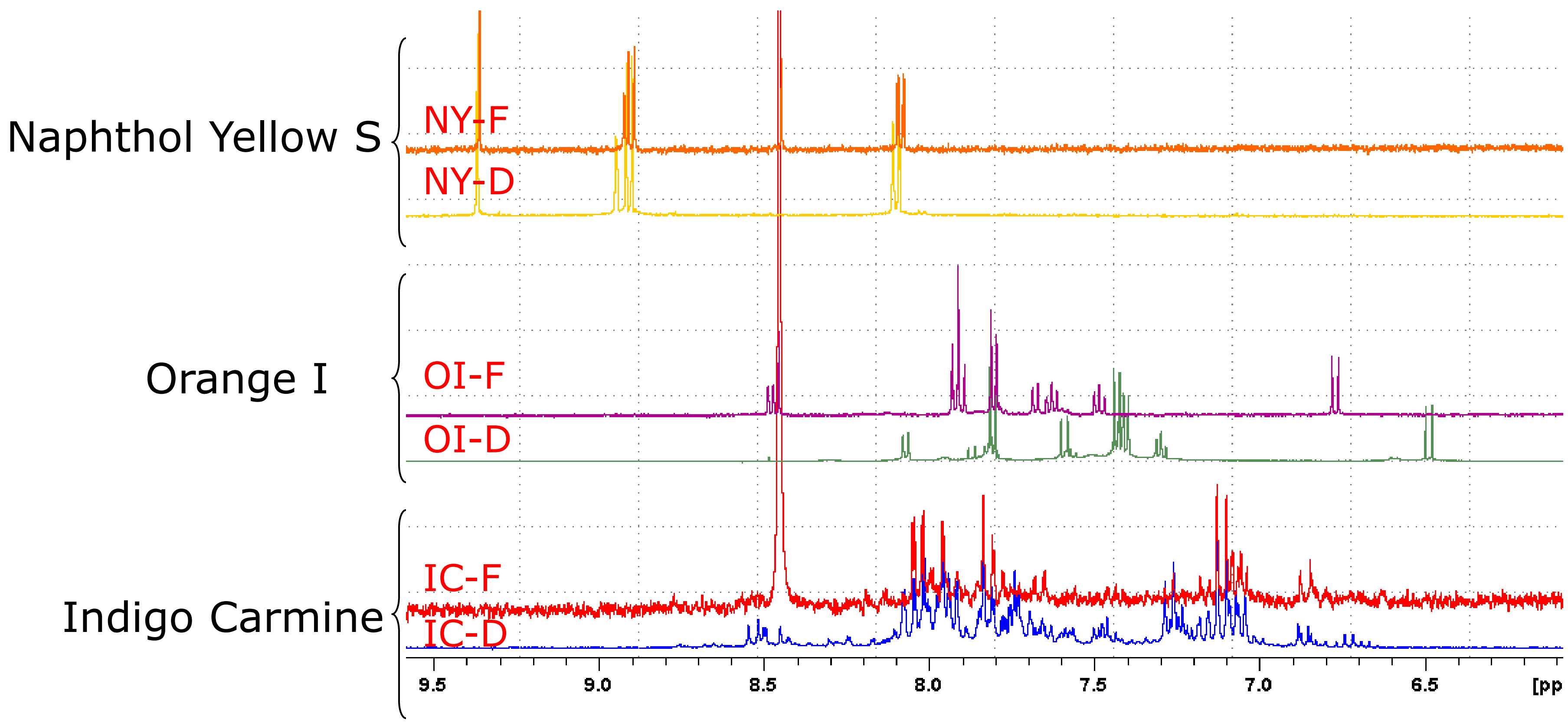
2. Standards of pure dyes and dyed wool

Peak shifting for basic dyes

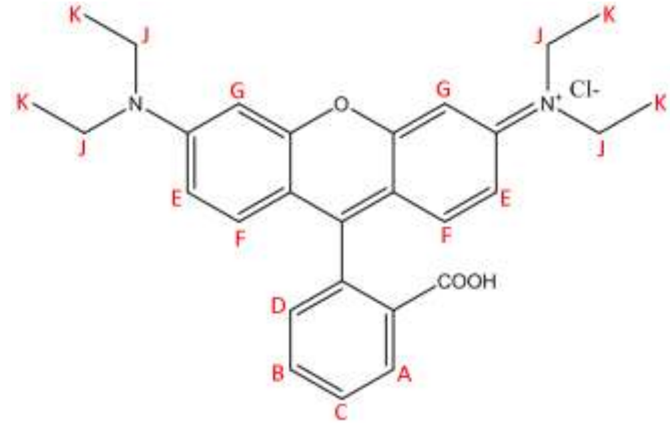


2. Standards of pure dyes and dyed wool

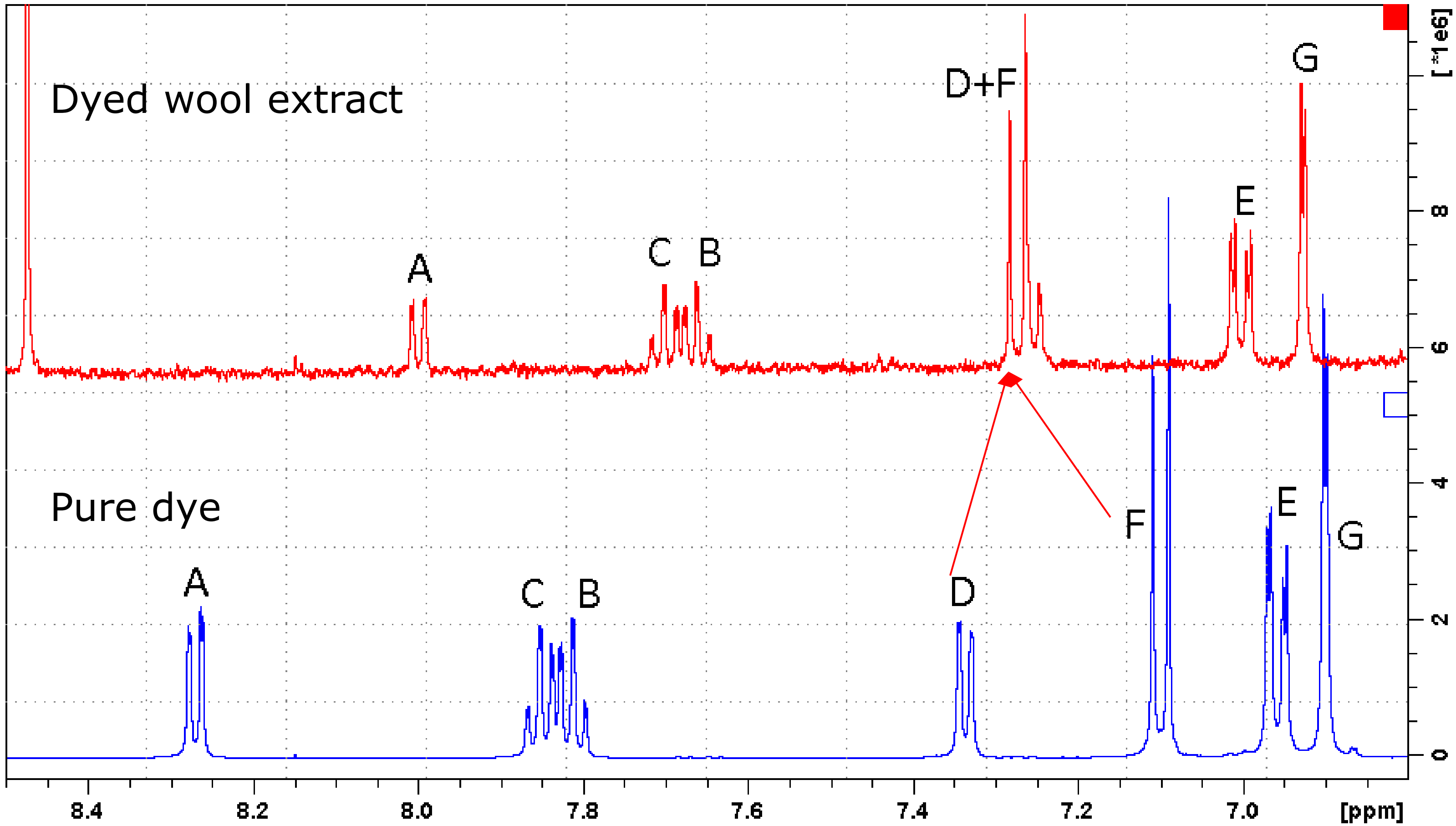
Peak shifting for acid dyes



