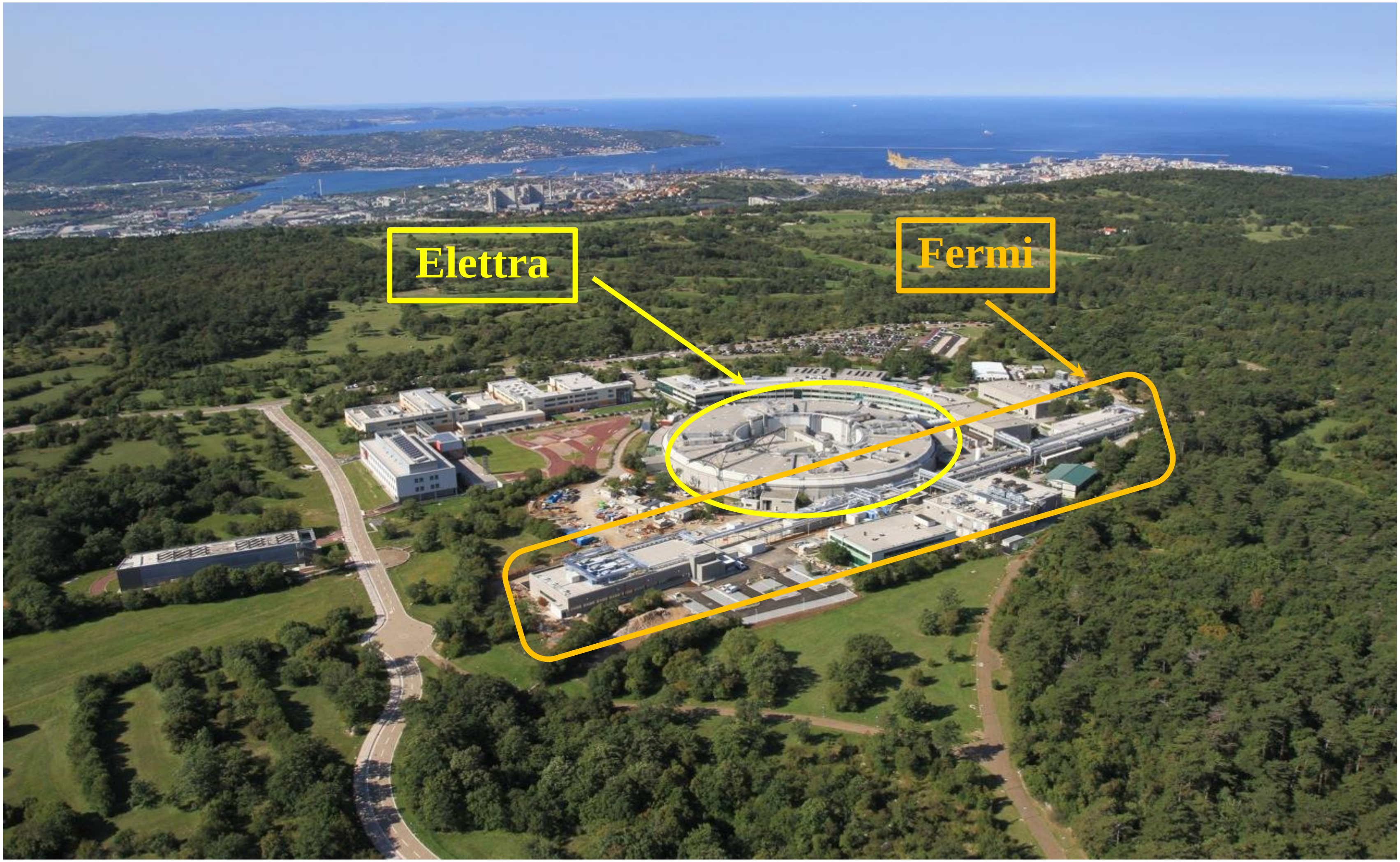
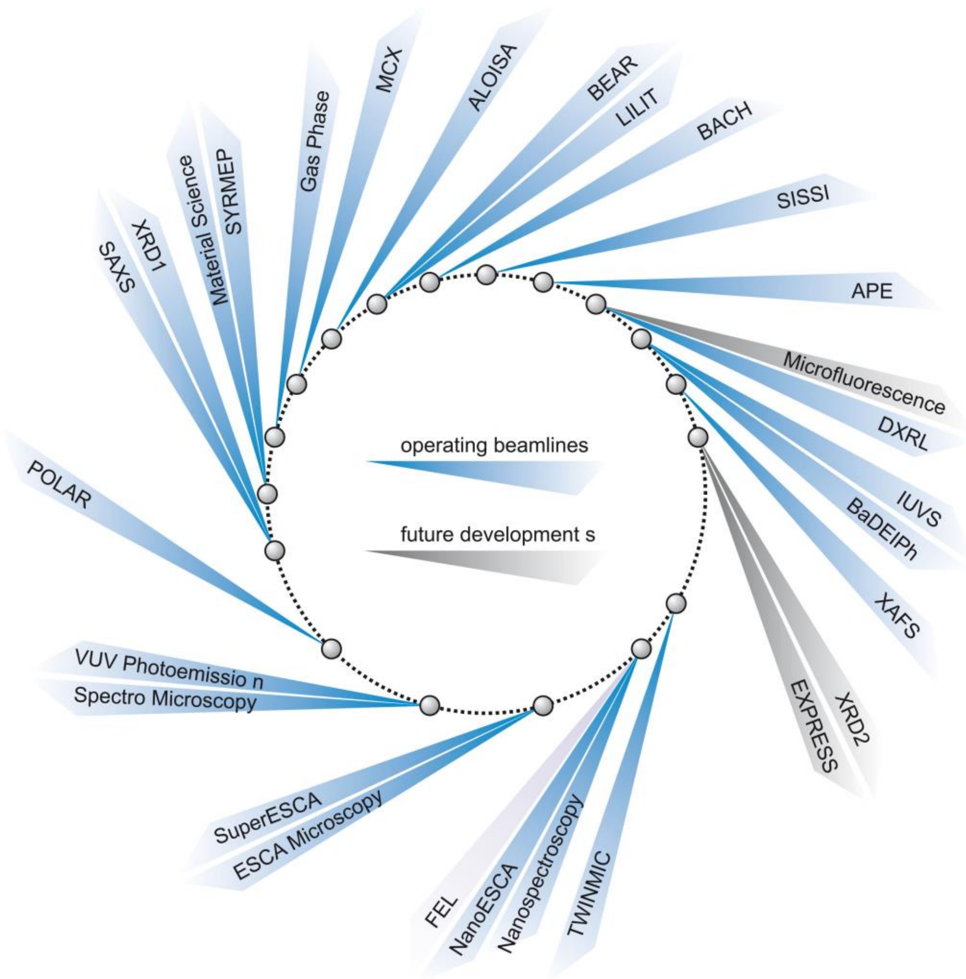
# Synchrotron Radiation and Cultural Heritage


**F. Zanini**

**Elettra - Sincrotrone Trieste**
**and**
**Scuola Interateneo di Specializzazione in Beni Archeologici**



Elettra
Fermi


MCX
ALOISA
BEAR
LILIT
BACH
SISSI
APE
Microfluorescence
DXRL
IUVS
BaDElPh
XAFS
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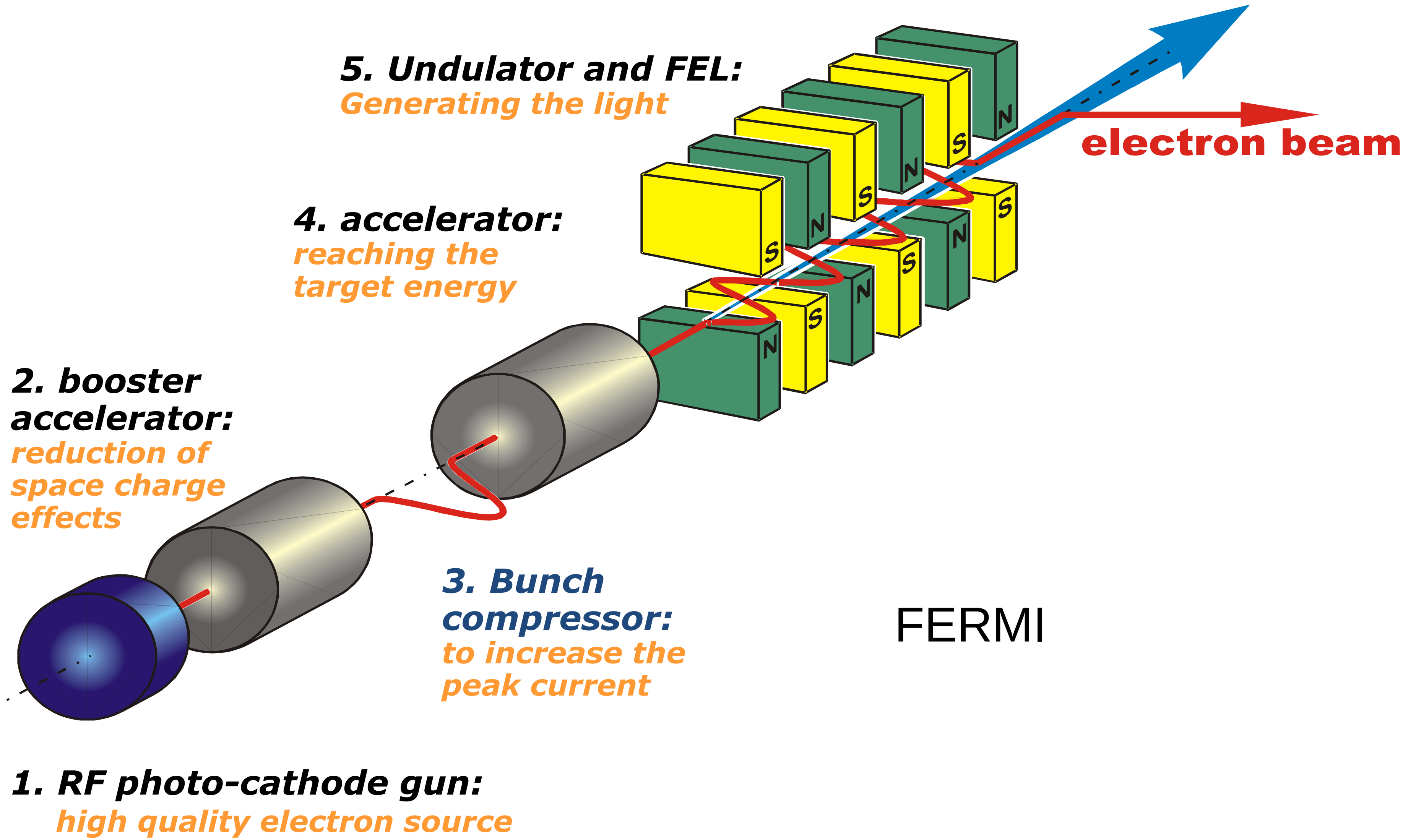
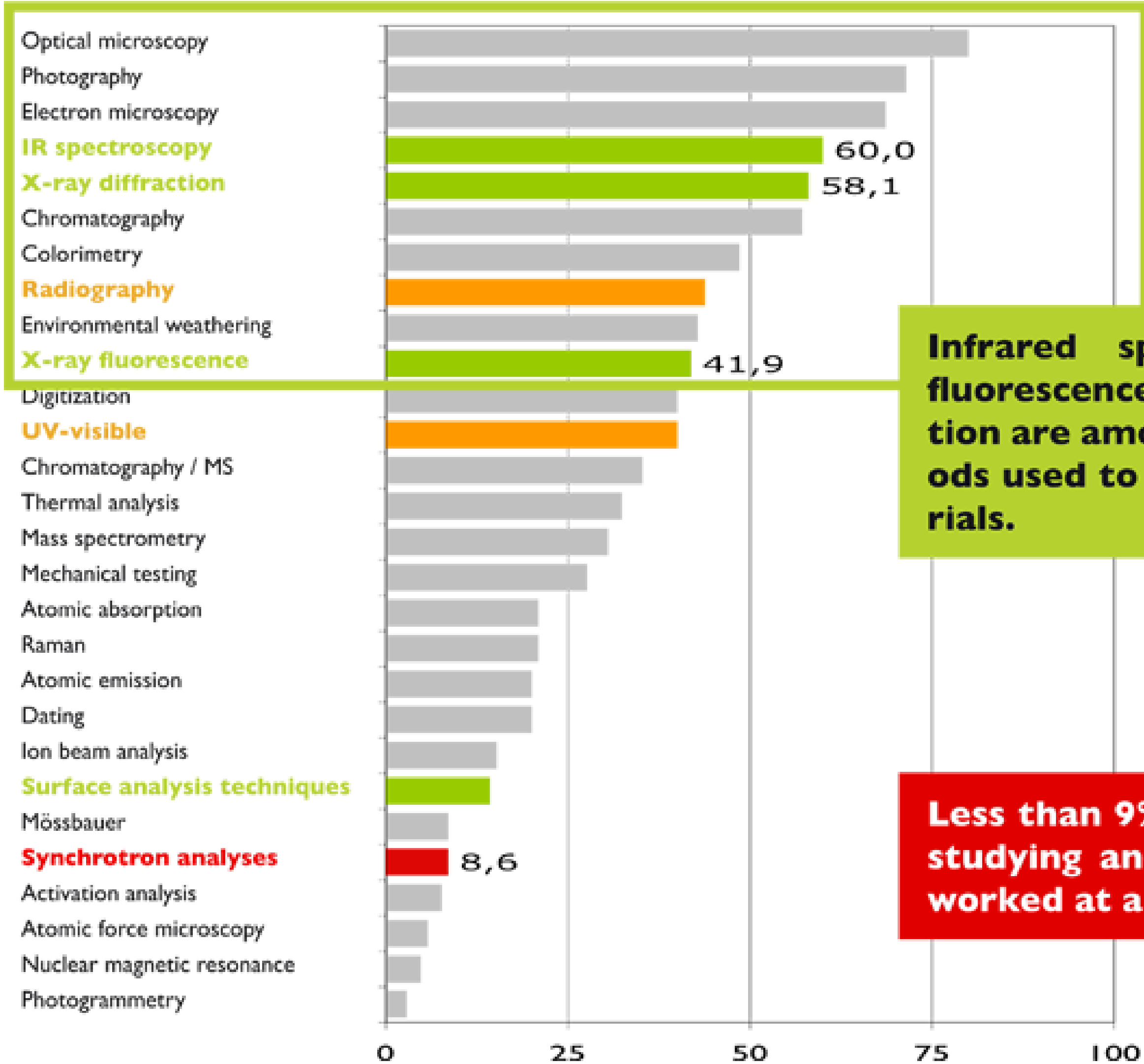
EXPRESS
TWINMIC
Nanospectroscopy
NanoESCA
FEL
ESCA Microscopy
SuperESCA
VUV Photoemissio n
Spectro Microscopy
POLAR
SAXS
XRD1
Material Science
SYRMEP
Gas Phase
operating beamlines
future development s

# FERMI


5. Undulator and FEL:
Generating the light
electron beam
4. accelerator:
reaching the target energy
2. booster accelerator:
reduction of space charge effects
3. Bunch compressor:
to increase the peak current
1. RF photo-cathode gun:
high quality electron source
S
N

**cultural heritage research**

European context




**Infrared spectrometry, X-ray fluorescence and X-ray diffraction are among the top 10 methods used to study ancient materials.**

**large potential**

**Less than 9% of the laboratories studying ancient materials ever worked at a synchrotron**

# Cetervm censeo, mvndvm non delendvm esse

- Samples of great historical and/or commercial value
- Monitoring of restoration and conservation protocols

