Elettra Sincrotrone Trieste

# Portable XRF-XRD for characterization of valuable objects

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# X-ray fluorescence

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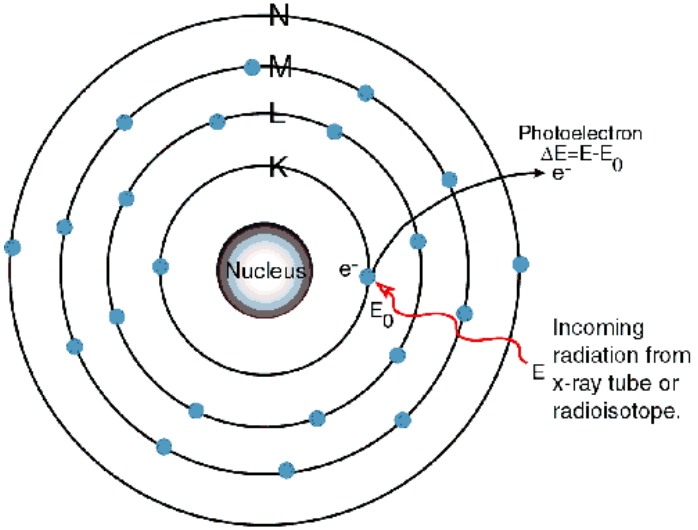


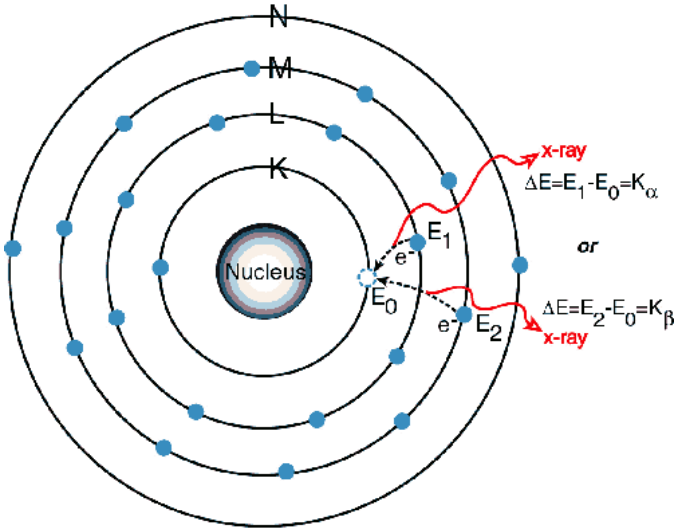


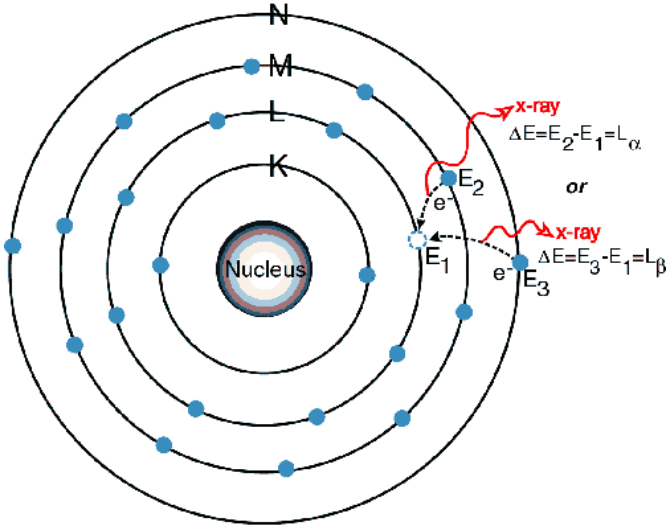


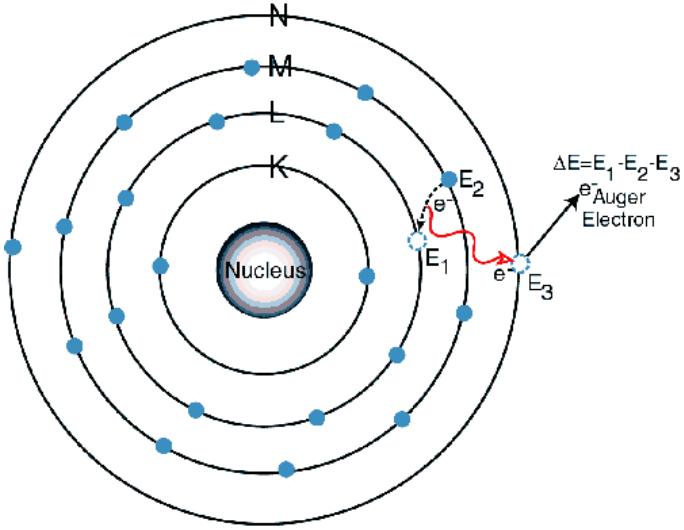

# De-excitation

There are two mechanism of de-excitation following the absorption of the incident X-ray photon:

- X-ray Fluorescece - XRF:
- An electron from a more external orbital is going to fill the vacancy, causing the emission of an X-ray photon with a caracteritic energy.

- Auger effect:
- An electron from a more external orbital is going to fill the vacancy, and a second electron is emitted.