Rhodamine B



K
J
N
G
O
N+
Cl-
E
F
COOH
D
B
A
C

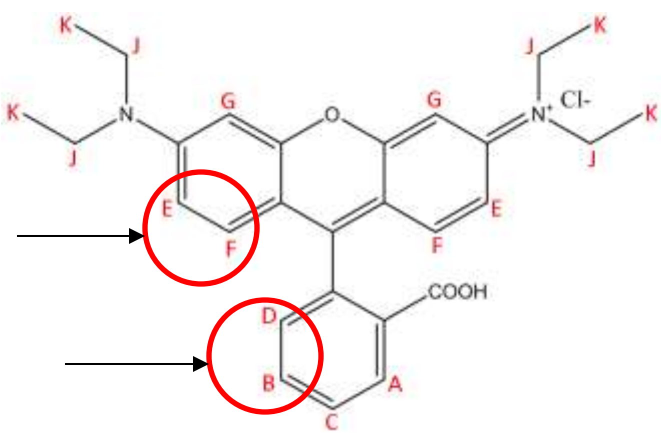


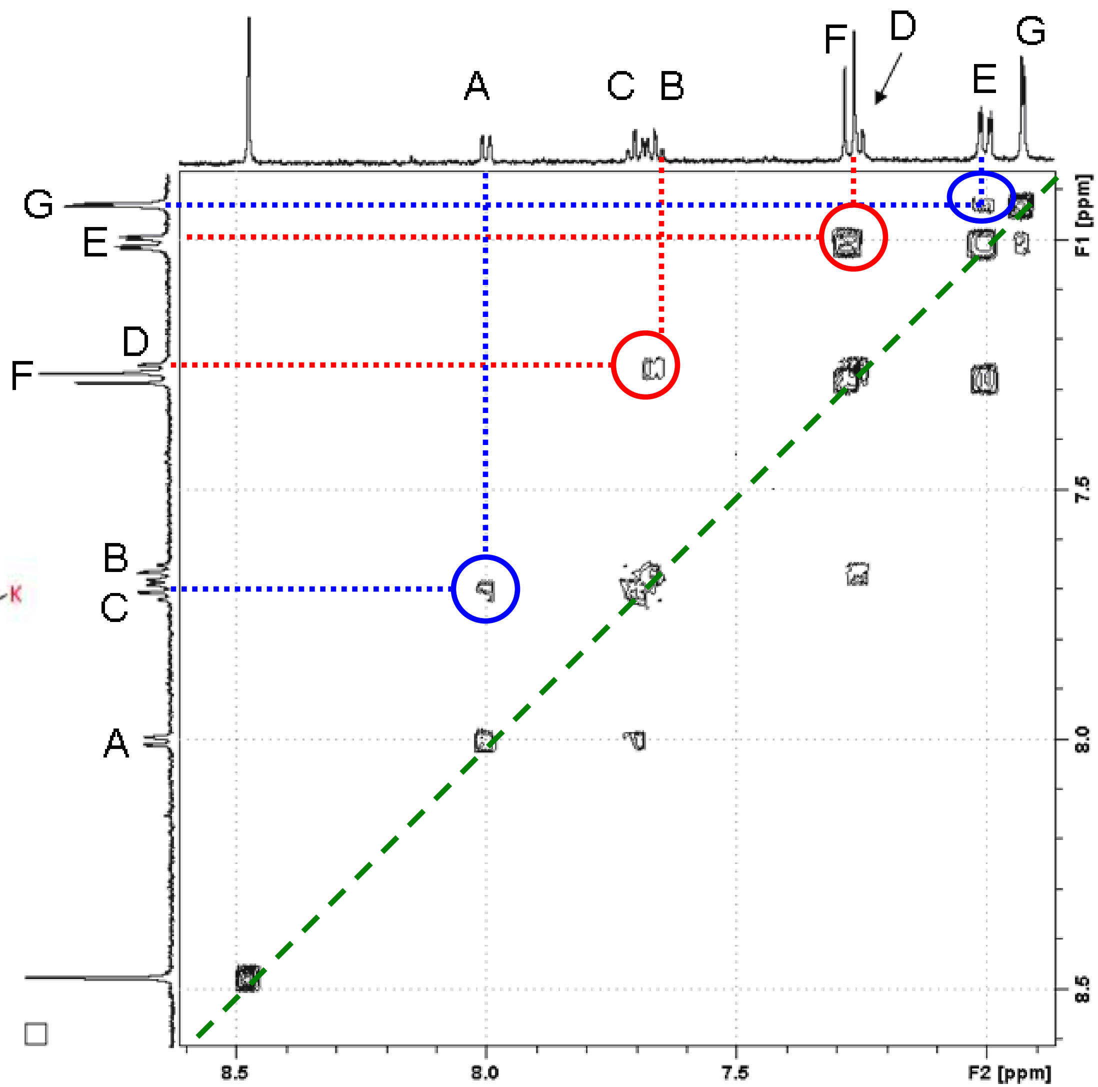
Dyed wool extract
A
C B
D+F
E
G
Pure dye
A
C B
D
F
E
G
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
[ppm]
[*1e6]
8
6
4
2
0