# Artis monvmentorvm qvi vnvm vidit nvllvm vidit, qui mille vidit vnvm vidit

- Use of several experimental techniques
- Examination of a high number of similar samples

# What do we offer?

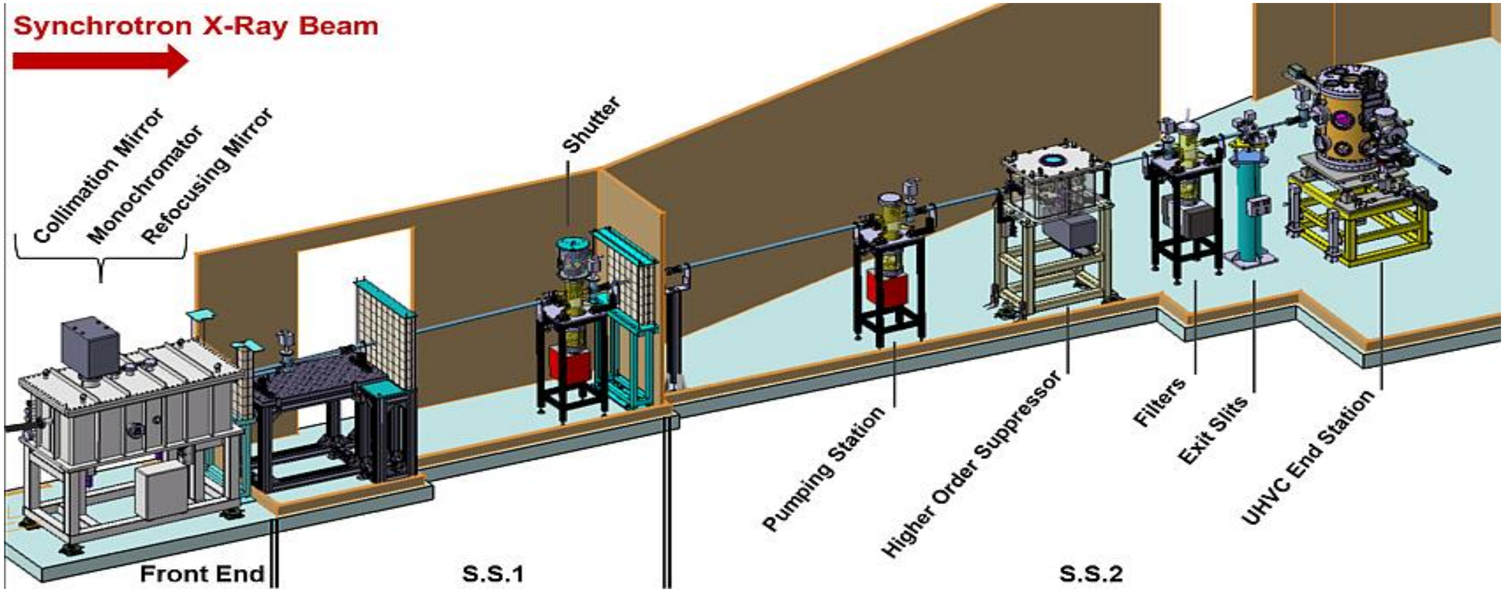
- Large portfolio of techniques
- Most techniques are non destructive or microdistructive
- Sinergies between conventional labs and large research infrastructures
- Easy access to thematic networks and fundings

# ECHO - Elettra Cultural Heritage Office

- Support to CH users:
  - proposal submission
  - sample preparation
  - experimental setup
  - data analysis and interpretation
- Dedicated evaluation panel
- Collaboration for regional and european calls
- Distributed archaeometry laboratory

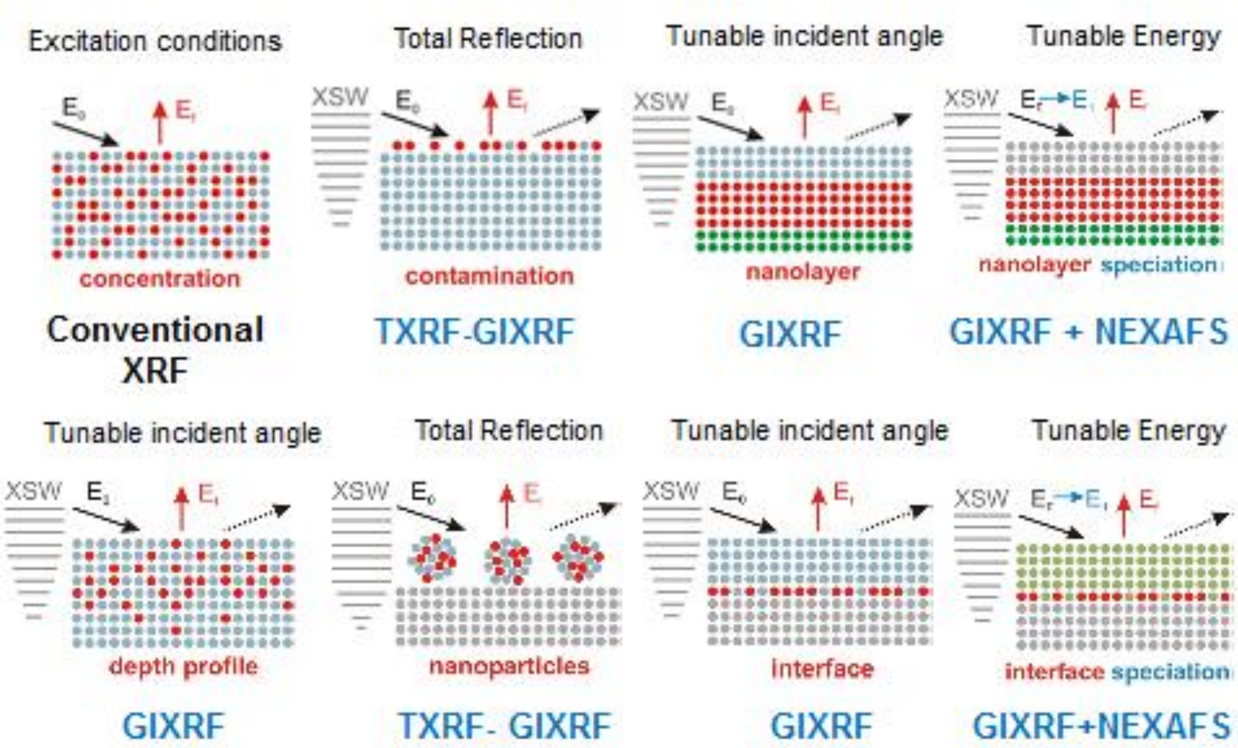
## ELETTRA X-Ray Fluorescence: a multi-purposes XRF beamline

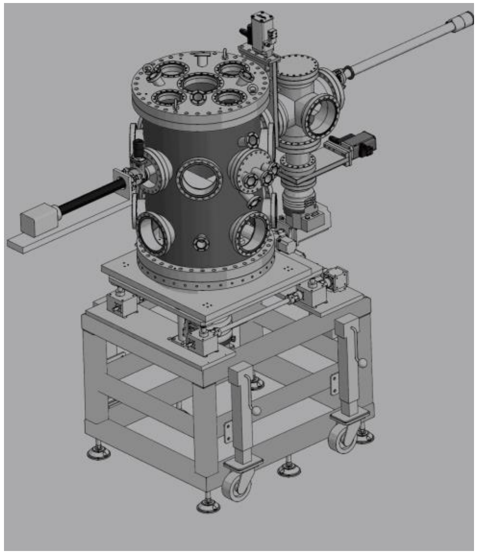
*Energy range:* 2 - 14 keV (0.7 - 14 keV with multilayers, 2016)
*Beam size:* at the exit slits (22.91 m from source) 250 X 50 $\mu m^2$
*Beam divergence:* 0.15 mrad (exit slits)
*Flux:* 5 $10^9$ ph/s @ 5.5 keV (2 GeV) or @ 7keV (2.4 GeV) (exit slits)
*End Station:* ***Ultra-high Vacuum Chambe***r for XRS in collaboration with IAEA.org International Atomic Energy Agency
**Techniques: TRXRF, GIXRF (GEXRF), XRR, XANES**
Beam size: ~250X120 $\mu m^2$ (sample position)



## TECHNIQUES:

- ❑ **GIXRF**
  Grazing Incidence X Ray Fluorescence Analysis
- ❑ **TXRF**
  Total Reflection X Ray Fluorescence Analysis
- ❑ **XANES / NEXAFS**
  Near Edge X ray Absorption Fine Structure



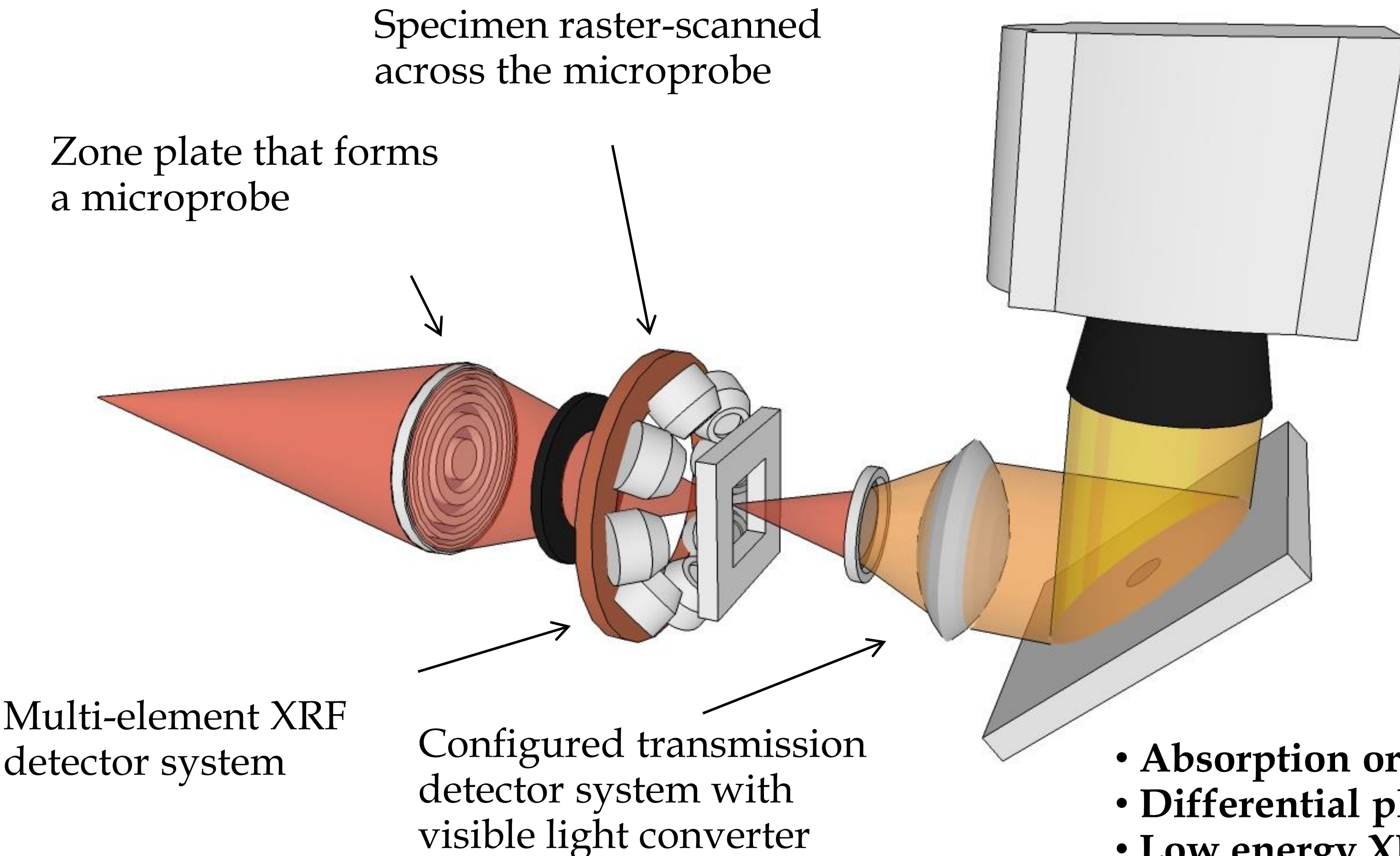



*(courtesy from B. Beckhoff, 2011)*

# APPLICATION FIELDS:

- Energy storage and conversion related micro- and nano-scaled heterogeneous materials
- Materials/Chemistry under extreme conditions (P, T), Microelectronics – Nanoelectronics
- Environmental samples – Speciation of nanoparticles
- Fundamental Parameters work – Metrology (reference-free analysis)
- Chemistry and other domains of material – Manufacturing / Reaction follow-up
- Detection, quantification and speciation of Trace elements – Contaminants
- Cultural Heritage

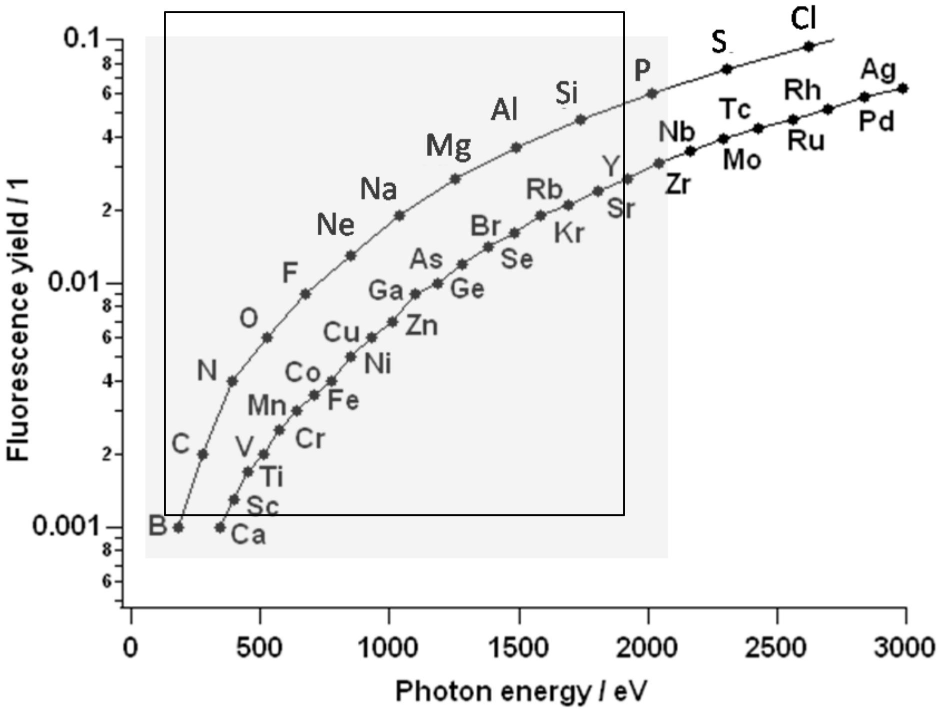
## **ELETTRA TwinMic:** the soft X-ray transmission and emission microscope

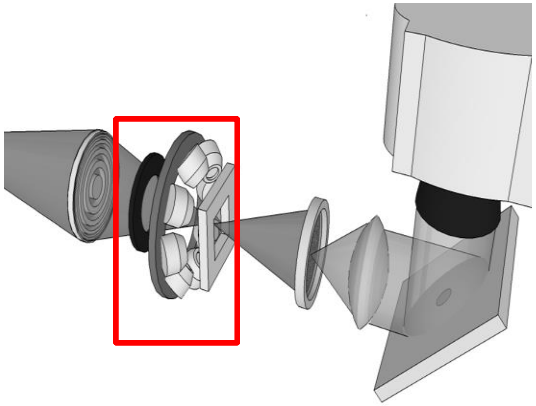



- **Absorption or transmission**
- **Differential phase contrast**
- **Low energy XRF**
- **Energy range: 400 - 2200 eV**
- **Spatial resolution: 100 - 1000 nm**