In the hard x-ray regime (> 2 keV), the emission of an XRF photon is the most probable phenomenon, compared to Auger emission, whereas at low energies the is the dominant one

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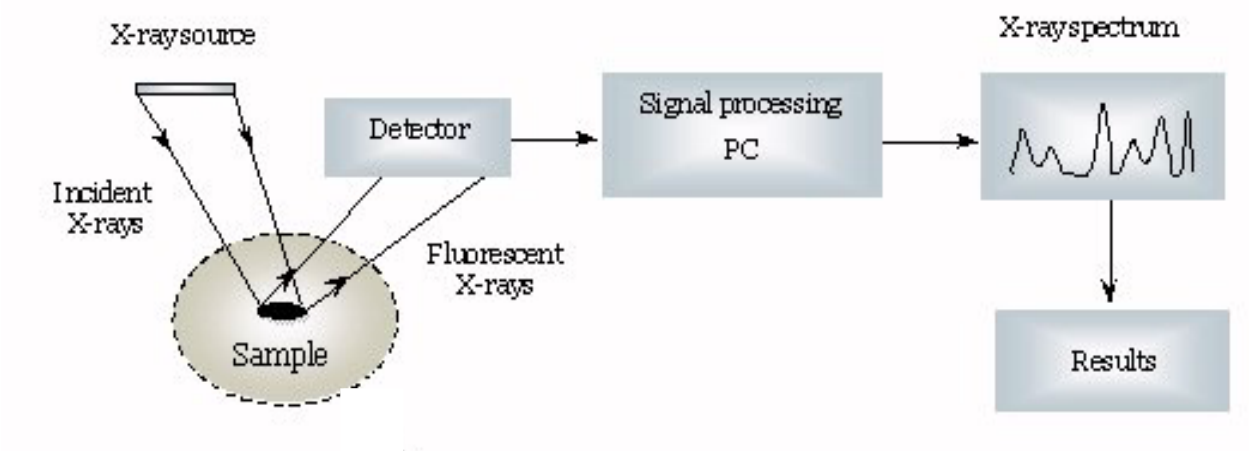
# XRF system




- Source: X-rays (X-ray tube, Radioactive source, sinchrtron light…)
- Detector: solid state (Ge, Si), phootomultiplier
- Signal processing: preamplifier + filter shaping + multichannel analyser
- PC + analysis software (qualitative and quantitative)

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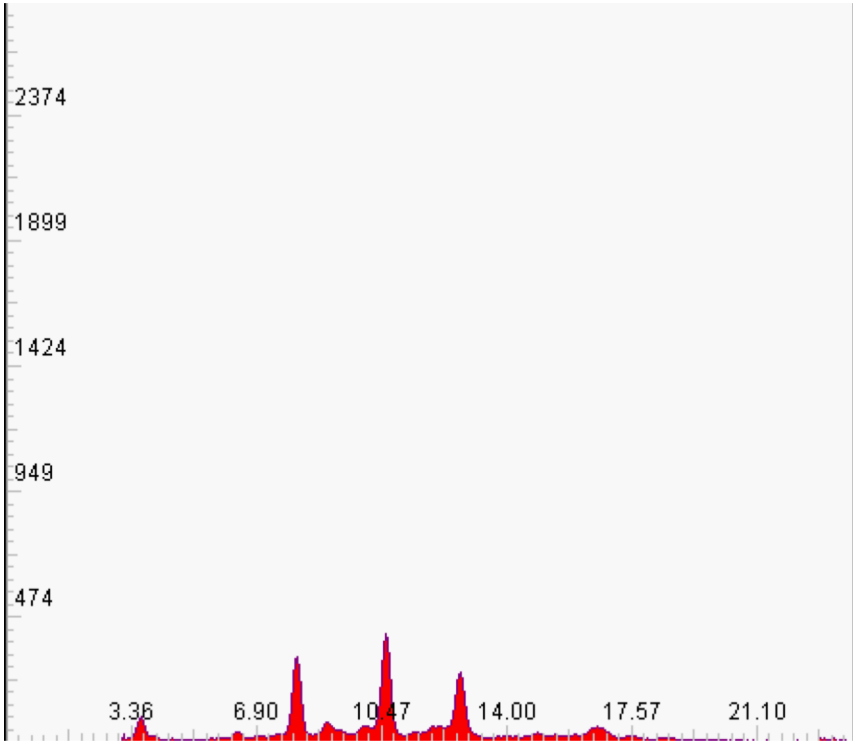
# Spettro XRF




- Histogram where the counts are represented versus the energy
- Calibration in energy performed with a known sample: the chemical elements present in the specimen are known
- Identification of the chemical elements present by using database where the emission energies for each chemical elements are tabulated

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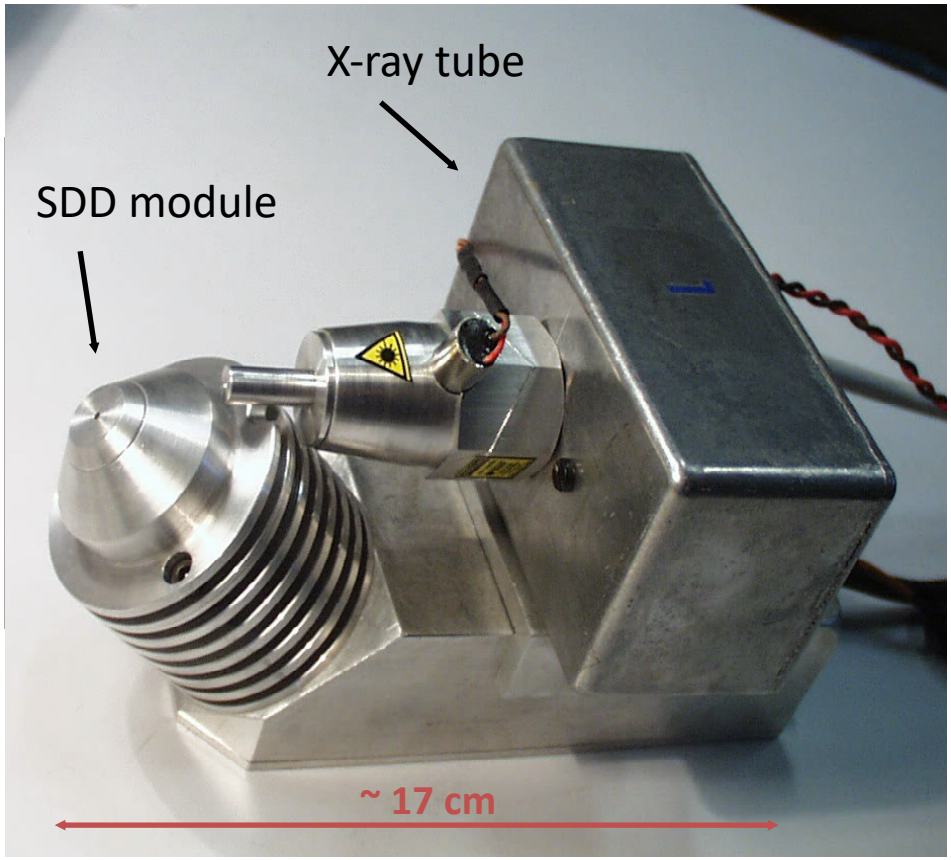
# Portable XRF spectrometer