2. Standards of pure dyes and dyed wool

Rhodamine B

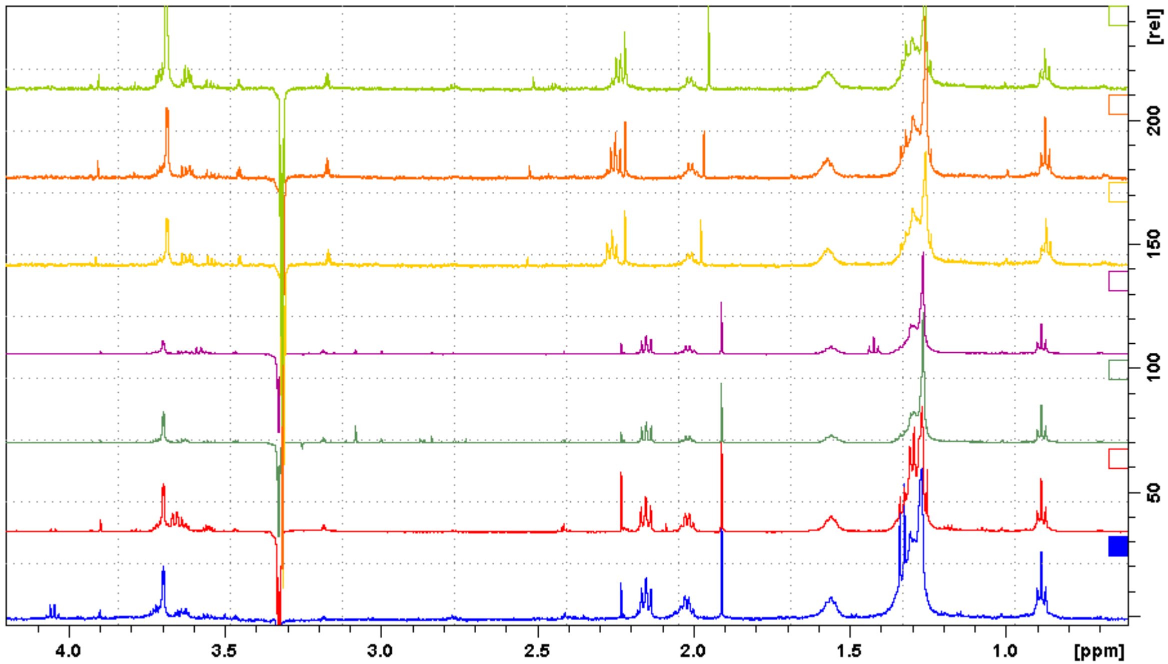
2D COSY NMR spectrum of dyed wool extract





2. Standards of pure dyes and dyed wool

Presence of a common lipidic matrix in all the extracts.



- Wool → lipid content about 2%
  - Free fatty acids
  - Sterols
  - Polar lipids

2. Standards of pure dyes and dyed wool

High amounts of a monounsaturated fatty acid were identified by NMR

Extract	***%MU***
Rhodamine B	***49,8***
Crystal Violet	***36,8***
Victoria Blue R	***44,3***
Naphthol Yellow S	***28,6***
Orange I	***31,1***
Indigo Carmine	***33,7***
Blank (undyed)	***50,8***

Marseille soap was used to treat the wool before dying

Marseille soap is made from olive oil

3. Oil colours of Remo Brindisi

Sample	
MOB 370	Blue colours
MOB 408	
MOB 410	
MOB 457	
MOG 111	Yellow colours
MOG 112	
MOG 435	
MOG 454	
MOV 286	Green colours
MOV 356	
MOV 429	
MOV 433	

List of pigments and extenders used in the colours analysed

Each colour has a different composition. A mixture of pigments is used in order to obtain the desired colour.

<u>Phthalocyanines</u>

- PB15 Phthalocyanine α
- PB15:3 Phthalocyanine β
- PG7 Chlorinated phthalocyanines
- PB16 Metal free phthalocyanine

<u>Other components</u>

• Organic:

- PY1 Hansa Yellow 1
- PY3 Hansa Yellow 3
- PY17 Disazo Yellow
- PY83 Diarylide yellow
- PO43 Perinone orange

• Inorganic:

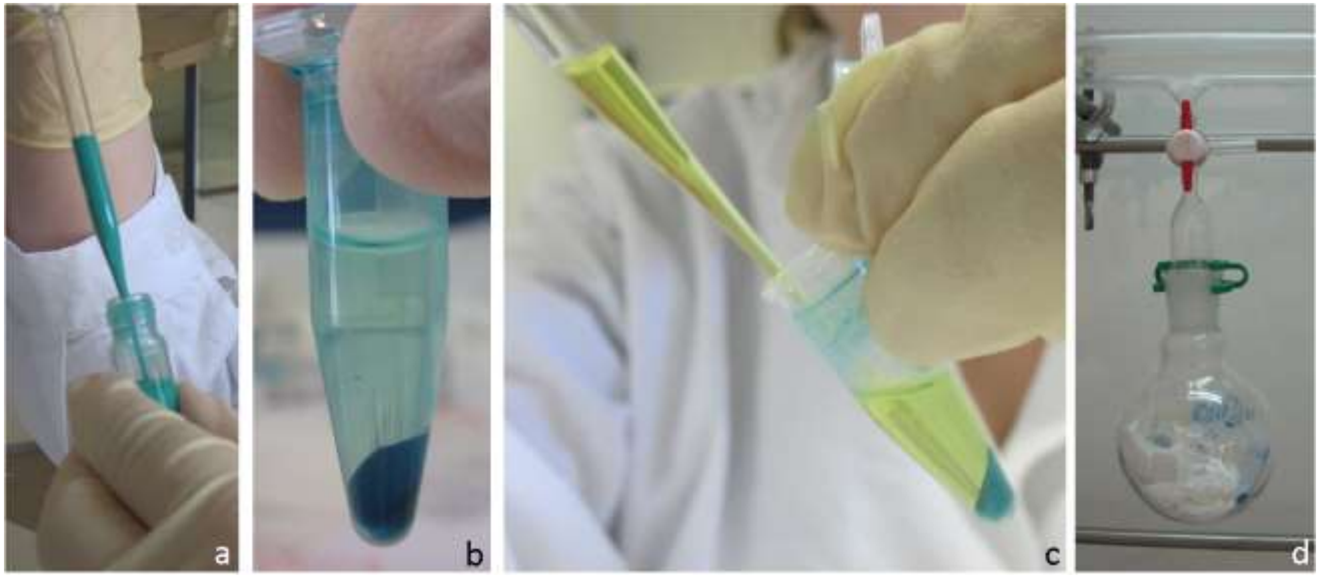
- PB29 Synthetic ultramarine
- PW4 ZnO (zinc oxide)
- PW6 TiO2 (titanium dioxide)

3. Oil colours of Remo Brindisi

- Objectives:
  - Characterization of organic modern synthetic pigments.
  - Evaluation of the state of conservation of the oil binder.