## ELETTRA TwinMic: the soft X-ray transmission and emission microscope

### Elements detected with LEXRF @ TwinMic:



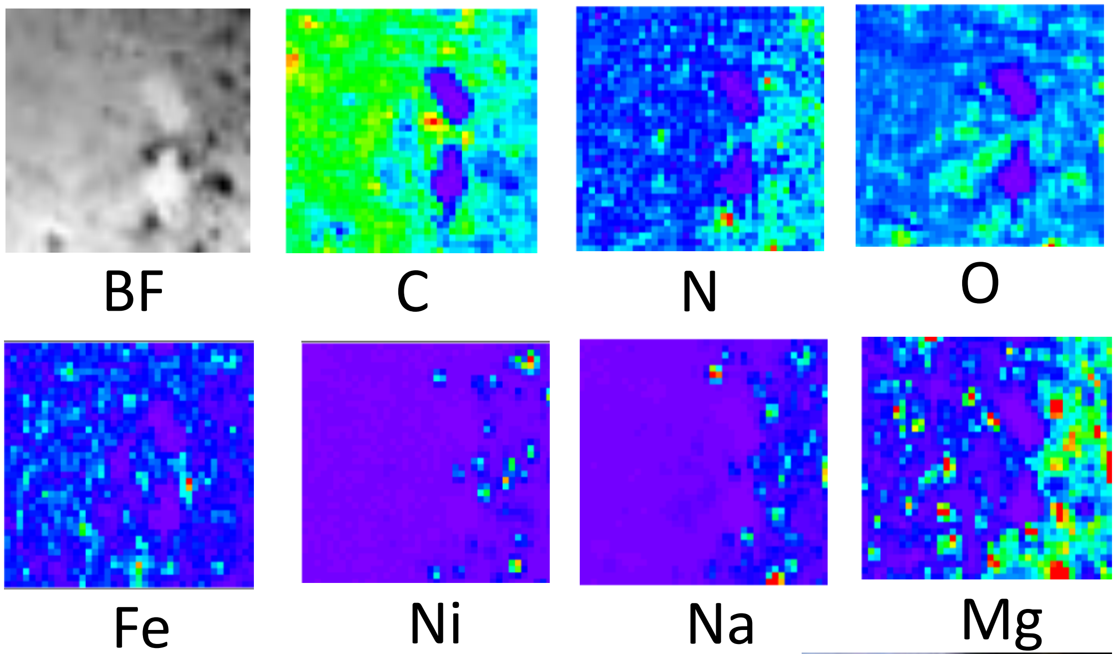



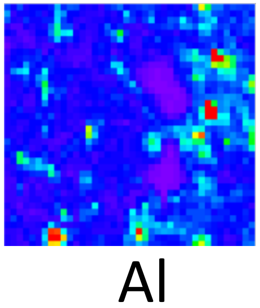
X-ray fluorescence: ~1000x better sensitivity than electrons (SEM-EDS) for trace elemental mapping. Better lateral resolution.

# ELETTRA TwinMic: the soft X-ray transmission and emission microscope

*I. Nemec & Ž. Smit, Uni Ljubljana, Slovenia*

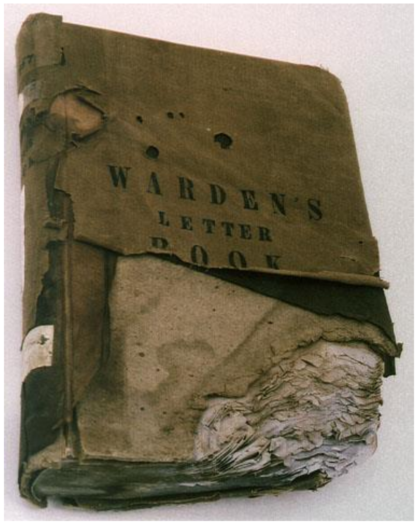
Analysis of the elemental distribution in paintings from **August Černigoj** (1898-1985)



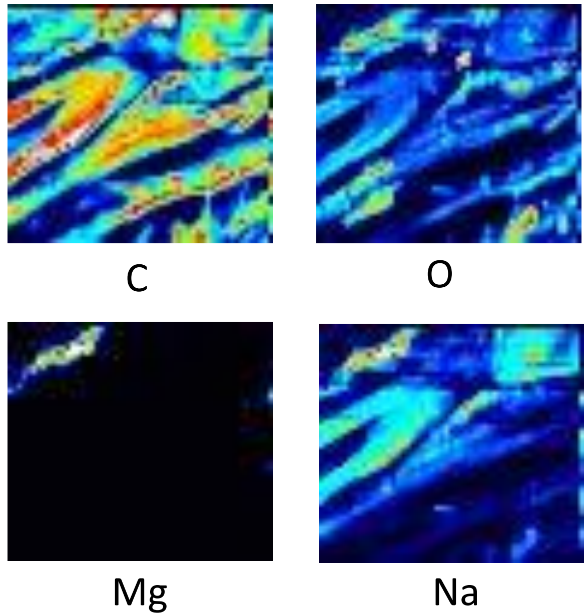

E = 1670 eV
40 μm x 40 μm,
40 x 40 pixels
15 s dwell/ px

**<u>ELETTRA TwinMic:</u> the soft X-ray transmission and emission microscope**



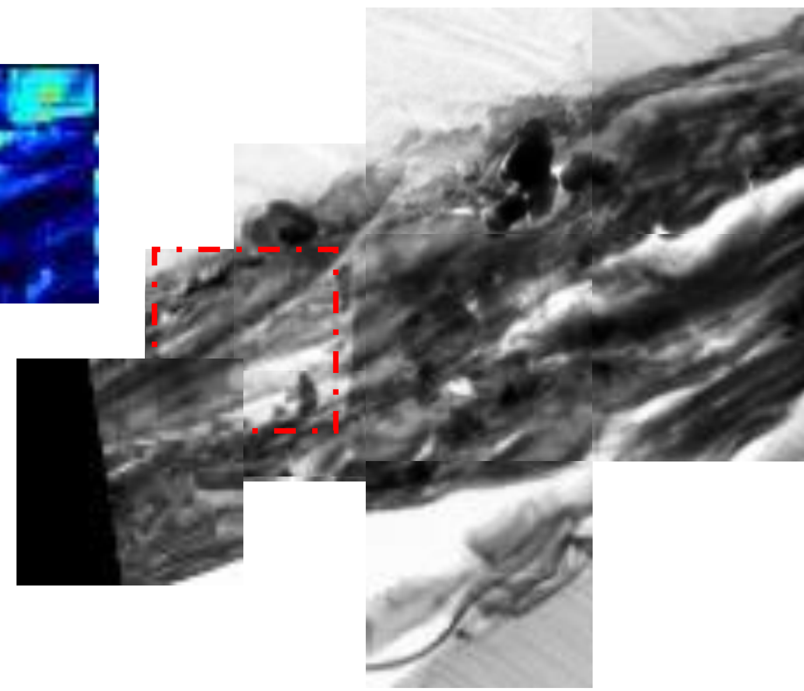
*A. Zappala, Dept of History of Art, Uni Udine, I*

Distribution of polymers ("Bookkeeper" Mg containing) for book conservation in paper




E = 1468 eV
65 µm x 65 µm,
50 x 50 pixels
15 s dwell/ px

Cross-section of a page of an ancient book



Absorption images

# ELETTRA MCX: Material Characterization by X-ray diffraction

Light source:

Bending magnet

Critical energy : 3.2keV (2.0) , 5.5keV (2.4)

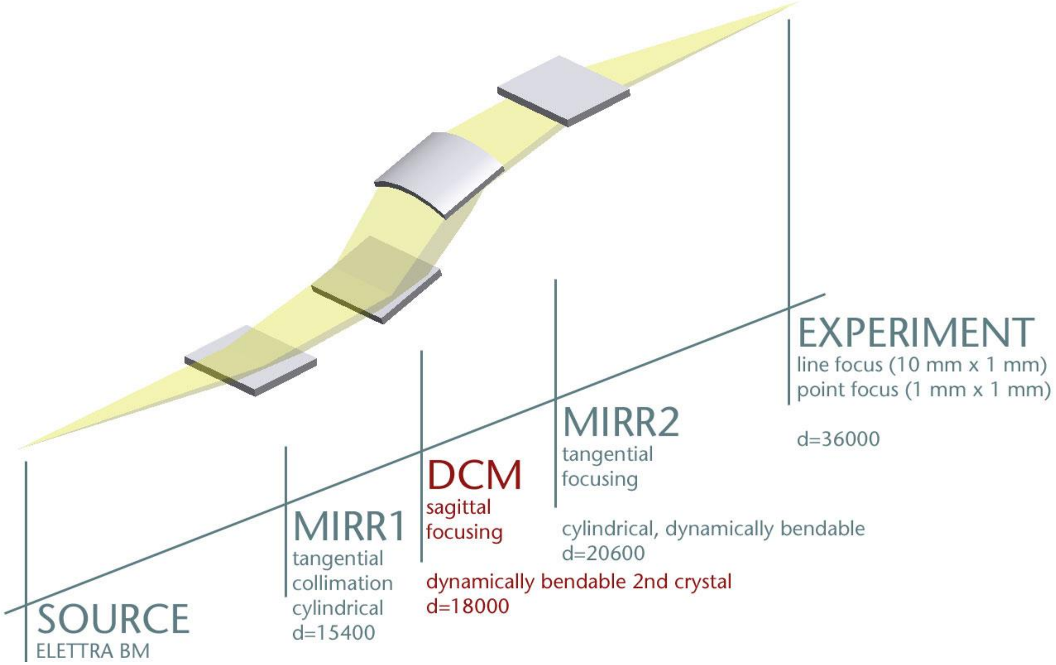
X-rays at sample:

Energy range : 6-22 keV

Photon flux : $10^{11}$ photons/sec

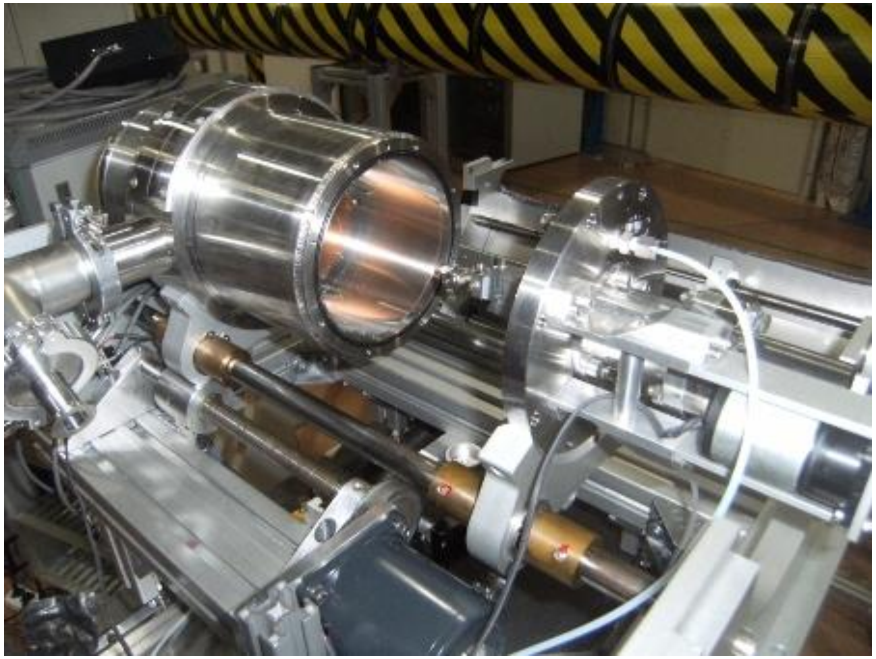
Beam size at sample : 10x1 $mm^2$ - 0.3›

Energy resolution : ΔE/E $2x10^{-4}$



## **ELETTRA MCX:** Material Characterization by X-ray diffraction

Four circle diffractometer



Furnace

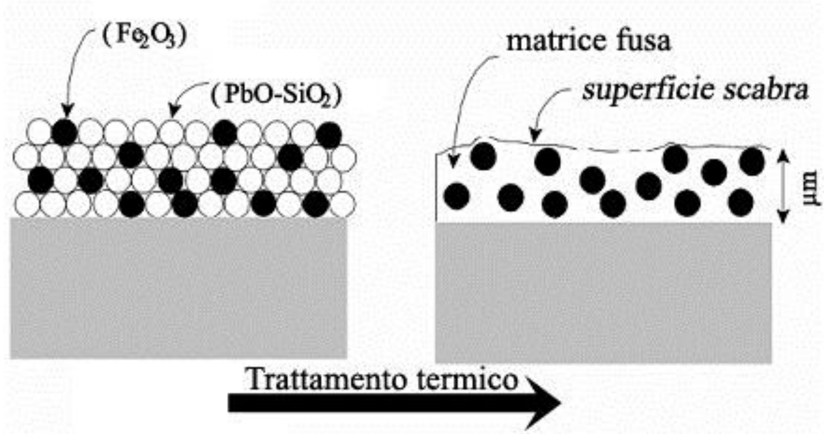
X-ray diffraction patterns are used as fingerprints to identify phases in mixtures. The example shows a fragment of a stained glass window from the Basilica of San Giovanni e Paolo in Venice

## Chiesa dei Santi Giovanni e Paolo XIII-XVI sec.

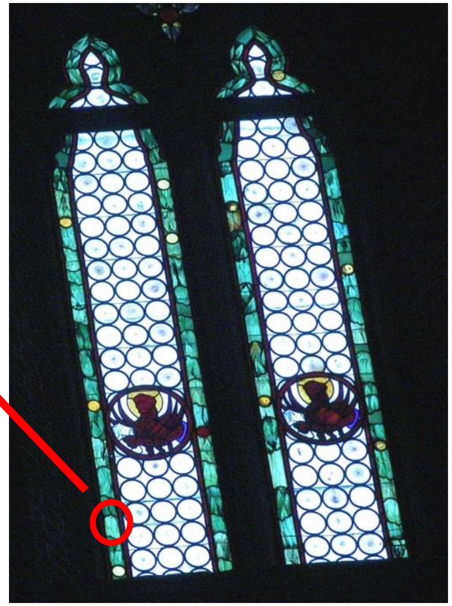
"La grande vetrata"
End XV century

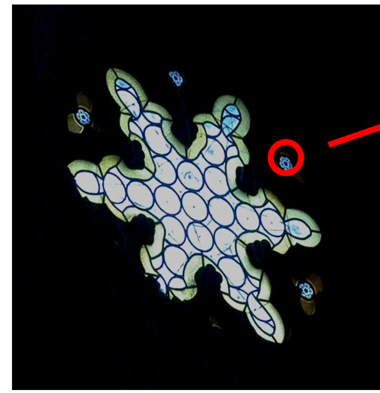
- Low melting glass ($SiO_2$, PbO,)
- Pigment (metal oxides)
- Paint medium (water, vinegar, oil)
- Firing to fuse the grisaille on the glass