Politecnico di Milano




- X-ray tube:

  OXFORD TF302
  (30kV,0.1mA,W anode)
- X-ray spot: 2mm
- Laser pointer aligned with the X-ray beam
- SDD:

  active area= 5mm$^2$

  thickness=280 μm
  Be window, 7.5 μm
  single Peltier stage

  FWHM=150eV @5,9 keV
  @T=-10°C
- Electronics board for automatic biasing

  Preamplifier

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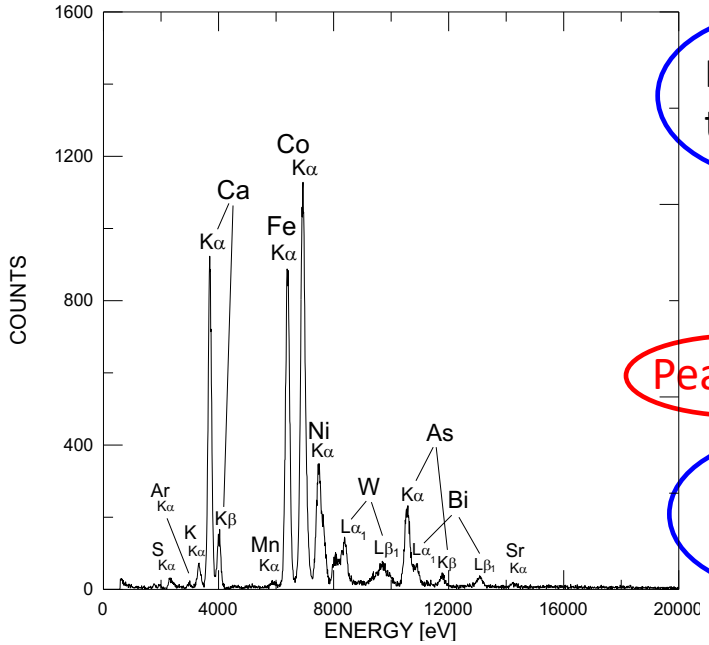
# XRF analyses

## Qualitative Analysis

Determination of the chemical element present in the sample (10-300 sec)

Univocally determined by the energy




## Quantitative Analysis

Measurement on a fresco painting of Lorenzo Lotto (XVI century) in Bergamo.

Fluorescence spectrum of a blu point of the blanket.

The identification of K, Fe and Co allows to determine the use of a "smalto veneto"

Determination of the chemical elemental composition of the sample (1-15 min)

Detector

Source

Inten
the s

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Peak ar

Geor
para
s

$$\left.\frac{(E_i)}{\vartheta_f}\right]h$$

$$\frac{E_i)}{\vartheta_f}$$

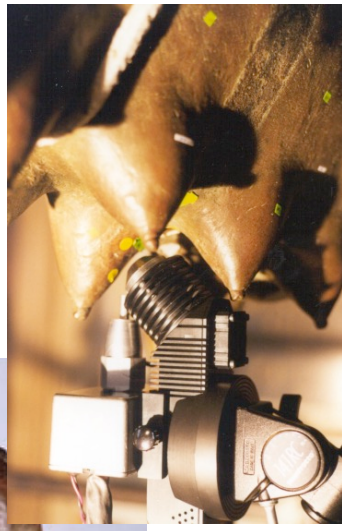
$$\mu^M(E_o) = \sum_{k=1}^{N} c_k \mu_k(E_o)$$

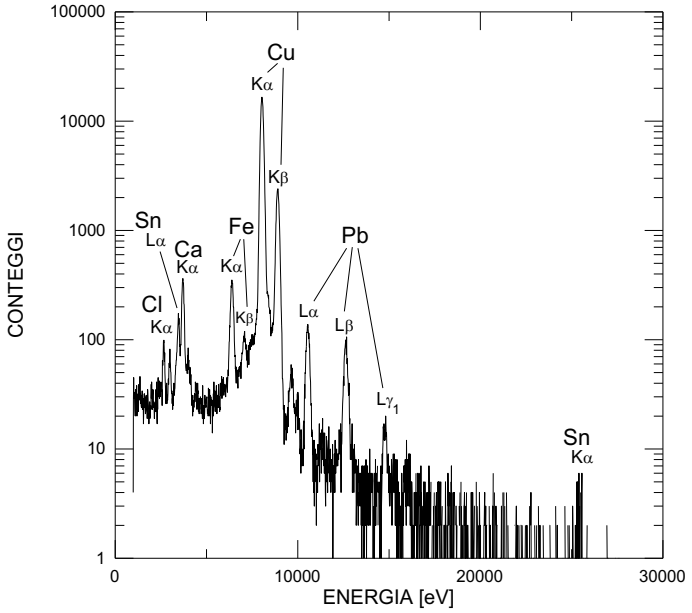
# Examples of XRF applications

## Non destructive XRF analyses on works of art

### Analyses on bronze statues at the Musei Capitolini in Rome

- The mobility and the portability of the instrument allows the analysis of small inaccessible parts of the sample
- Measurements directly at archaeological sites