3. Oil colours of Remo Brindisi

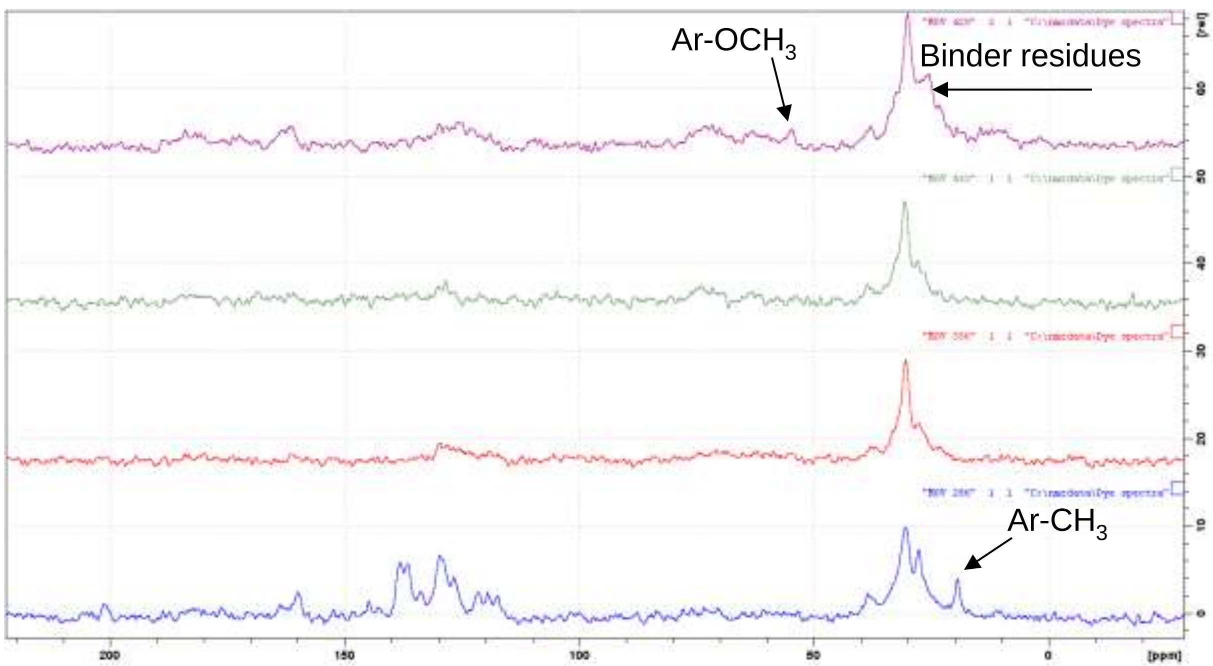
- Preparation of the samples
  - Paint in a vial
  - Acetone added (a)
  - Precipitation by centrifugation (b)
  - Acetone with binder removed (c)
  - Excess acetone dried from sample (d) → SS-NMR

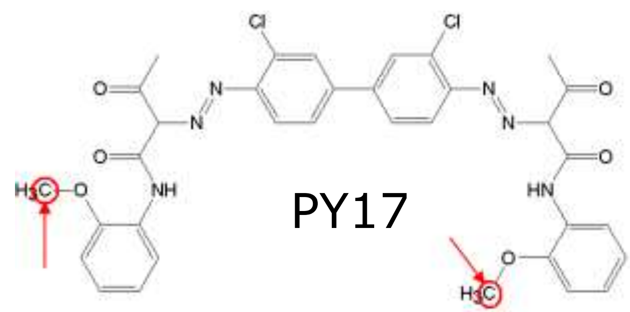


3. Oil colours of Remo Brindisi

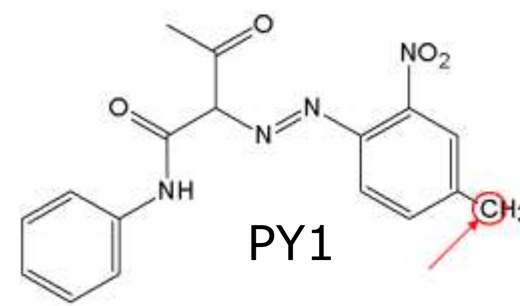
- Solid state CP-MAS NMR analysis
  - High amount of sample
  - Information not significant enough

Green colours





PY17



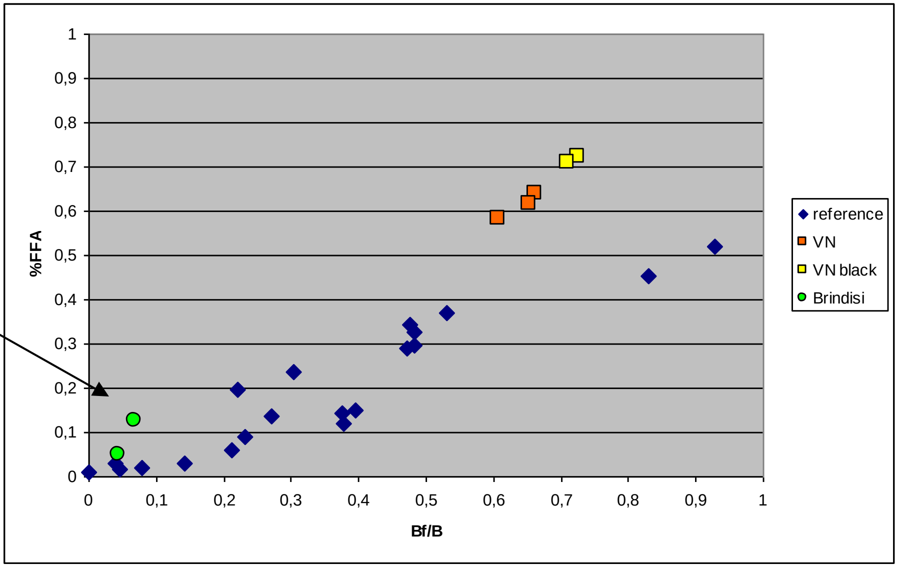
PY1

3. Oil colours of Remo Brindisi

Glycerides analysis

	Sample			
	MOB457	**MOG454**	**Fresh linseed oil**	**Linseed oil 5 yrs**
TG	**88,21**	**76,44**	**95,4**	**30,9**
1,2-DG	3,26	6,14	2,7	19,6
1,3-DG	6,58	8,30	1,9	20,9
MG	0,58	3,97	0	28,7
GL	1,37	5,14	0	-

The colours look like new !



Aknowledgements

Valeria Corradetti, Six months internship at the NMR laboratory – UoC, Greece.

MSc in Science for the conservation-restoration of cultural heritage, University of Bologna, September 2014.

Dr. E. Kartsonaki, UoC.

S. Sfakianaki, M.Sc., UoC.

Prof. Silvia Prati, University of Bologna, Italy.