Grisaille technique



SSGP1/2





SSGP3

SSGP2


SSGP2

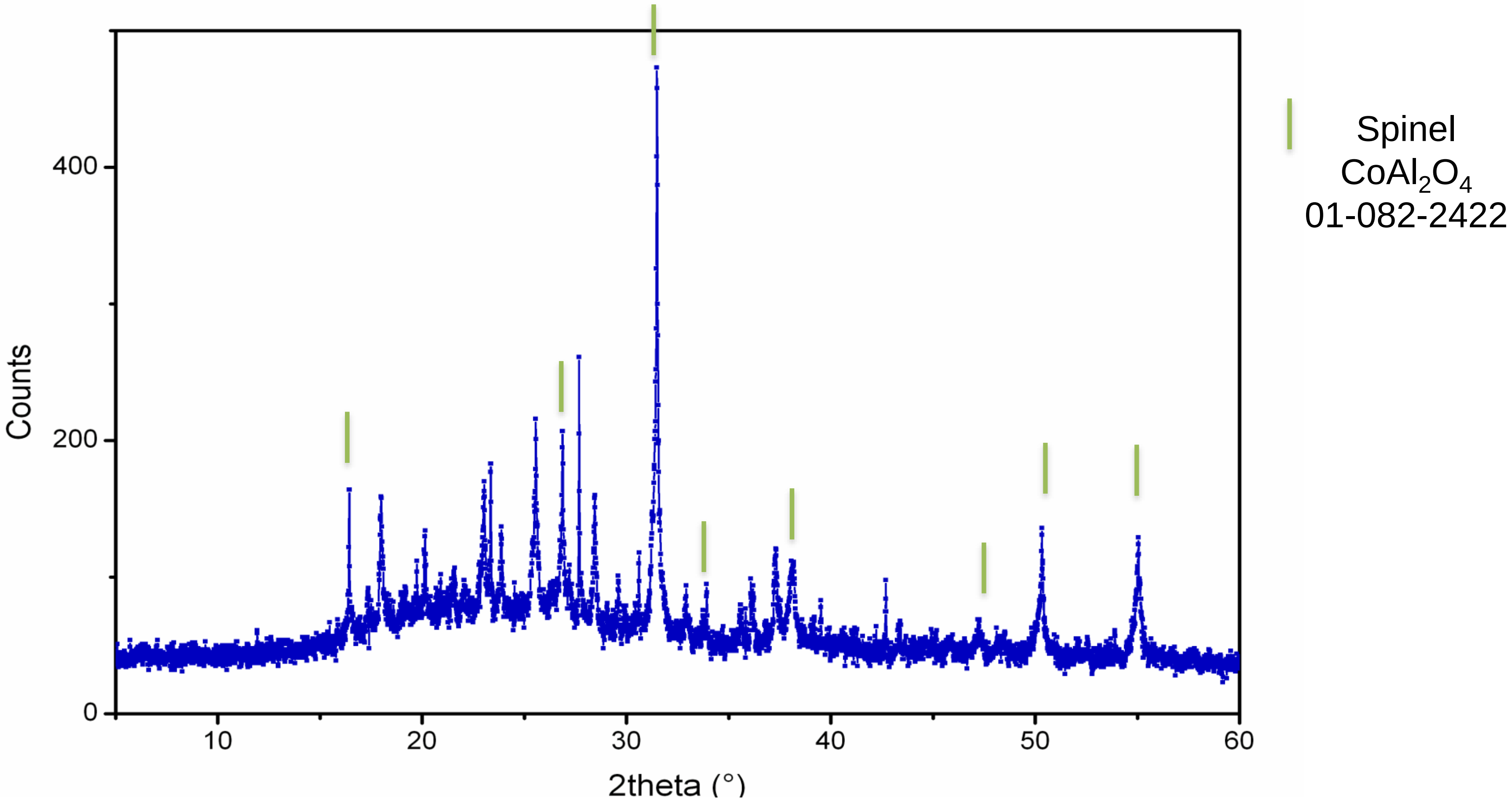
SSGP3

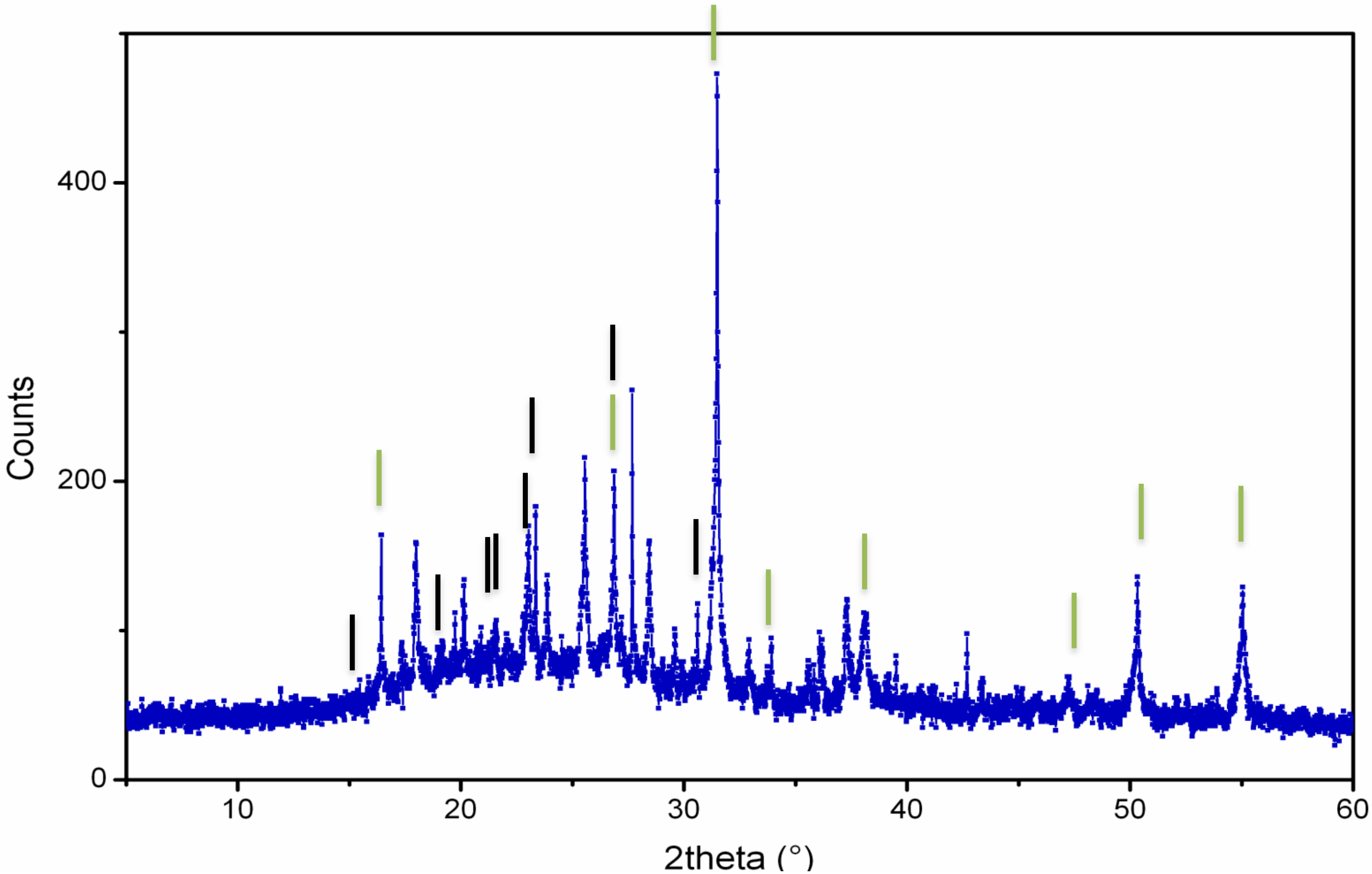
| Sample | Glass | Grisaille | Patina |
|---|---|---|---|
| SSGP1 | Green | Dark | Brown |
| SSGP2 | Green | Brown | White |
| SSGP3 | Light yellow | Blue | White |

**SSGP2**


**SSGP2**

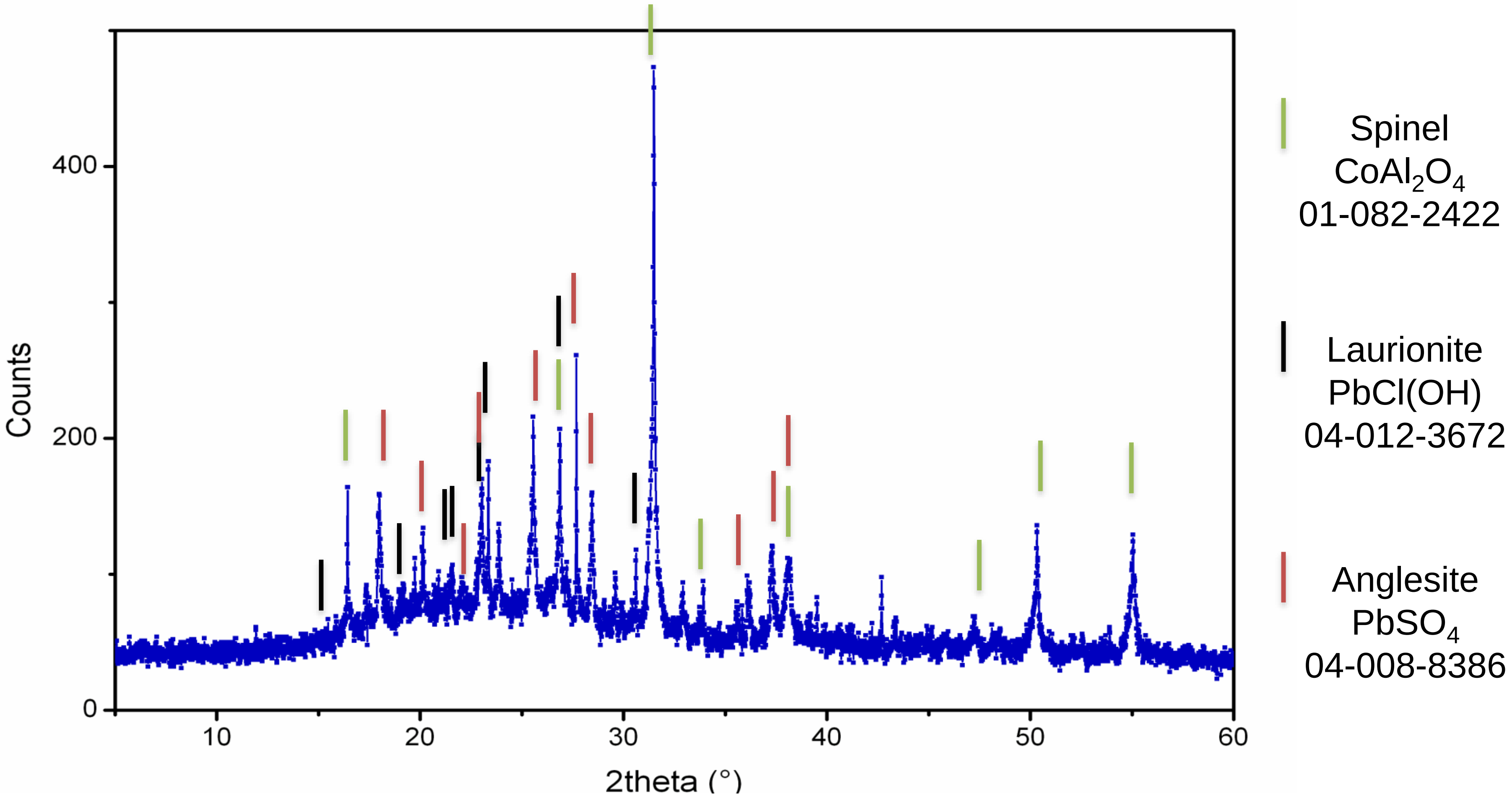
**SSGP3**


400
200
0
Counts
10
20
30
40
50
60
2theta (°)
Spinel
$CoAl_2O_4$
01-082-2422



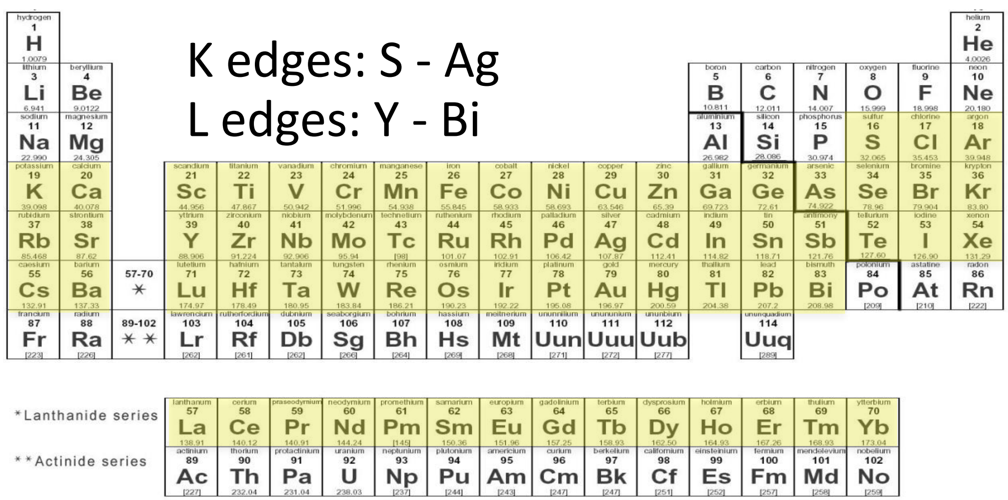

Spinel
$CoAl_2O_4$
01-082-2422

Laurionite
PbCl(OH)
04-012-3672

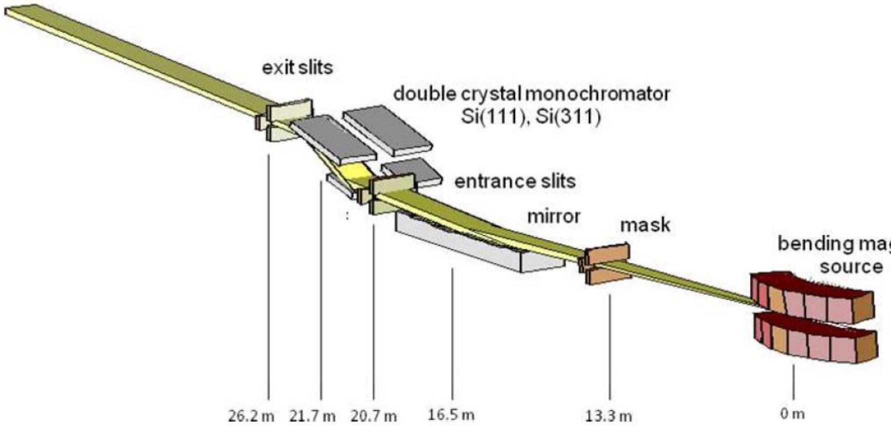

Counts
400
200
0
10
20
30
40
50
60
2theta (°)
Spinel
$CoAl_2O_4$
01-082-2422
Laurionite
PbCl(OH)
04-012-3672
Anglesite
$PbSO_4$
04-008-8386