**Lupa Capitolina**

C. Fiorini, A. Gianoncelli, A. Longoni, "A new portable spectrometer based on Silicon Drift Detector for non-destructive analyses on the cultural heritage", proceeding of the Workshop Nazionale "Microelettronica e beni culturali", Firenze, 19 marzo 2001, pp. 74-83, 2002

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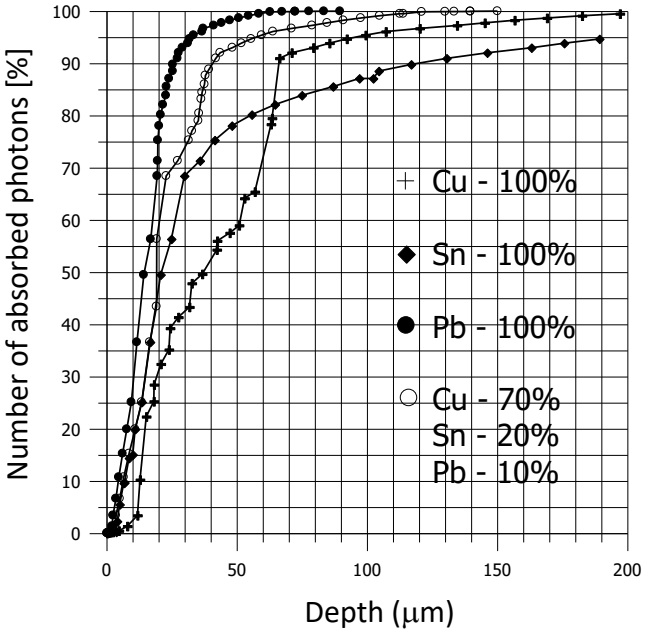
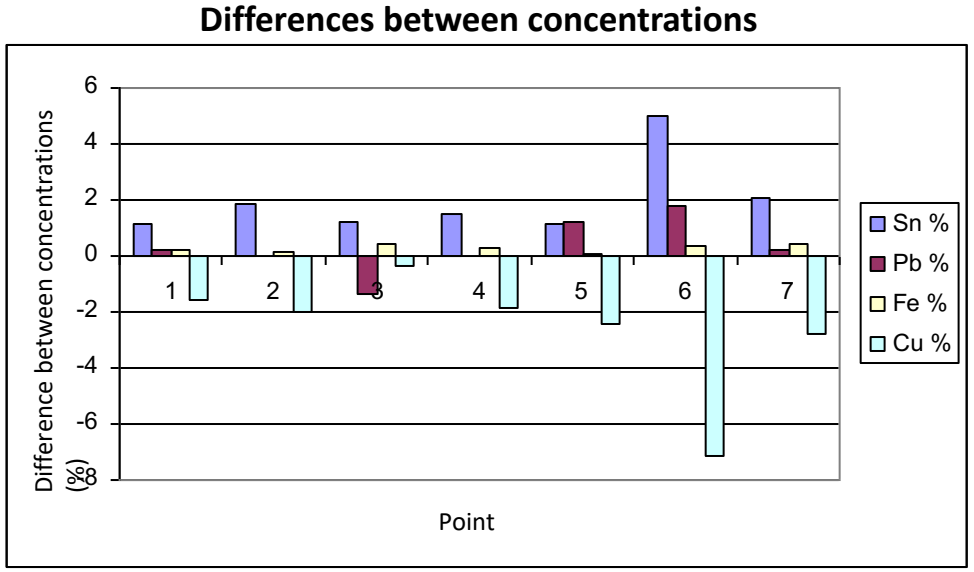
# Superficial Patina




- The X-ray beam penetration depth is about 35-40 μm in the above bronze alloy

- On average the chemical concentration of Fe and Sn is bigger in the region covered by patina

- In principle it is possible to calculate some correction factors to evaluate the chemical composition of the alloy without patina

A. Longoni, A. Gianoncelli, C. Fiorini“ ‚Uno spettrometro XRF portatile di elevate prestazioni per analisi non distruttive di opere d'arte ‚” *Alta Frequenza*, Vol. 13, N°2, 2001