Dr. Ulla Knuutinen, University of Helsinki, Finland.

Prof. D. Anglos, UoC and IESL-FORTH, Heraklion Crete.

Prof. E. Caponetti, Dr. A. Spinella, University of Palermo, Italy.

Dr. E. Kouloumpi, National Gallery, Athens, Greece.

Thank you !!

Contemporary Works of Art

Oulu City Art Museum, Finland

The last milk platform,
Jan-Eric Andersson, 1992

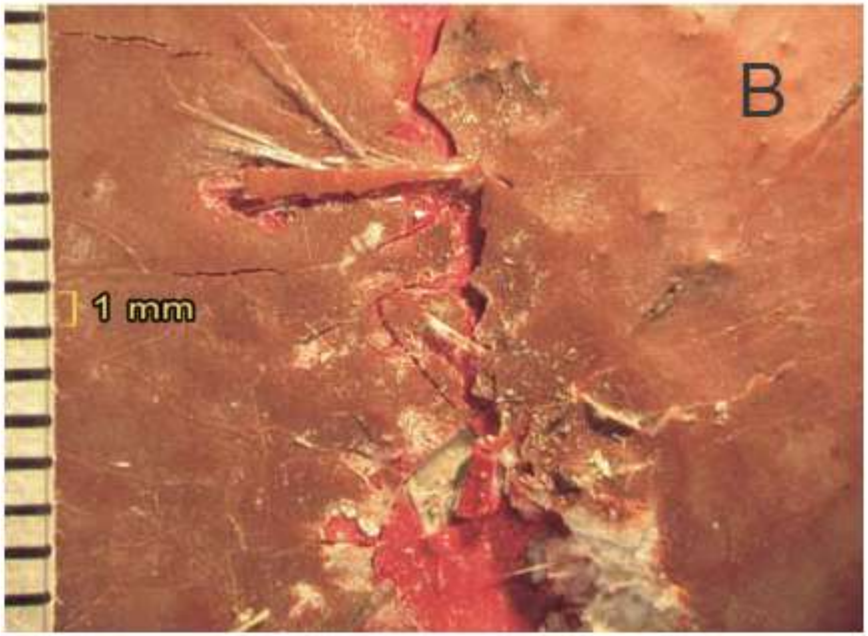
The Cocotte with two dogs,
Karry Tykkylainen, 1987

UP resin degradation

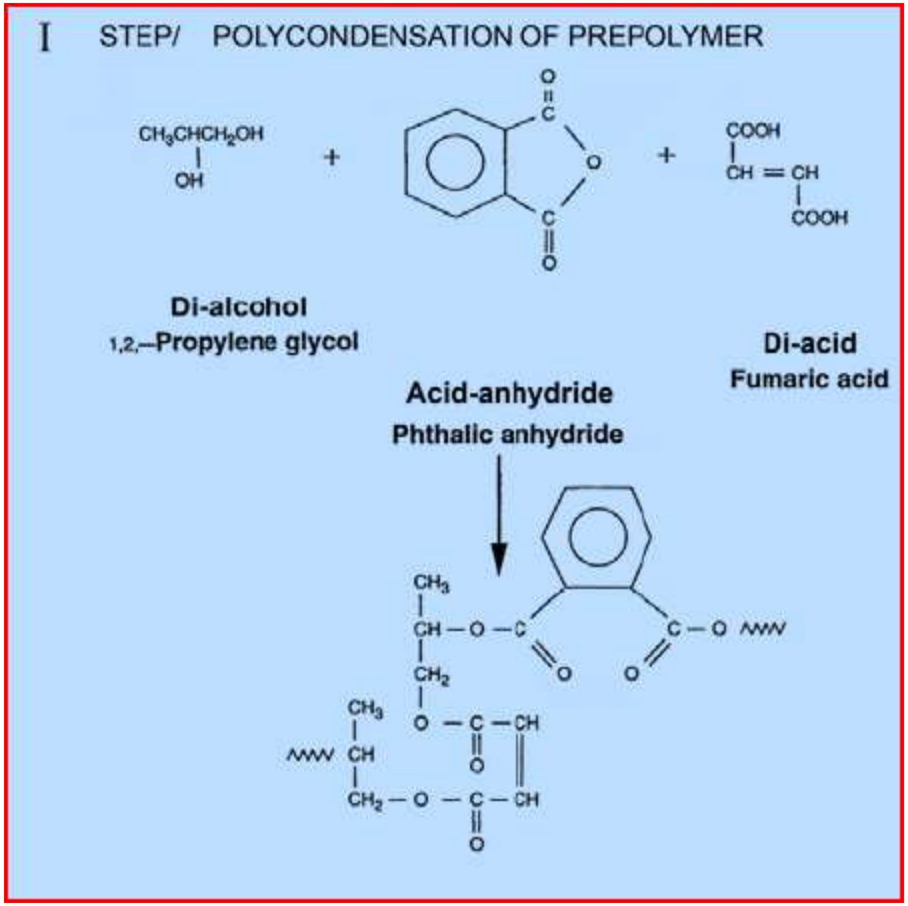
- Works of art made by glass-reinforced UP resin
- Exhibited outside for several years