# ELETTRA XAFS: X-Ray Absorption Fine Structures

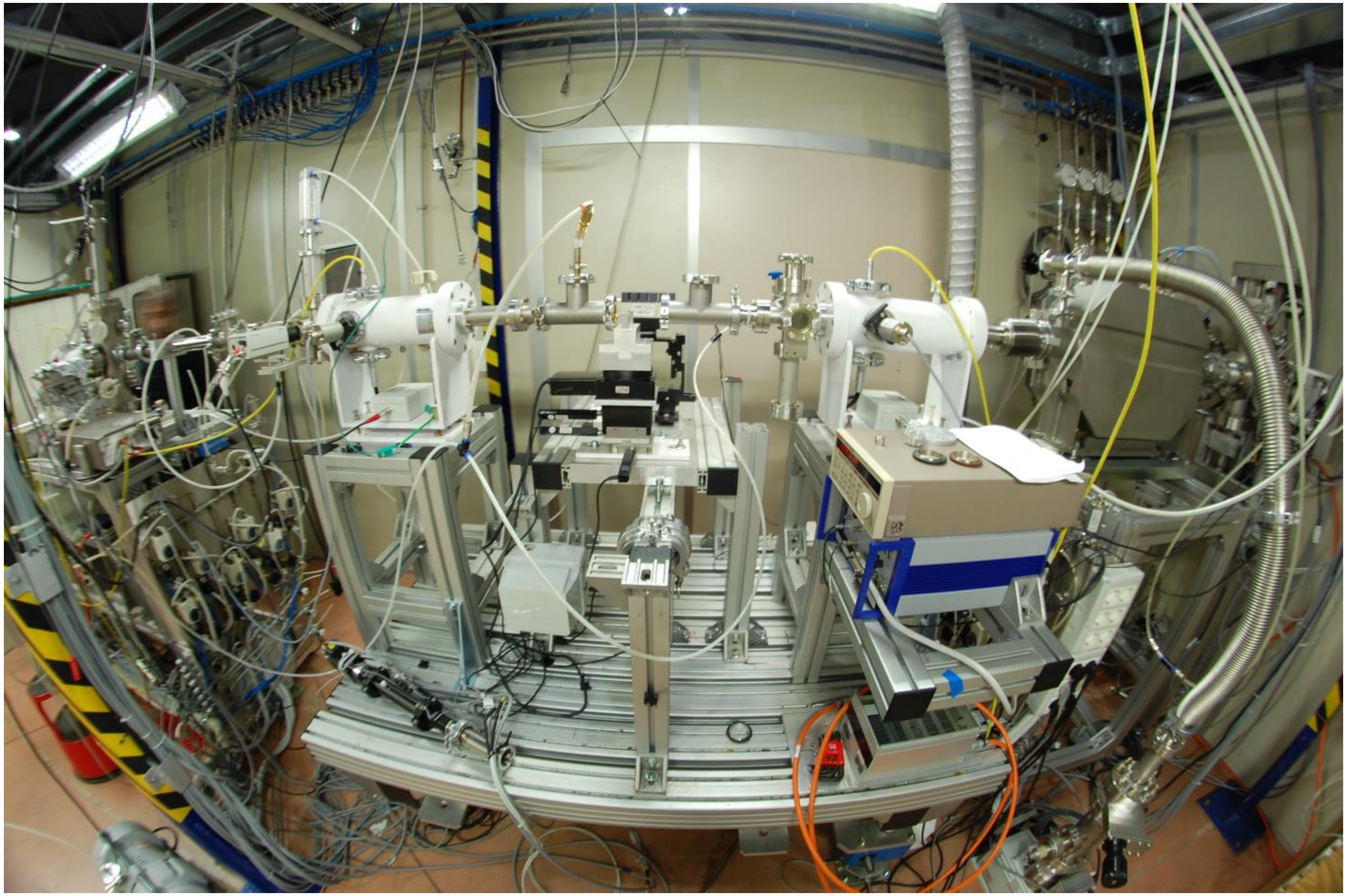
| | |
|---|---|
| Source | Bending magnet |
| Flux | $10^9$ - $10^{11}$ |
| Resolution ΔE/E | $10^{-4}$ (Si 111), $5x10^{-5}$ (Si 311) |
| Spot size | max 26 x 2 (H x V) $mm^2$ |
| Energy range | 2.4 - 27 keV |



- Double flat crystal double cam Kohzu apparatus
- Operating angular range 5 – 75 degrees
- Two pairs of crystals: Si 111 (2.4 <E < 22 keV) and Si 311 (4 < E 27 keV)
- Harmonic rejection for E < 9 keV provided by detuning the second crystal




- Cylindrical mirror
- Vertical collimation -> Parallel 2 mm height beam upstream the monochromator
- fixed grazing angle (3 mrad)
- Pt coated (cutoff : 27 keV) (no interference with Pt $L_3$ data)
- Optically active dimensions (1000 x 60 $mm^2$)



Experiments can be performed in transmission or fluorescence mode, in vacuum or in air, at low or high temperature (10 to 2000 K).

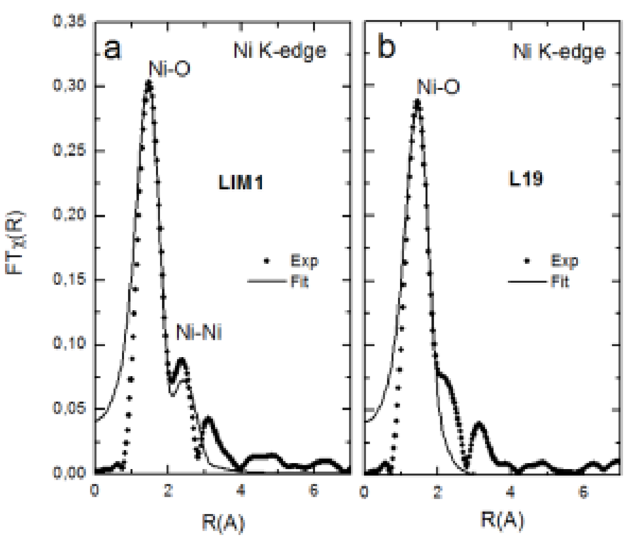
## *A comparative study of Hispano-Moorish and Italian Renaissance lustred majolicas by using X-ray absorption spectroscopy (XAS) (G. Padeletti et al,* **J. Anal. At. Spectrom., 2015, 30, 738-744***)*

*Lustre technique was developed in Iraq and spread to Egypt, Persia and finally to Spain; from there, lustre was introduced in Central Italy where it was used to decorate the most beautiful majolicas.*

*It has to be pointed out that the Italian artisans developed their own style, hence the blue pigment and lustred regions of lustred majolica shards from Hispano-Moorish (LIM1) and Italian (L19) productions were compared…*

XAS measurement at the Cobalt, Nickel and Copper K-edge...

**Differences were found at the blue pigment**




Cobalt: poor crystallinity of the Co environment. Main contribution of $Co^{2+}$ ions at tetrahedral sites, however a contribution of octahedric $Co^{2+}$ is found in Hispano-Moorish production

Nickel: is present as NiO, and Italian majolicas present higher cristallinity for the Ni enviroment (up to the second coordination shell; Ni-O-Ni)

Copper: similar spectra, and indicate that Cu is close to $Cu^{2+}$ , even though edge modifications suggest a started reduction of the Cu ions

# *A comparative study of Hispano-Moorish and Italian Renaissance lustred majolicas by using X-ray absorption spectroscopy (XAS)* *(G. Padeletti et al,* ***J. Anal. At. Spectrom., 2015,30, 738-744****)*

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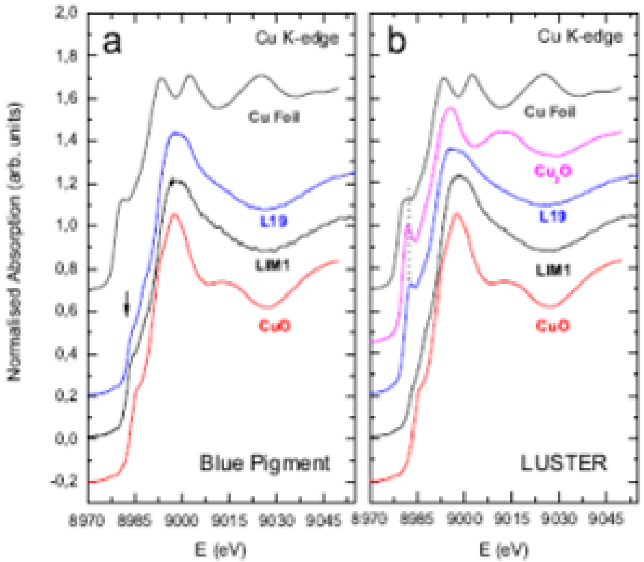



**Significant differences were found at the lustre!**

Copper XANES spectra are compared: L19 has a behaviour matching $Cu_2O$. The behavior of LIM1 matches CuO, indicating, for this sample a lower reduction degree

***In this case, an interpretation could be made considering the use of different technological procedures generating different efficiency in the reducing phase and consequently copper ions in different oxidation states***

## SISSI: Synchrotron Infrared Source for Spectroscopy and Imaging

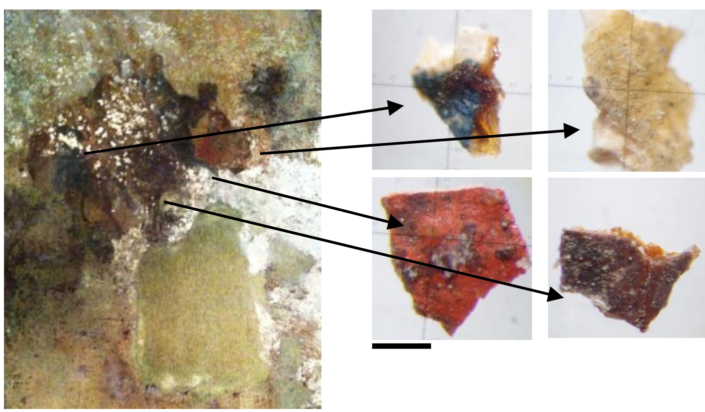
**1st Branch** - Solid State
Optimized for spectroscopy from Far to Near Infrared

**2nd Branch -** Life Sciences
Optimized for FTIR Microscopy and Imaging in the Mid Infrared


Vertex 70 in vacuum Interferometer
Hyperion 1000 Vis-IR microscope
Cryostat
Near, MIR, FIR detectors

Vertex 70 $N_2$ purged Interferometer
Hyperion 3000 Vis-IR microscope
Bidimensional FPA imaging detector and single point MCT detector

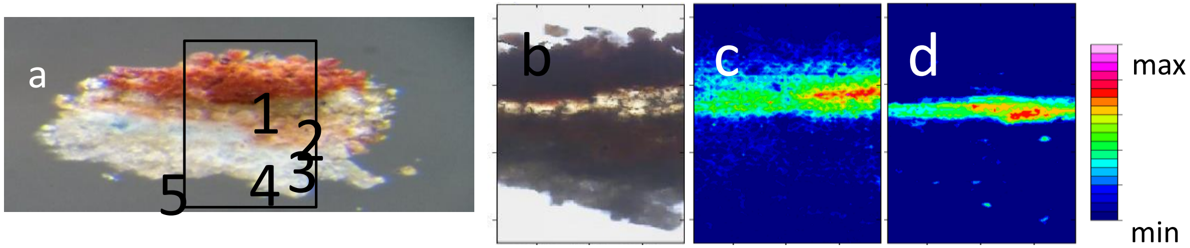
**SISSI:** **Synchrotron Infrared Source for Spectroscopy and Imaging**

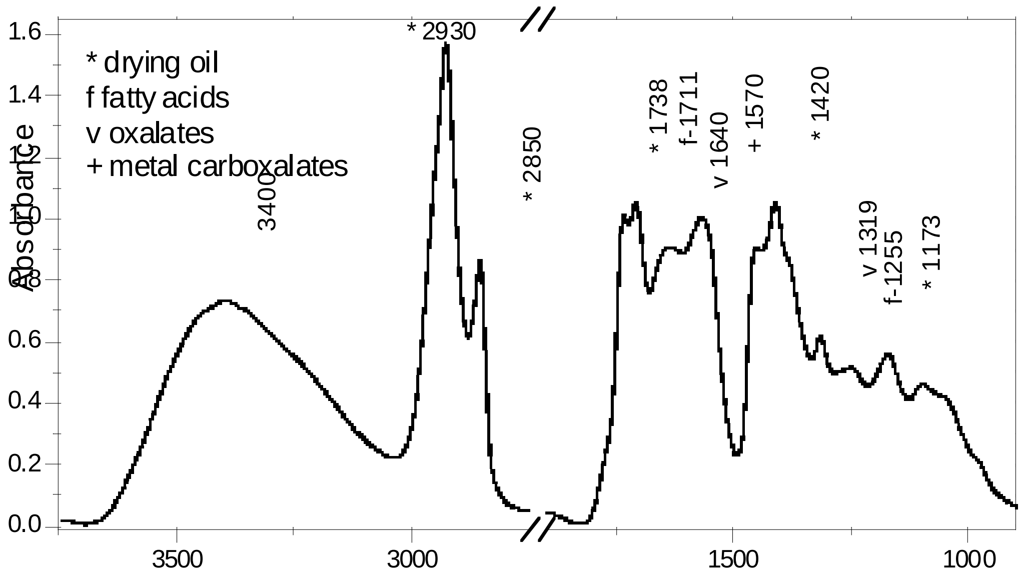


- Identification of the materials
- Understanding of the painting technique
- Study of the alteration mechanisms

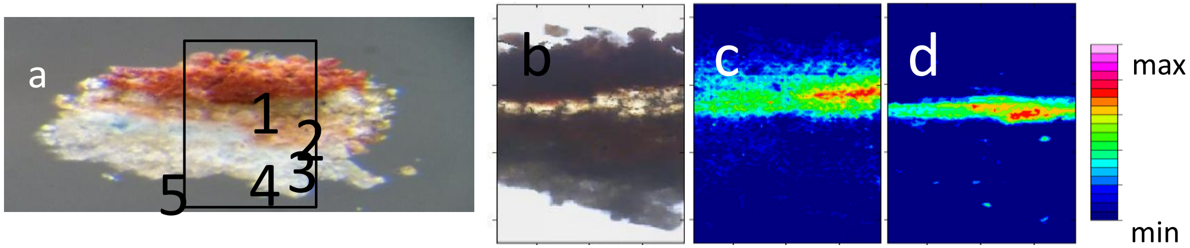
Z.E. Papliaka et al., Anal. Bioanal. Chem. 407 (2015), 5393

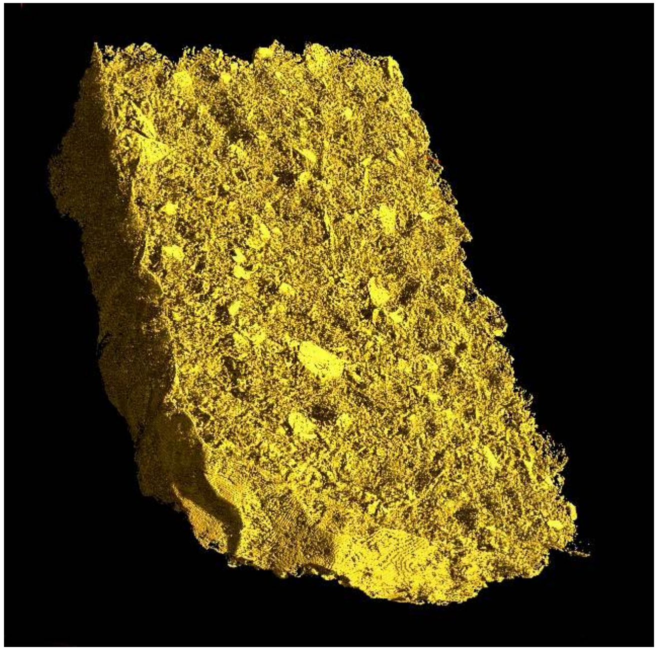
# **SISSI:** Synchrotron Infrared Source for Spectroscopy and Imaging