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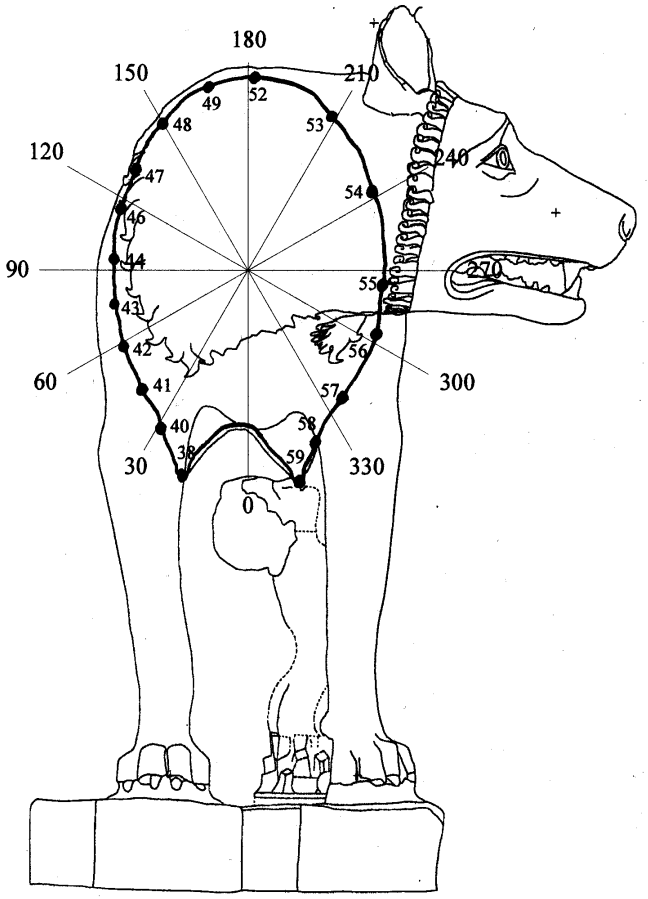
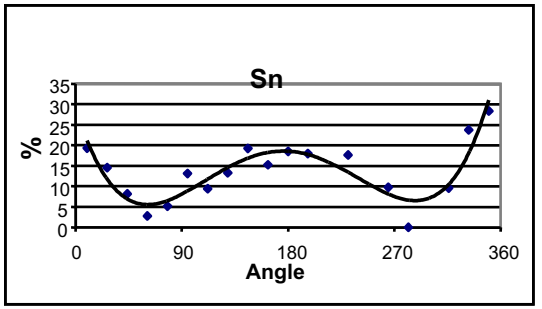
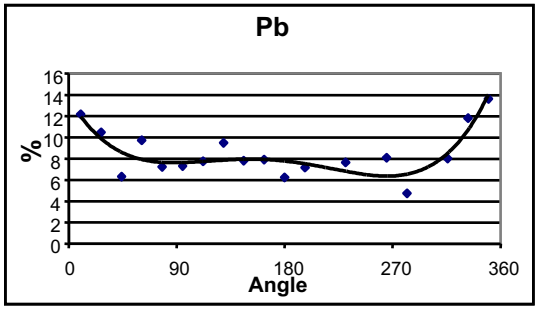
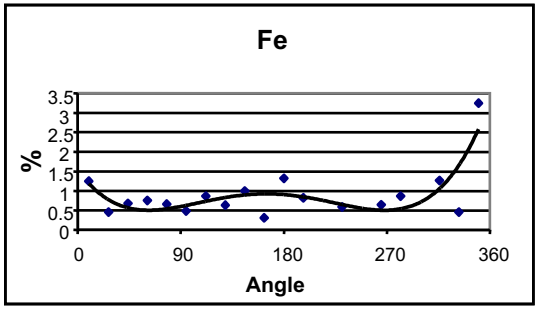
# Distribution of the chemical elements

Analisys of the circumference of the statue: ~ 5cm separation between points

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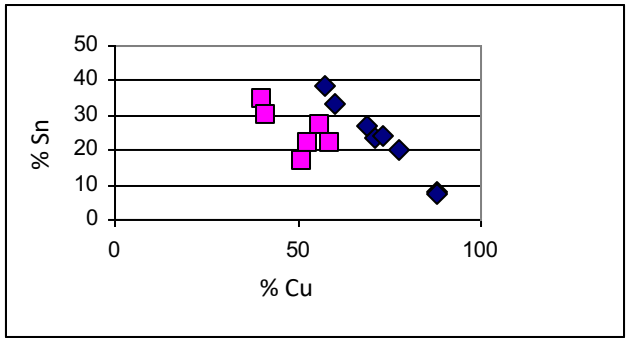
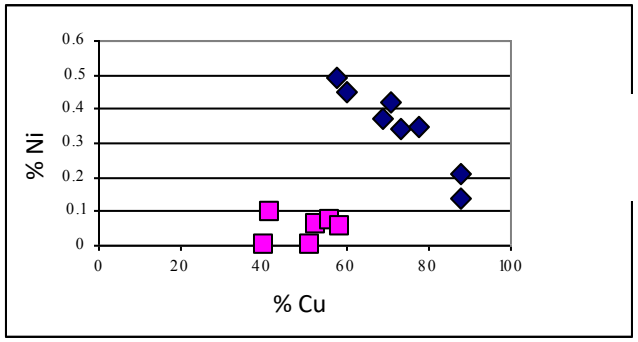
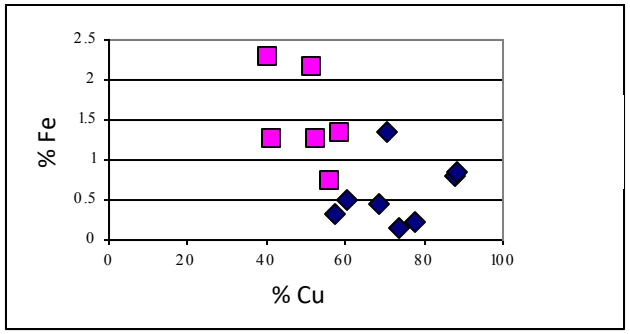
# Quantitative analysis on a bronze st

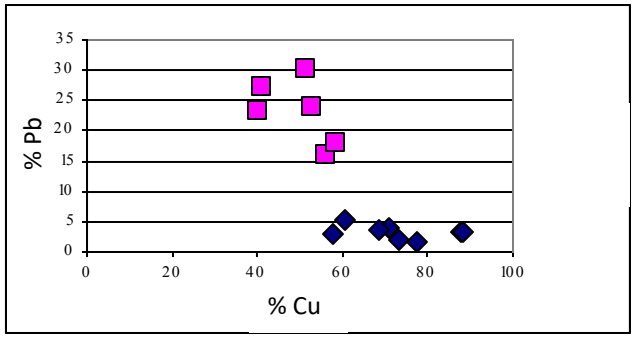


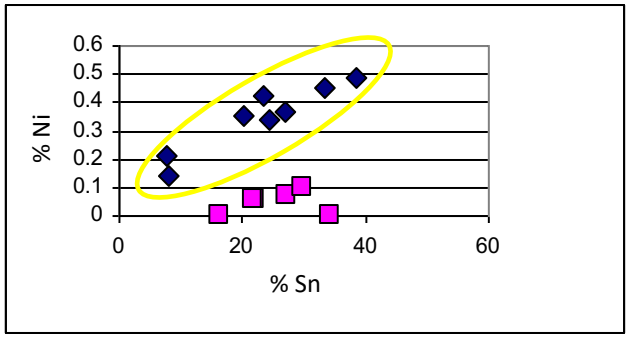




= body

= head




- Correlog e
head and
-The grap s have
been real erial
(maybe in
- From th e head
Ni is prob