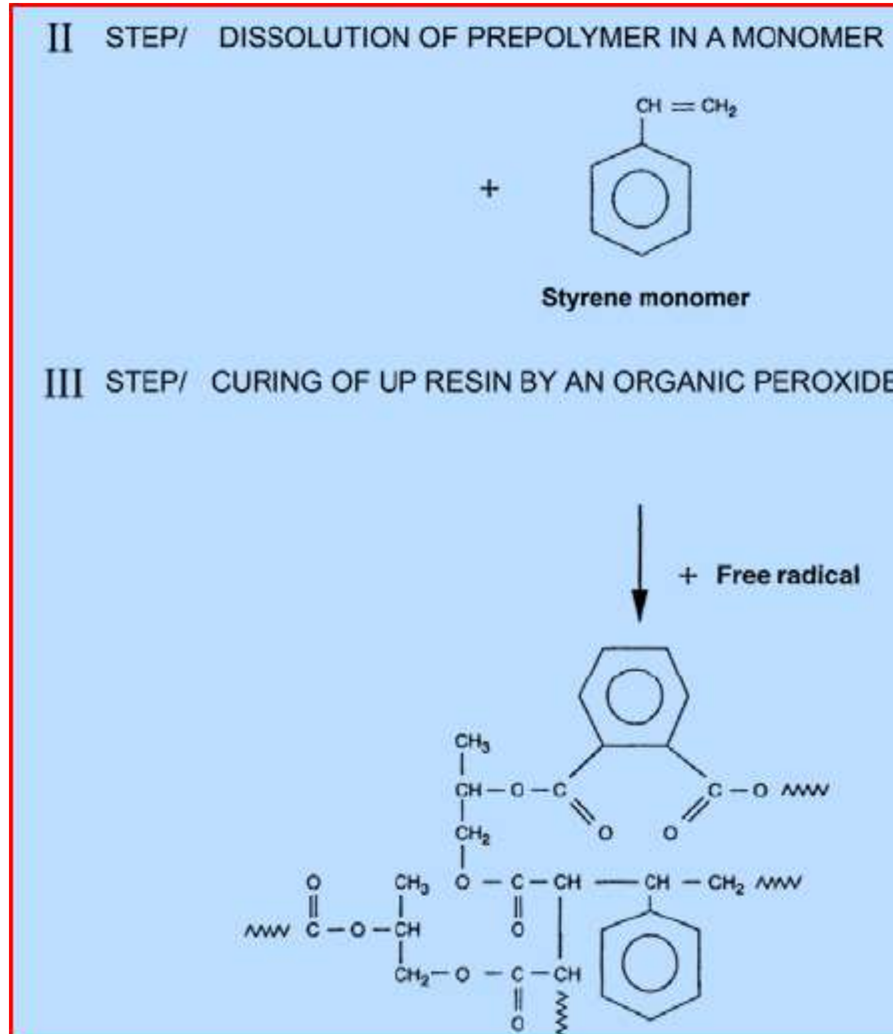
  -37 to 32 ^{o}C, 55-89 % RH,

Yellowing, cracks, air inclusions



Synthesis and curing of a UP resin to make a hard thermoset material



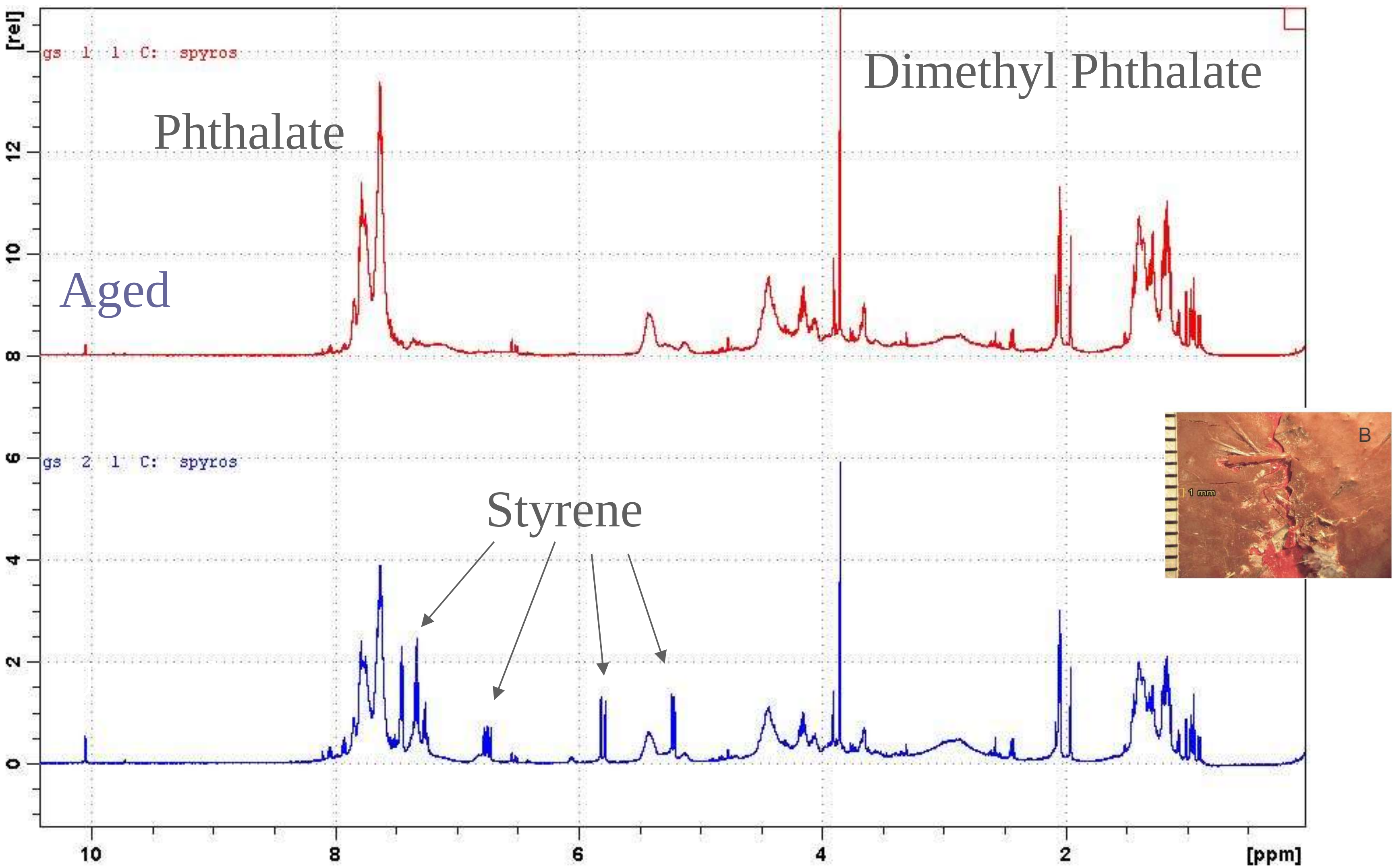


UPR analysis plan

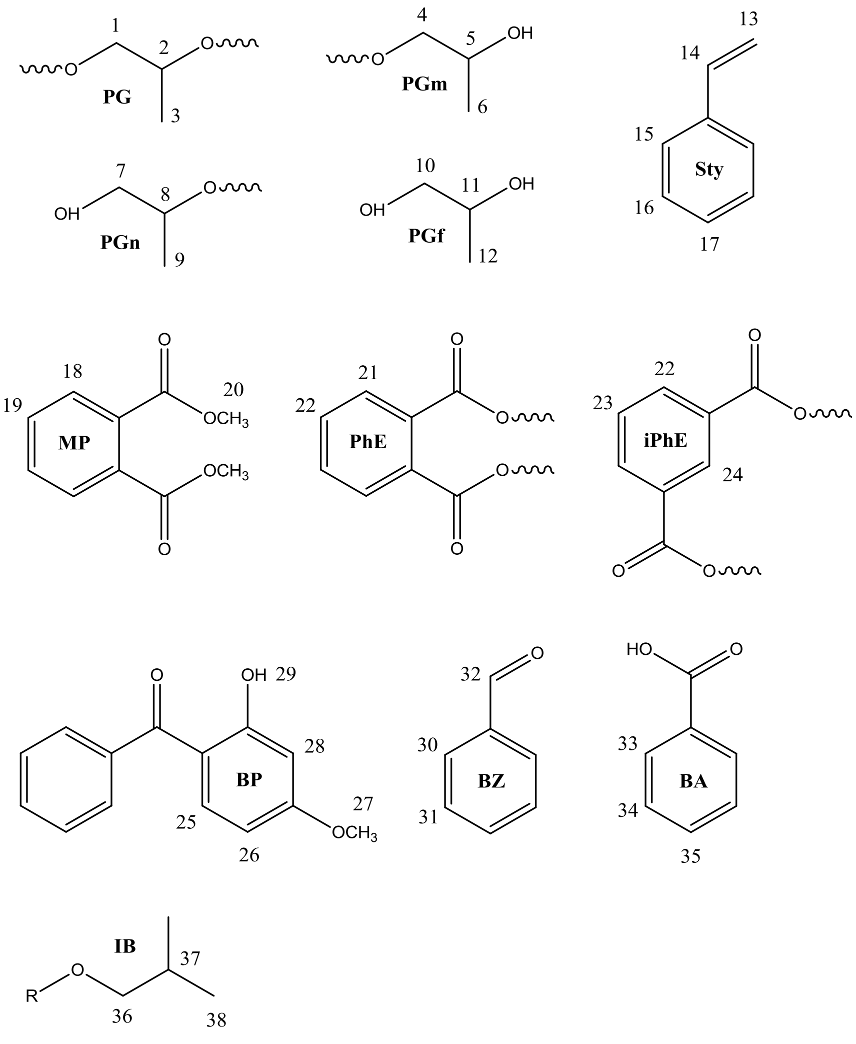
- Prepare reference UPR resins according to artist’s directions
- Age UPR under different environmental conditions (heat, humidity, UVB, etc)
- Measure mechanical properties
- Analyze reference and actual samples by NMR spectroscopy