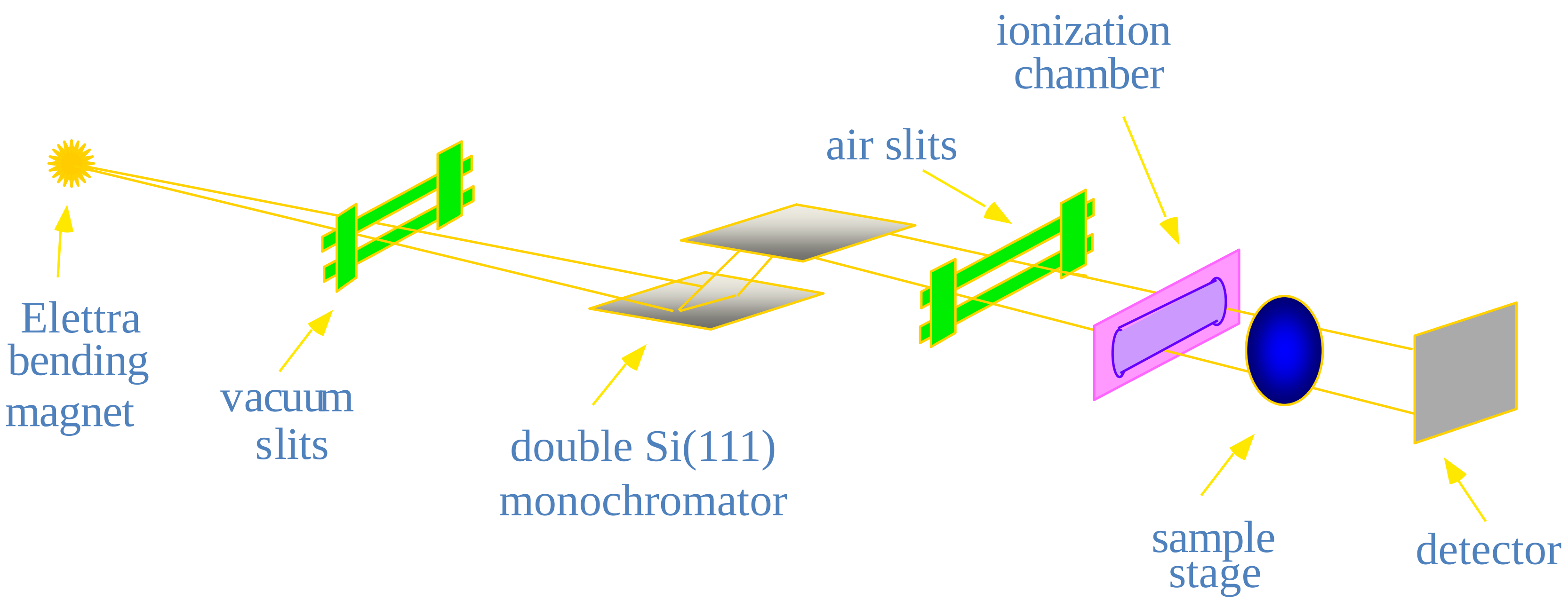



**<u>SISSI:</u> Synchrotron Infrared Source for Spectroscopy and Imaging**



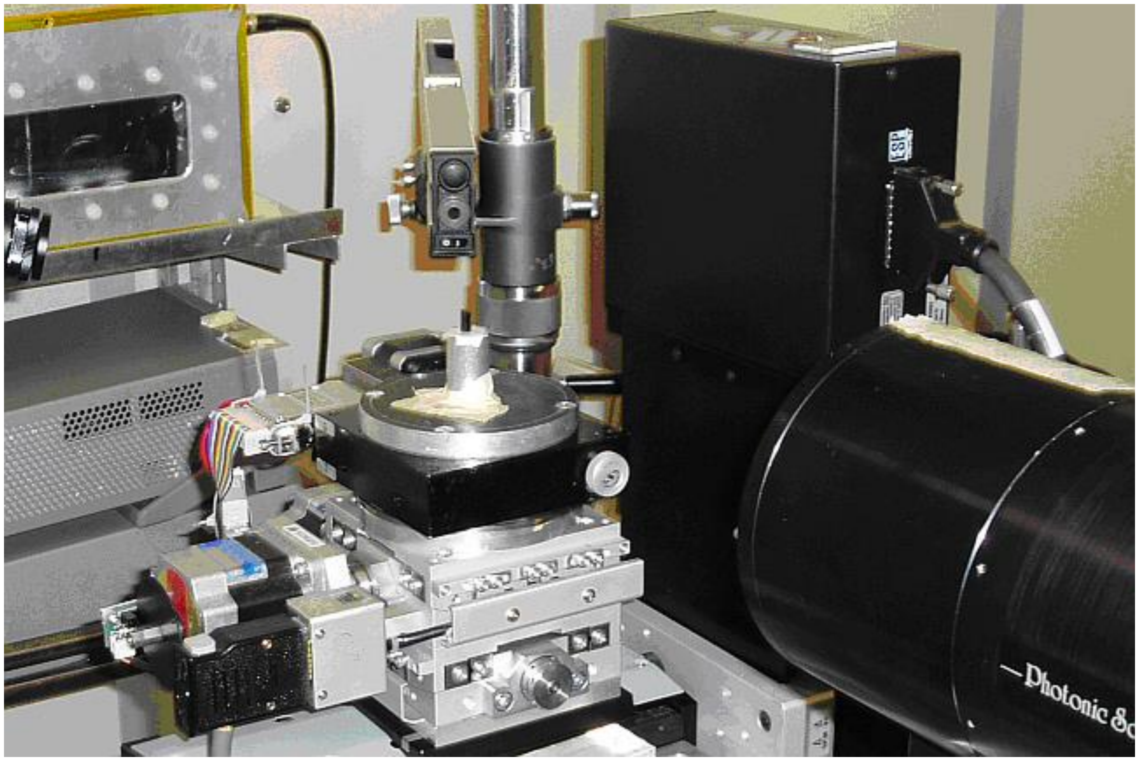



**SYRMEP:** **SYnchrotron Radiation for MEdical Physics**




- Energy range: **8.3 ÷ 35 keV**, Bandwidth **ΔE/E ≅ 2x10$^{-3}$**
- Beam size at sample (h x v) ≅ **150 mm x 4-6 mm**
- Source size (FWHM) s (h x v) ≅ **230 μm x 80 μm**
- Typical fluxes @15 keV ≅ 7 * 10$^{8}$ phot./mm$^{2}$ s (@ 2.4 GeV, 180 mA)
- Source-to-sample distance: **D ≅ 23 m**

**<u>SYRMEP:</u> SYnchrotron Radiation for MEdical Physics**



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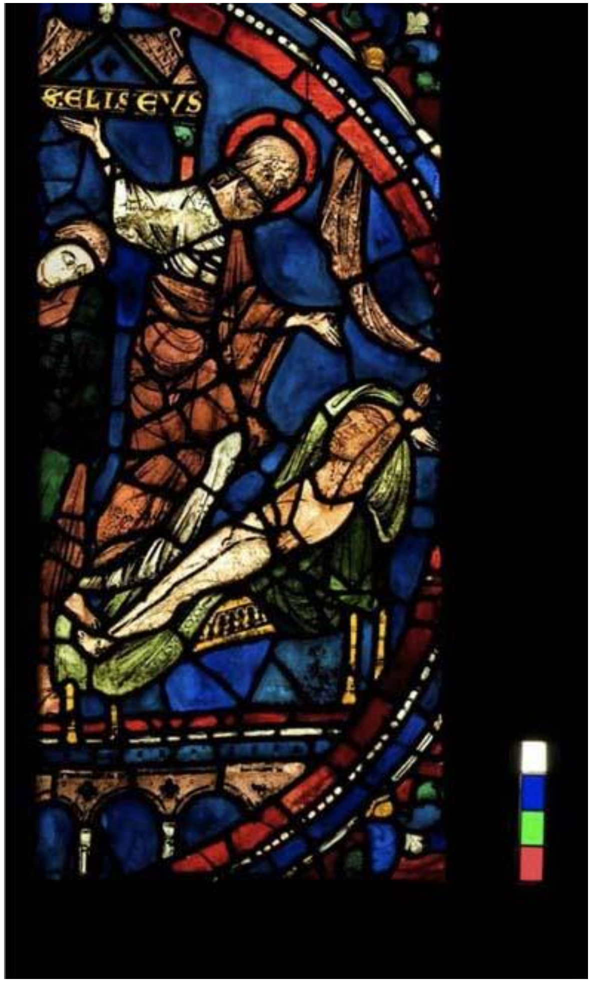
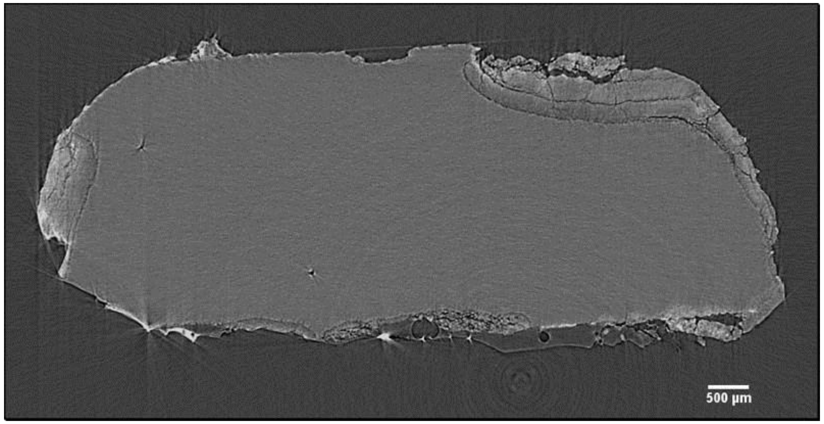
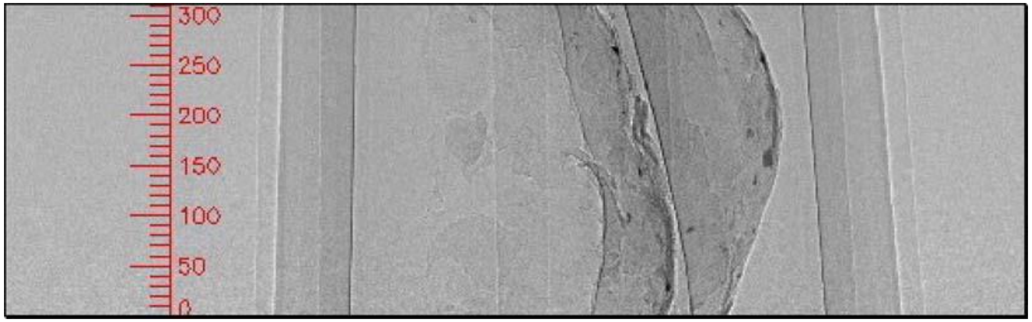


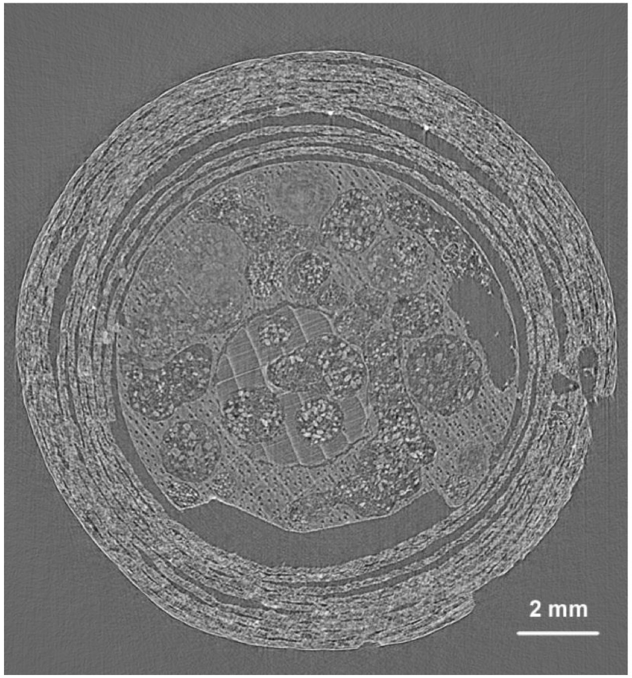

**Chartres Cathedral**
**Window 37**
**La Passion typologique**

H. Römich et al., NTJ 13 (2008) 30



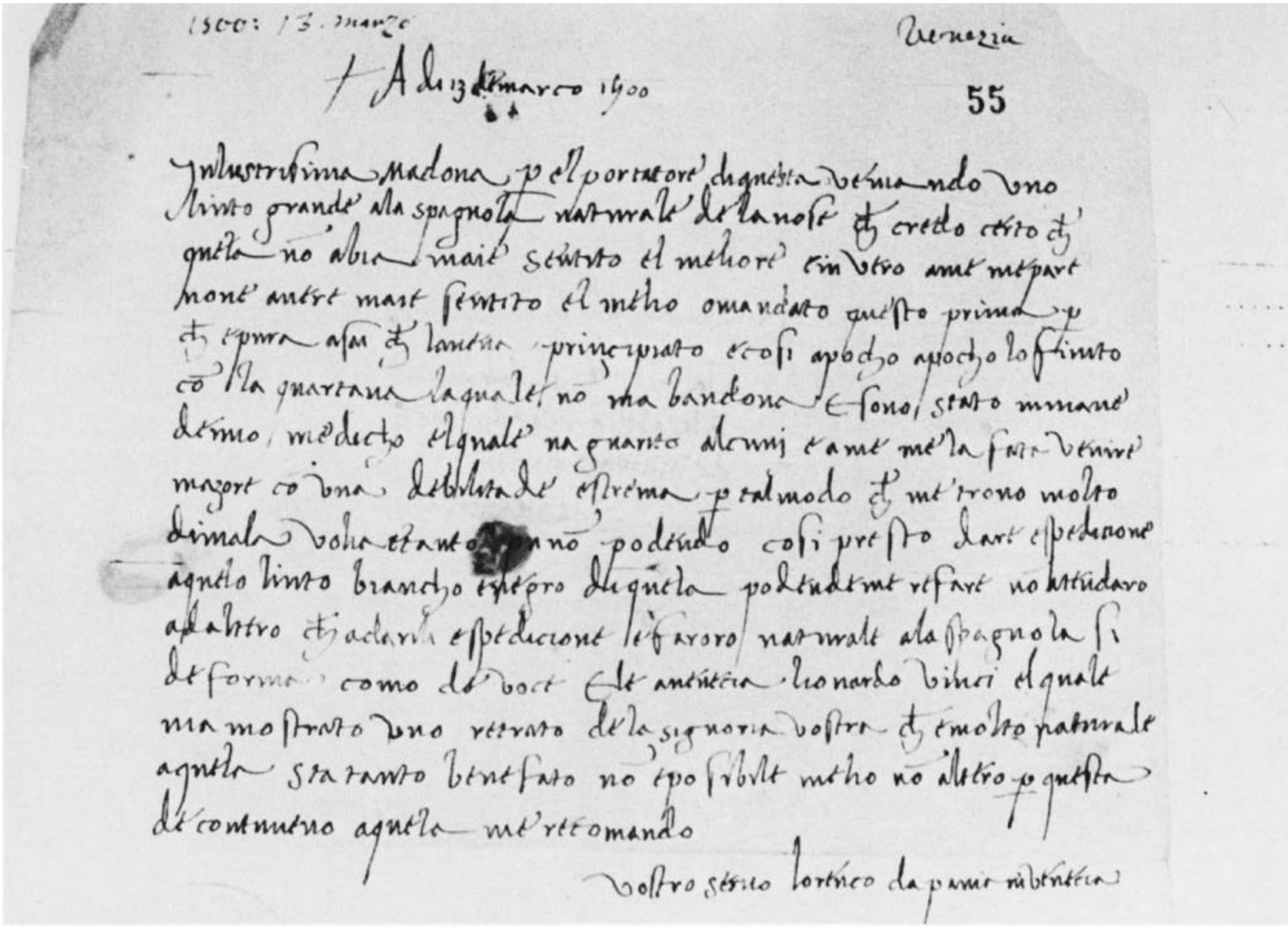

Viacryl flakes from Bourges
(window 9, panel 4)