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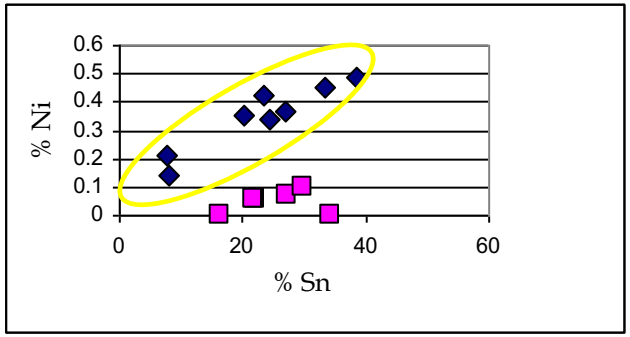
# Quantitative analysis of a bronze statue

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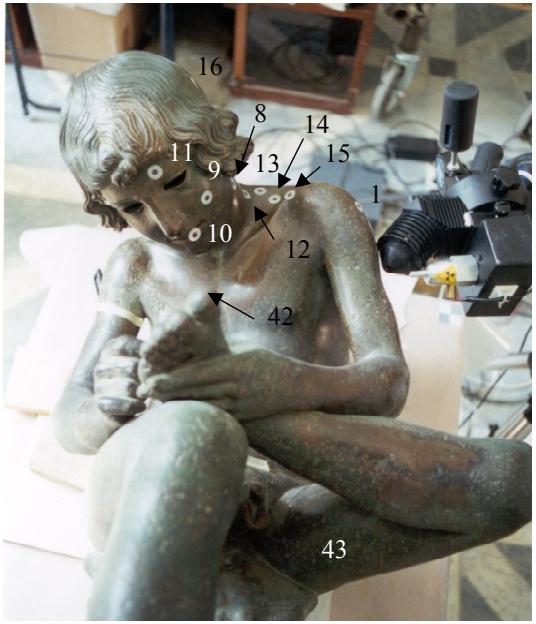


- Head: Ni is probably an impurity linked to Sn

| Sn | Fe | Pb | Zn | Ni | Cu |
|---|---|---|---|---|---|
| 23,2 | 0,6 | 3,5 | 0 | 0,3 | 72,4 |

**Head**

| Sn | Fe | Pb | Zn | Ni | Cu |
|---|---|---|---|---|---|
| 25,3 | 1,5 | 22,9 | 0 | 0 | 50,3 |

**Body covered by green patina**

| Sn | Fe | Pb | Zn | Ni | Cu |
|---|---|---|---|---|---|
| 15,07 | 0,58 | 12,09 | 1,32 | 0,16 | 70,89 |