Norpol 450-500

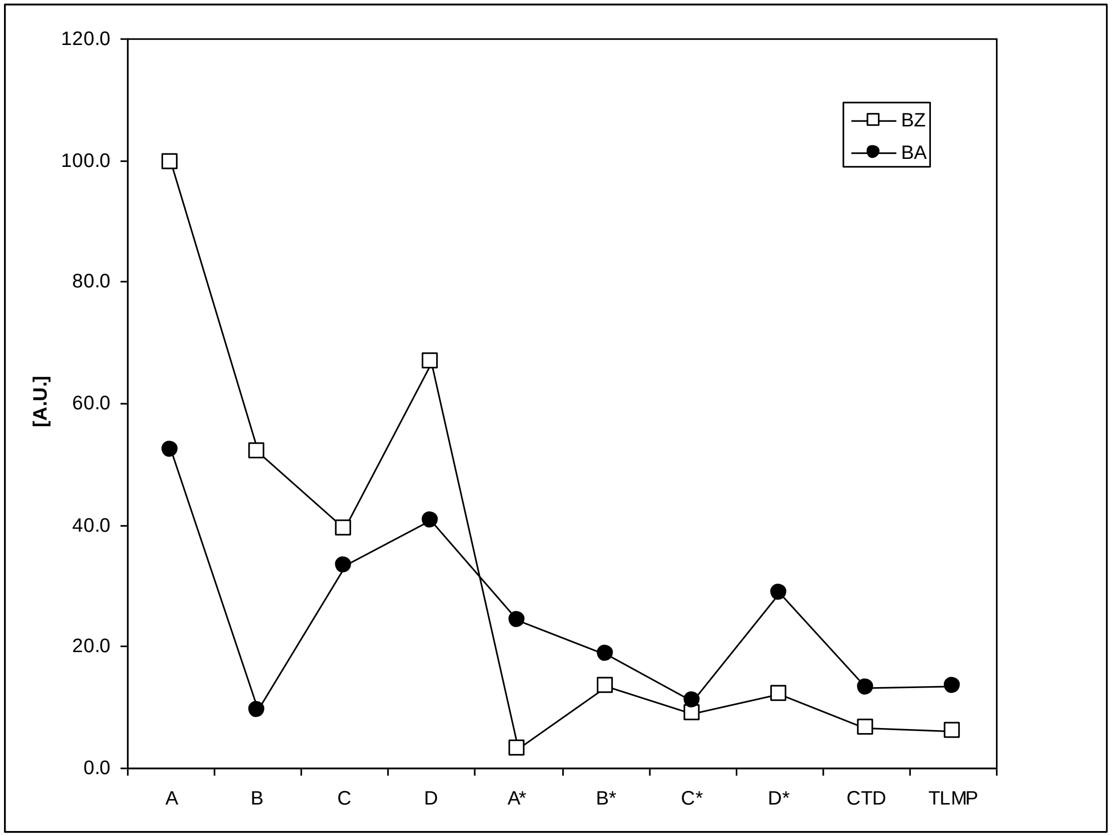
^{1}H NMR spectra of acetone extracts

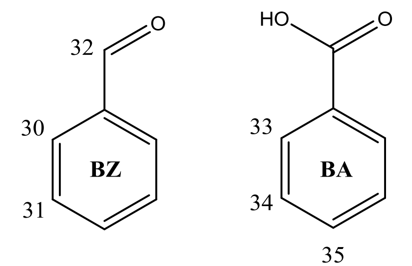


Organics in UPR resins

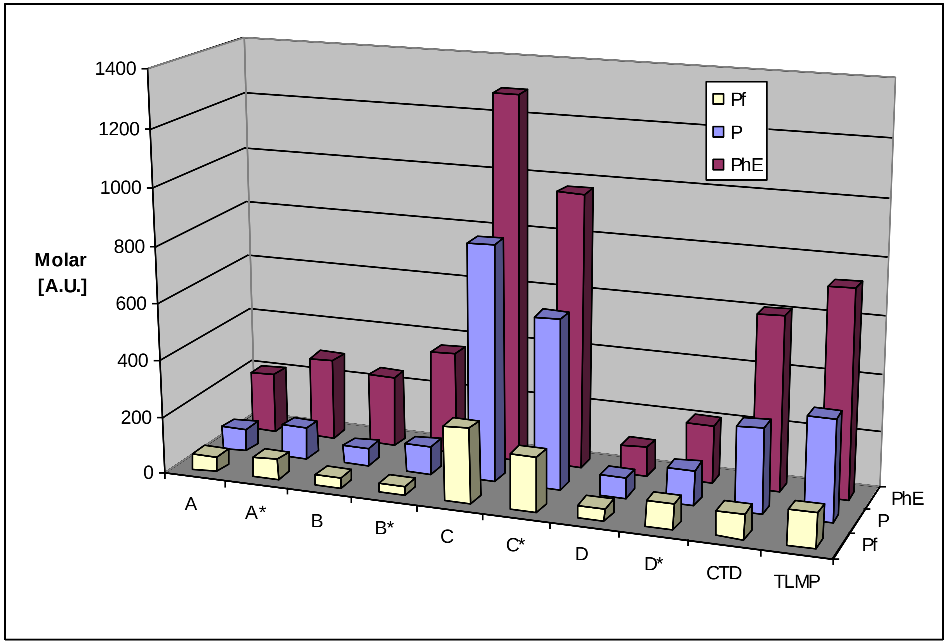


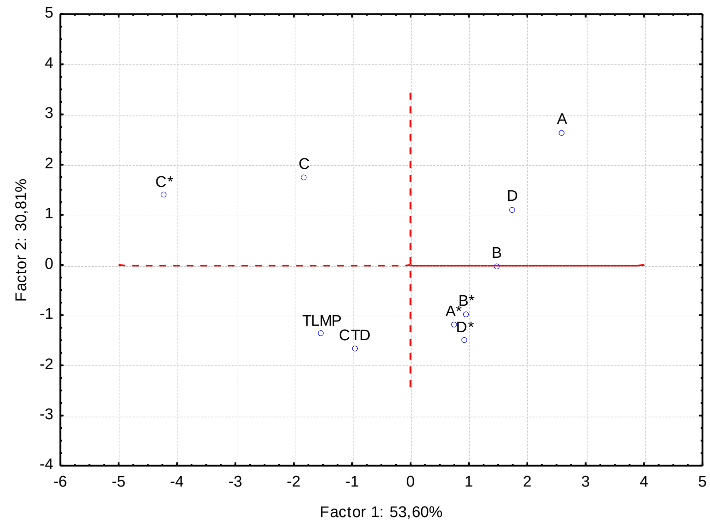
UPR aging: benzaldehyde (BZ) and benzoic acid (BA)

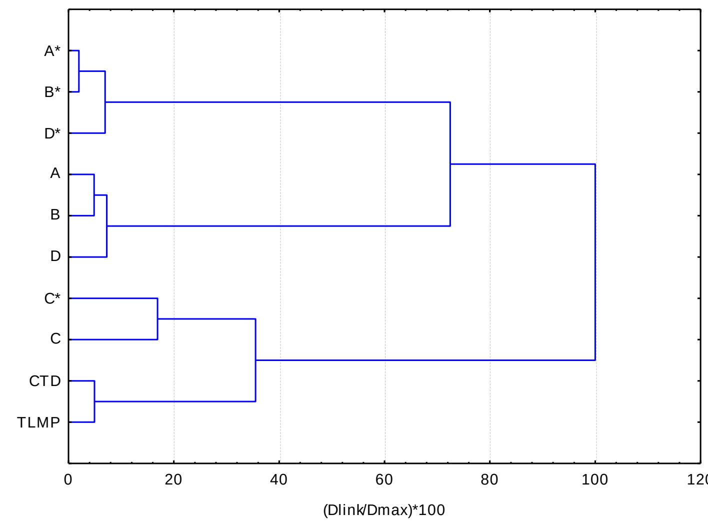




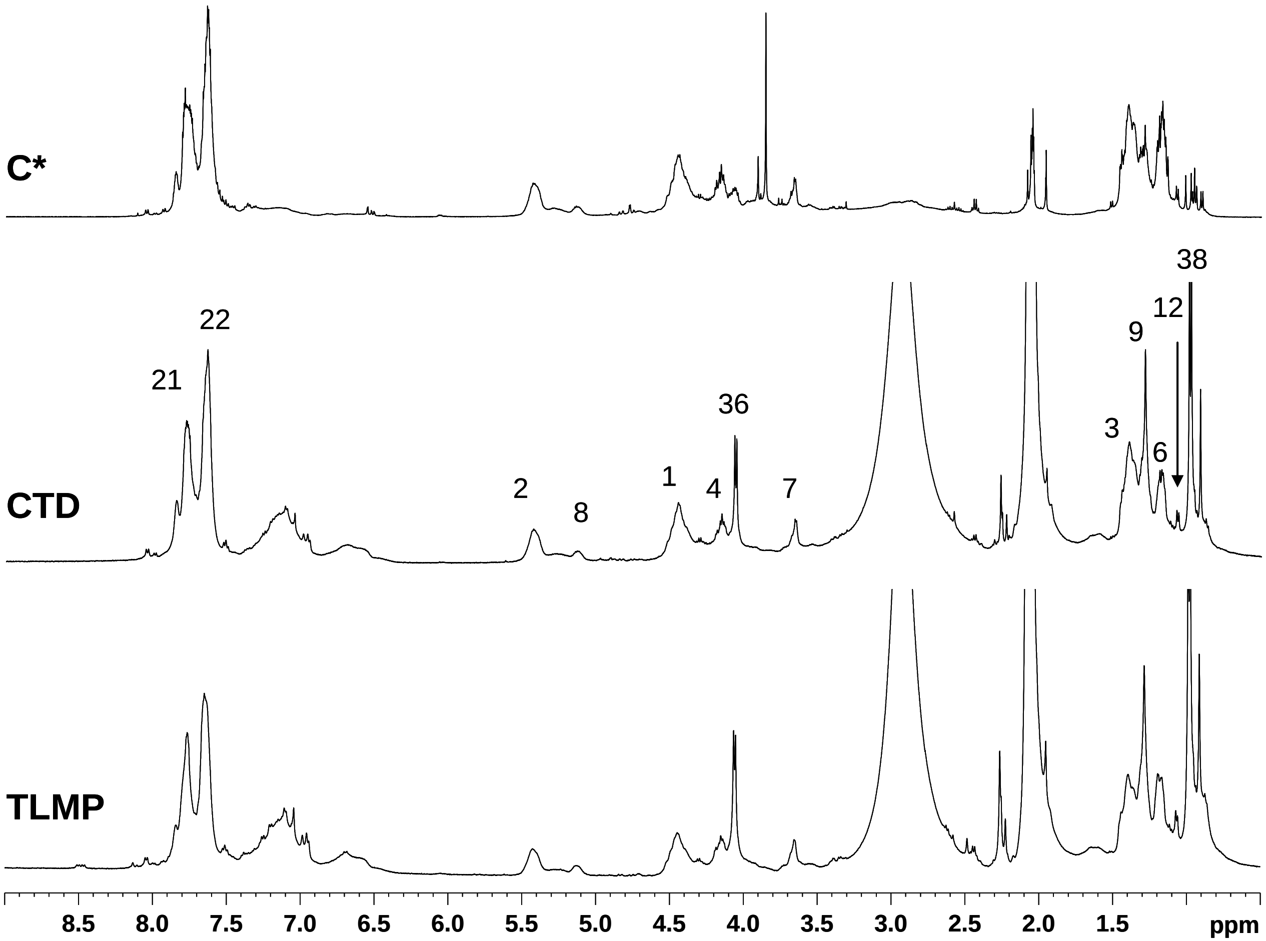
Chemometrics of UPR samples: PCA and cluster analysis







UPR reference resin C was used!



G. Stamatakis, U. Knuutinen, K. Laitinen, A. Spyros Anal. Bioanal. Chem. 398, 3203(2010)

From the chemist to the artist

- Exposure of works of art made from UP resins in the open air should be avoided.
- Use high quality UP resins containing UV stabilizers
- Care must be taken by the artist so that curing is completed and no residual solvents remain
- Use resistant top-coats to protect works of art