**SYRMEP:** **SYnchrotron Radiation for MEdical Physics**




**Paper-pipes organ, Lorenzo Guscasco da Pavia (1494)**

B. Bentivoglio-Ravasio et al., J. Ent. Acarol. Res. 43 (2011) 149


1500: 13. marzo
Venezia
+ Adi 13 de marzo 1500
55

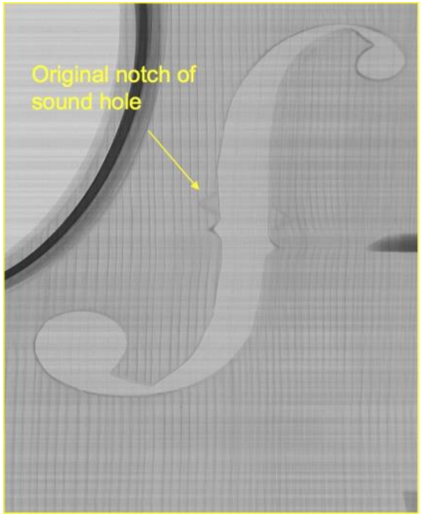
Jllustrissima Madona p el portatore de questa ve mando uno
liuto grande ala spagnola naturale dela nose et credo certo che
questo no abia mai sentito el meliore cum vetro ami me pare
non e mai sentito el meio o mandato questo prima p
che epura asai che lavevo principiato e cosi apocho apocho lo finito
co la quartana laquale no ma bandona e sono stato in mane
de mo medecho elquale ma guarito alcuni e ame me la fa venire
mazore co una debilitade estrema p tal modo che me trovo molto
di mala voia e tanto piu no podendo cosi presto dare espedicione
aquello liuto biancho e p ro de quela podendo me refare no atendaro
ad altro che a darli espedicione le faroro naturale ala spagnola si
de forma como de voce. E le a Venetia Lionardo Vinci el quale
ma mostrato uno retrato dela signoria vostra che e molto naturale
aquella sta tanto bene fato no e posibile meio no altro p questa
de continuo aquella me recomando

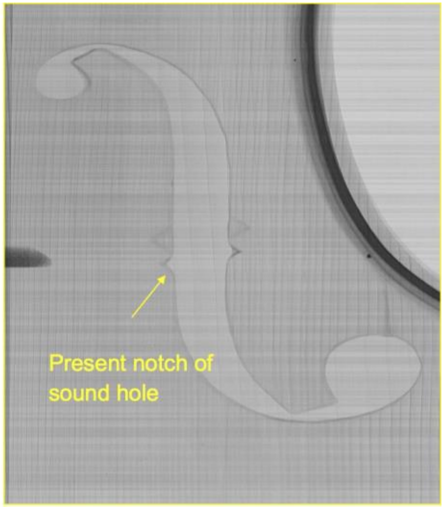
Vostro servo Lorenzo da pavia in Venetia

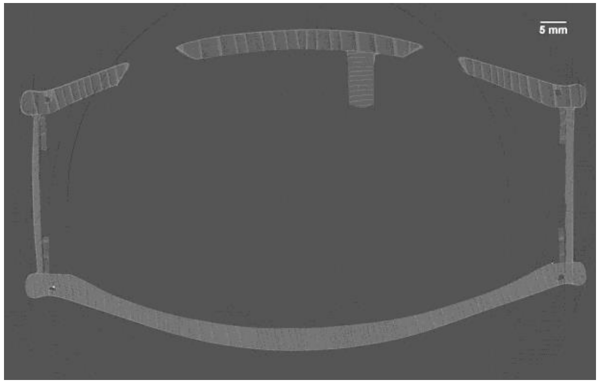
**Correspondence between Lorenzo Gusnasco and Isabella d'Este**

# **SYRMEP:** SYnchrotron Radiation for MEdical Physics

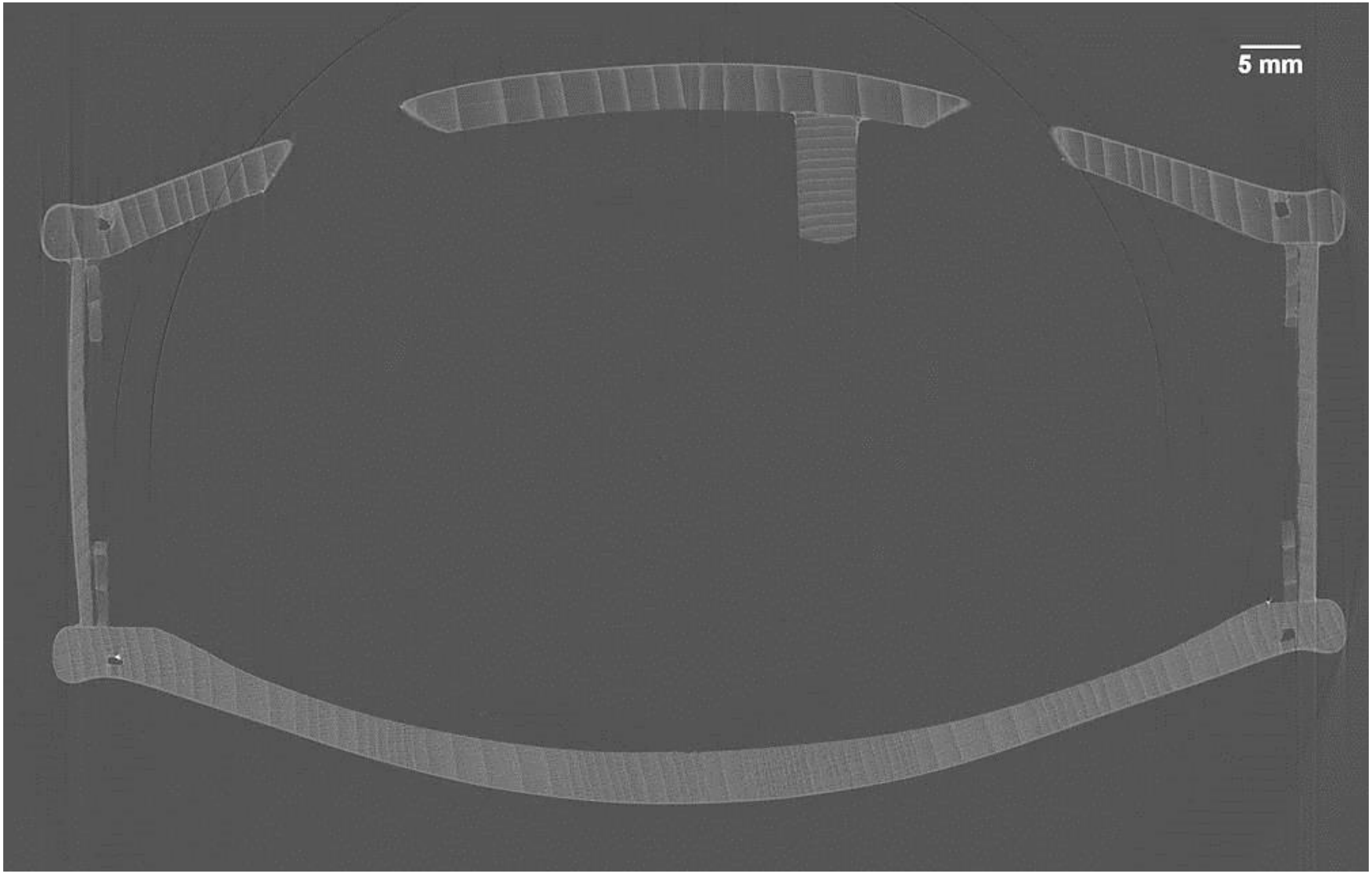
F. Zanini, Strad 123 (2012) 36

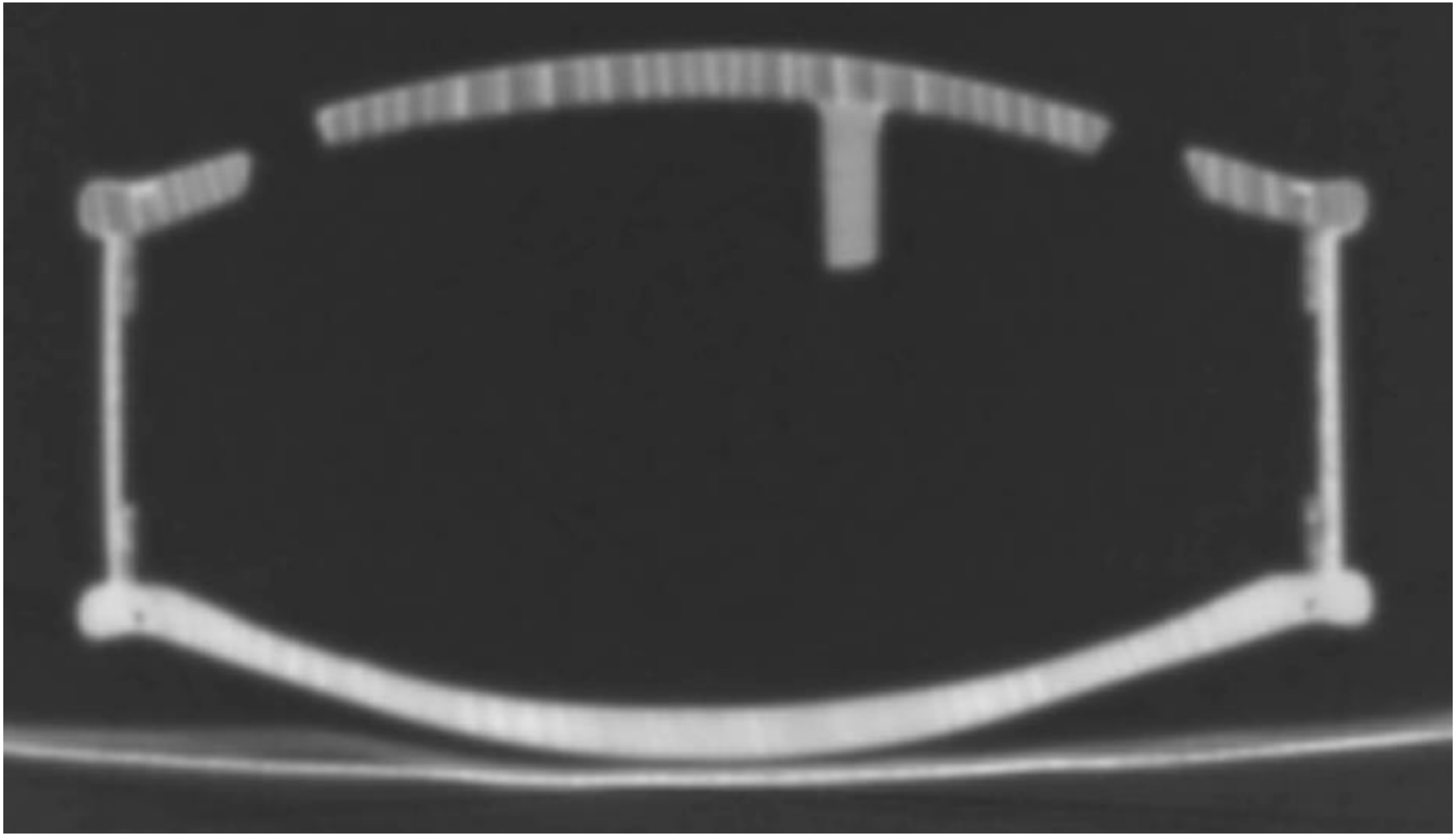


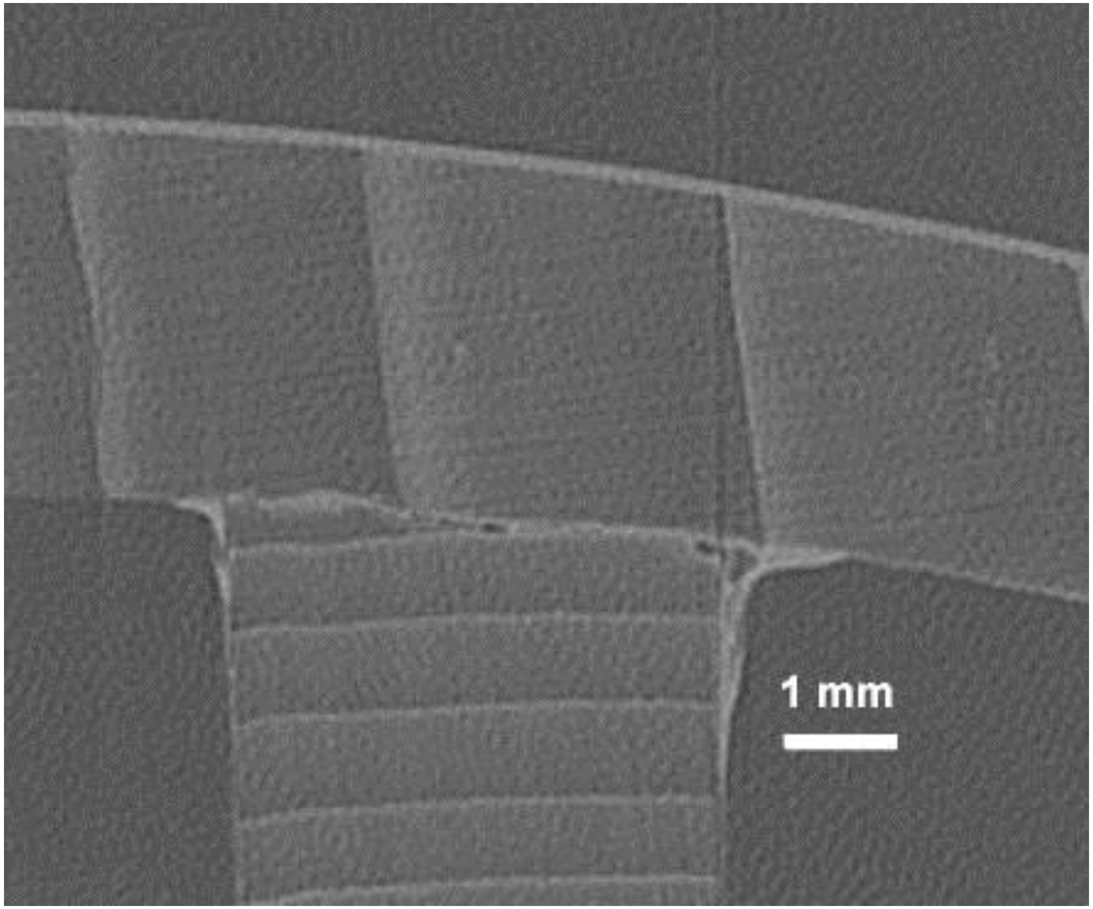




**G. B. Guadagnini
Herrestal Violin
Milano 1753**


5 mm

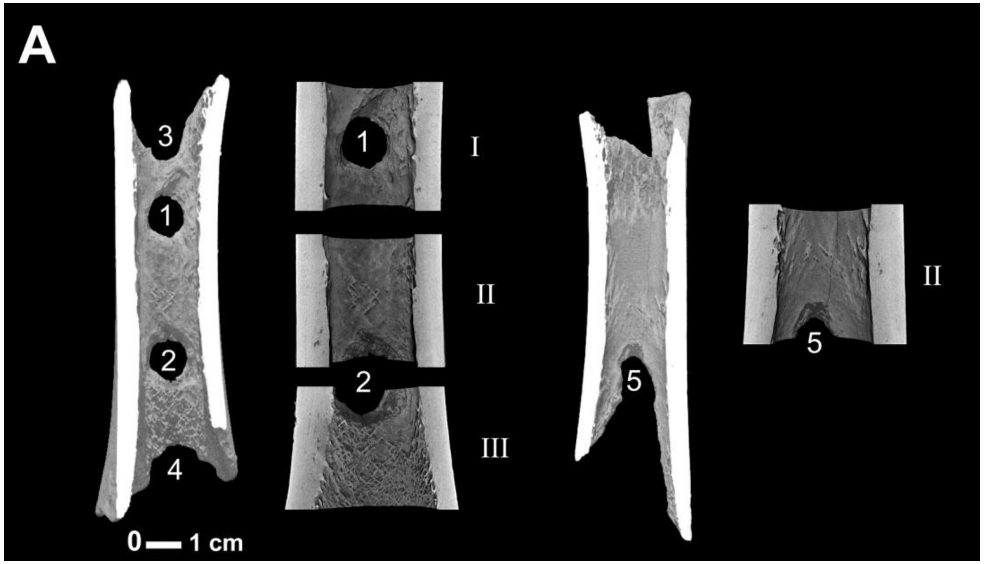





Detail showing the bass bar and the glue used to attach it to the front plate.