**Apparently repaired zones**

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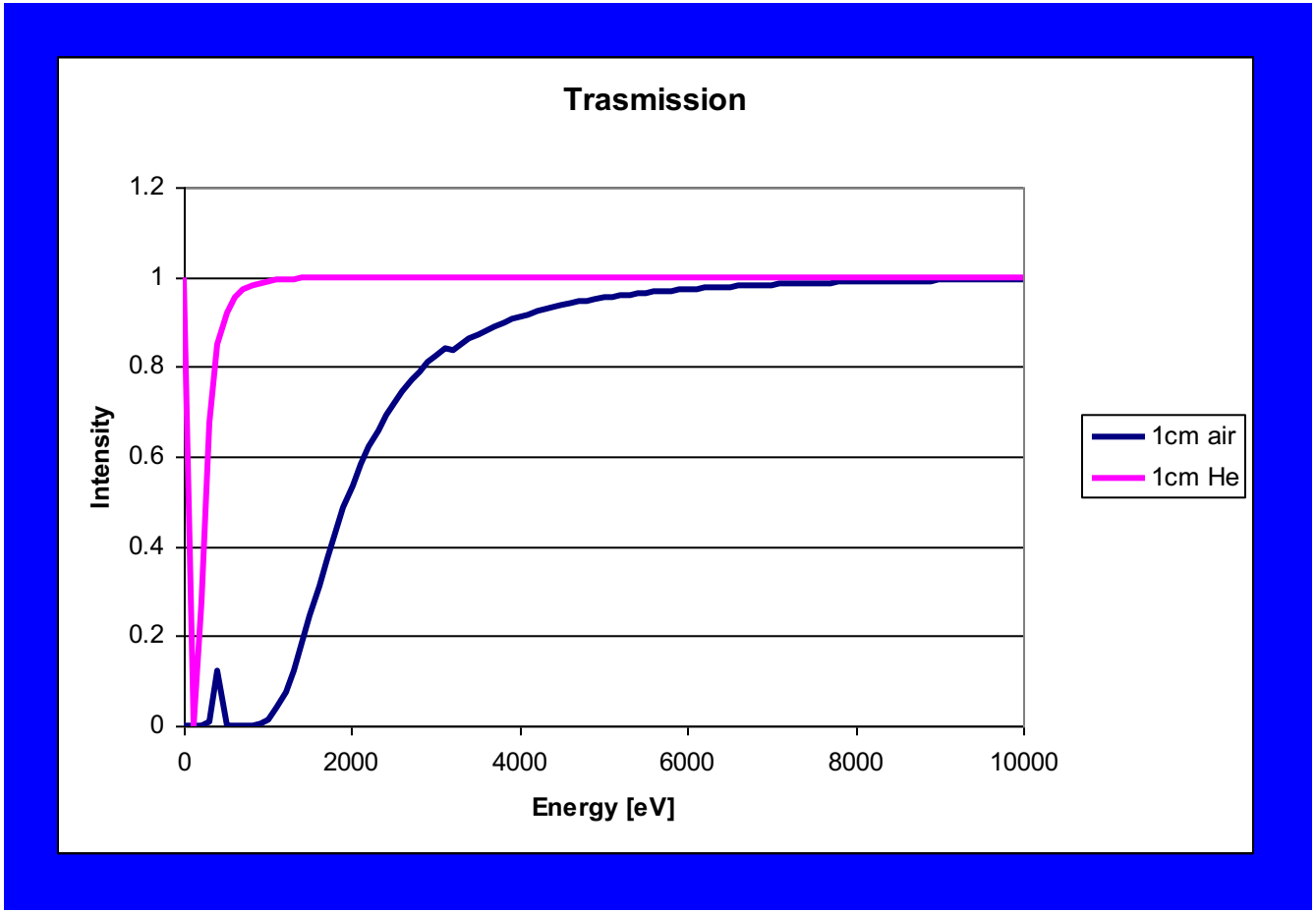
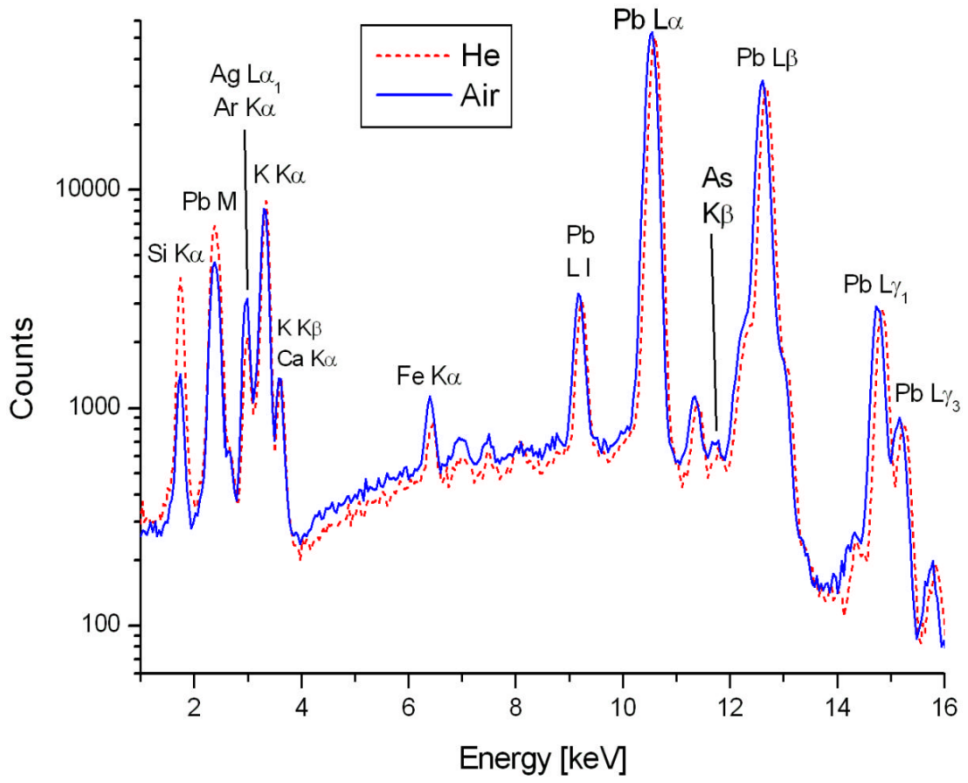
# Transmission of gases



# Transmission in Air and He




The presence of air between sample and detector limits the identification of light elements.

By filling the path between sample and detector with He, a gas lighter than air, the X-ray emitted by Si are less absorbed during their path towards the detector.

A. Gianoncelli, J. Castaing, A. Bouquillon, A. Polvorinos, P. Walter, "Quantitative elemental analysis of Della Robbia's glazes with a portable XRF spectrometer and its comparison to PIXE methods", X-ray Spectrometry Vol. 35, N° 6, 365-369, 2006.