## **SYRMEP:** SYnchrotron Radiation for MEdical Physics

The Divje babe *flute*
Mousterian, about 50000 years old, Slovenia




C. Tuniz et al., Archaeometry 54 (2012) 581

## **SYRMEP:** SYnchrotron Radiation for MEdical Physics

The Lonche *mandible*

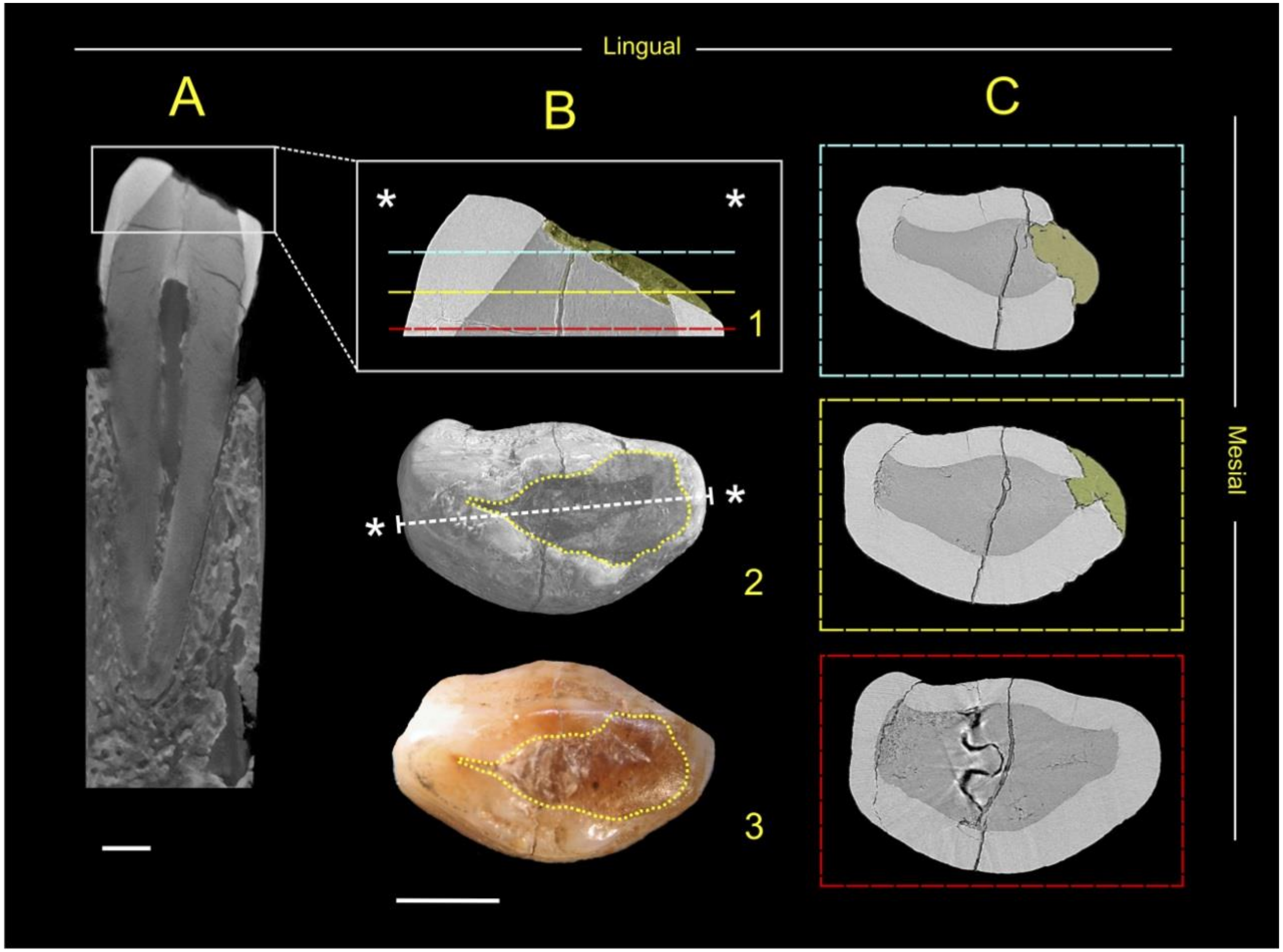
*Upper Pleistocene, about 6500 years old, Slovenia*

*Left canine shows presence of beeswax Inside a vertical crack*

*Earliest known evidence of therapeutic dental filling*

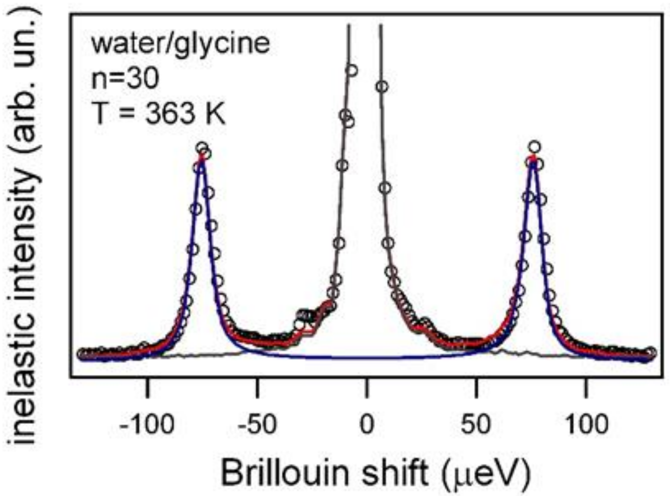
F. Bernardini et al., PLoS ONE 7 (2012)

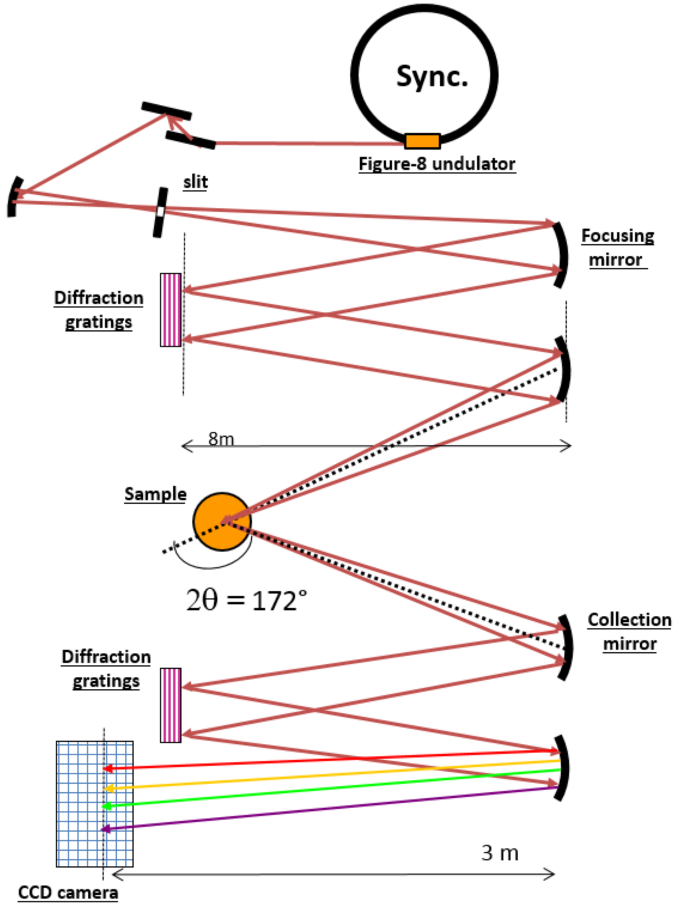
## SYRMEP: SYnchrotron Radiation for MEdical Physics



## IUVS: Inelastic UltraViolet Scattering

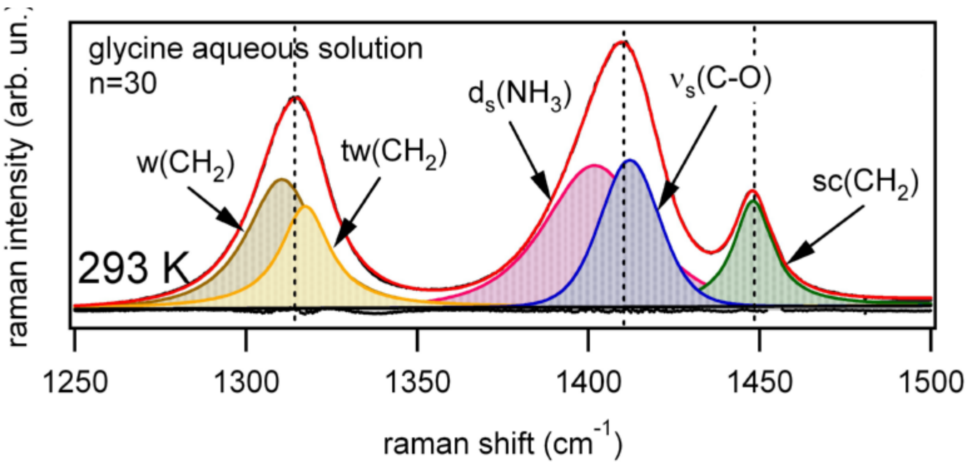
# Brillouin set-up

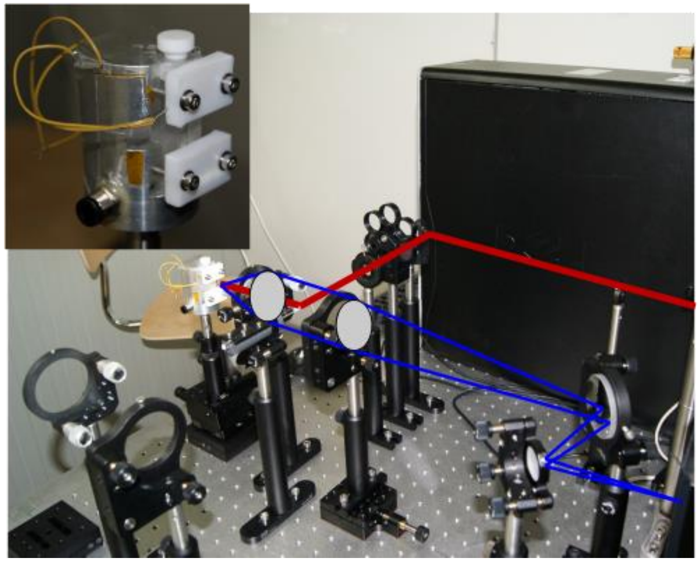


**IUVS:** **Inelastic UltraViolet Scattering**

# Raman set-up



# IUVS: Inelastic UltraViolet Scattering

**Main features of the Brillouin set-up:**

a) Beam @ sample:
→ $E_i = 4 \div 12$ eV
→ $10^{10} \div 10^{13}$ ph/s
→ 1x0.5 $mm^2$ spot

**b) DE ≈ 7÷20 meV**
**c) $E_o$-$E_i$ ≈ ± 1000 meV**
**d) S(Q,E) in one shot**
**e) "Easy" Q-change**

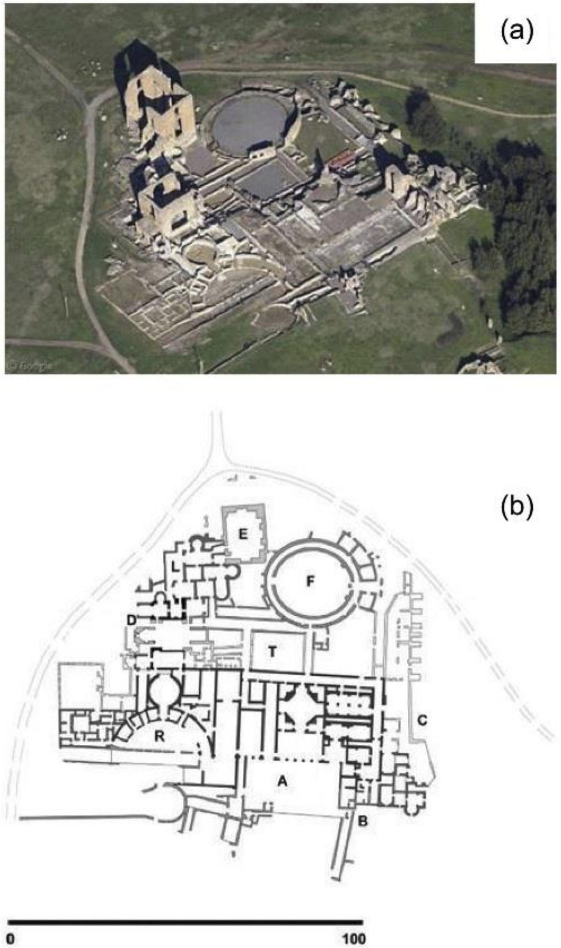
**Main features of the Raman set-up:**

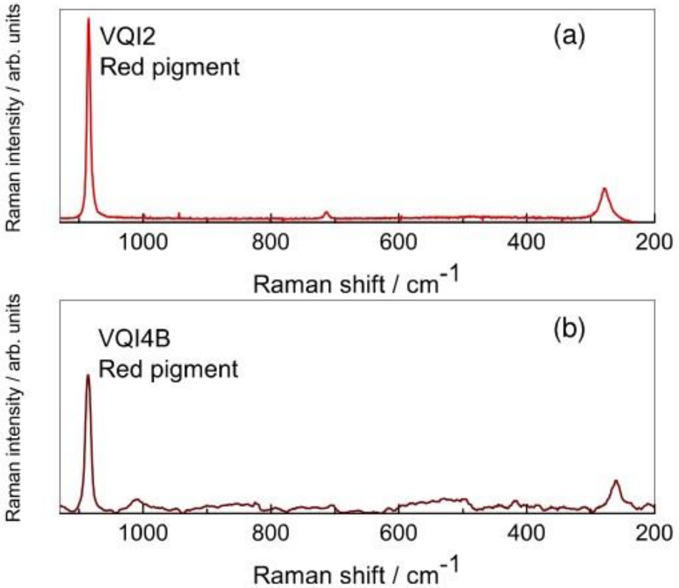
a) Beam @ sample:
→ $E_i = 4.6 \div 6.2$ eV (200 - 270 nm)
→ 10 μW (@ 270 nm)
→ 100 μm diameter spot

**b) Experimental resolution**
**1 $cm^{-1}$ @ 270 nm**

**Upgrade in progress:**
**Extention of the UV range below 200 nm**

## IUVS: Inelastic UltraViolet Scattering




UV-Raman scattering for the characterization of bulk minerals and pigments at *Villa dei Quintili*

V. Crupi et al., Vibrational Spectroscopy 83 (2016) 78

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