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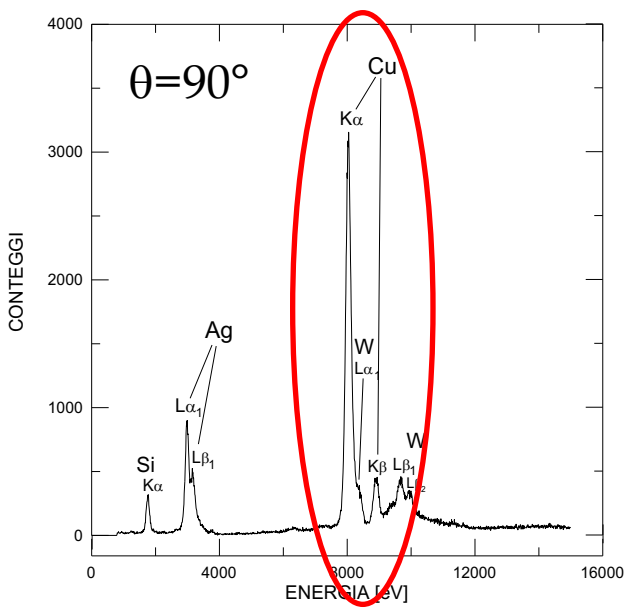
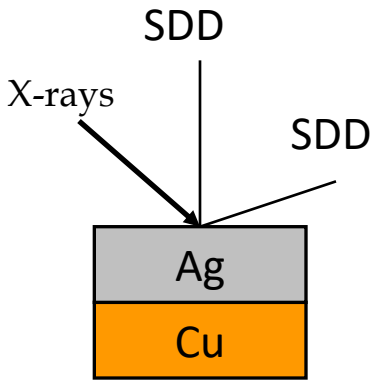
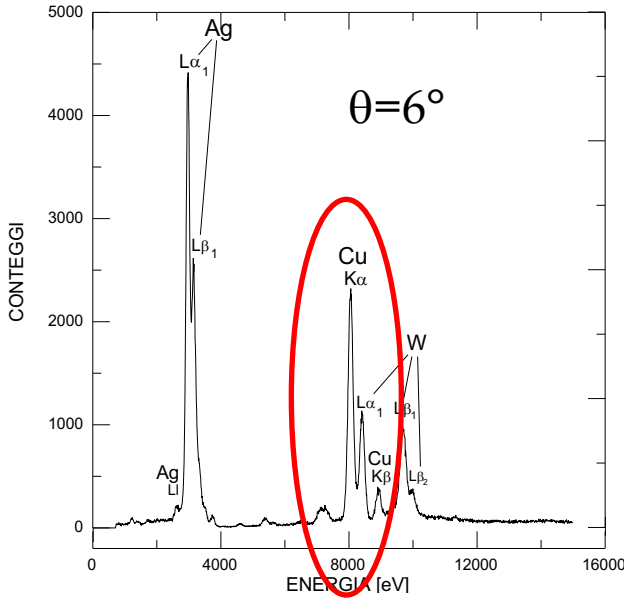
# Determination of the thickness of coatings deposited on a metallic substrate

- Strong angular dependence of the XRF intensity
- Fluorescence intensity of the substrate attenuated by the coating layer: attenuation depending on the coating thickness *h*
- This method requires no calibration

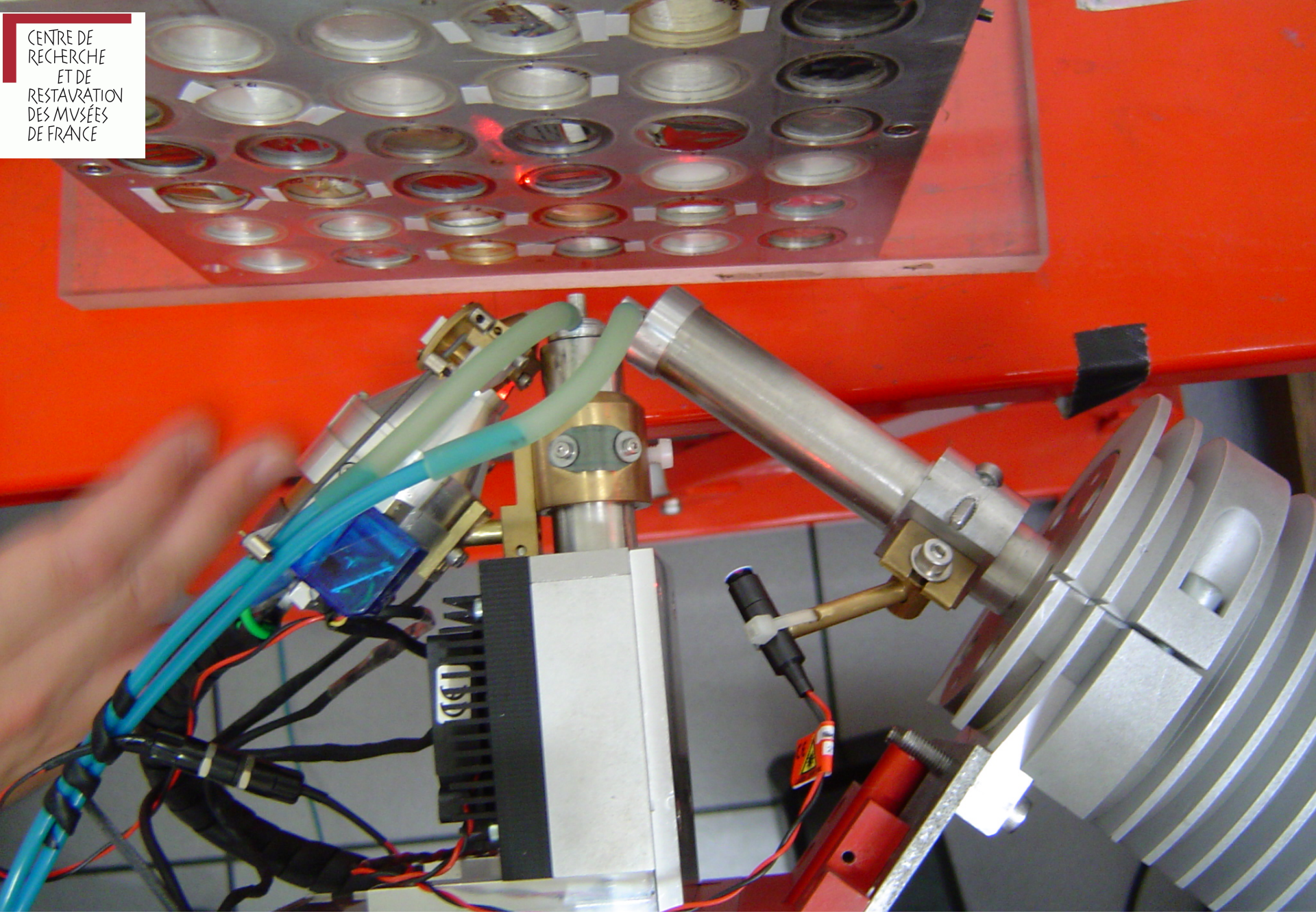


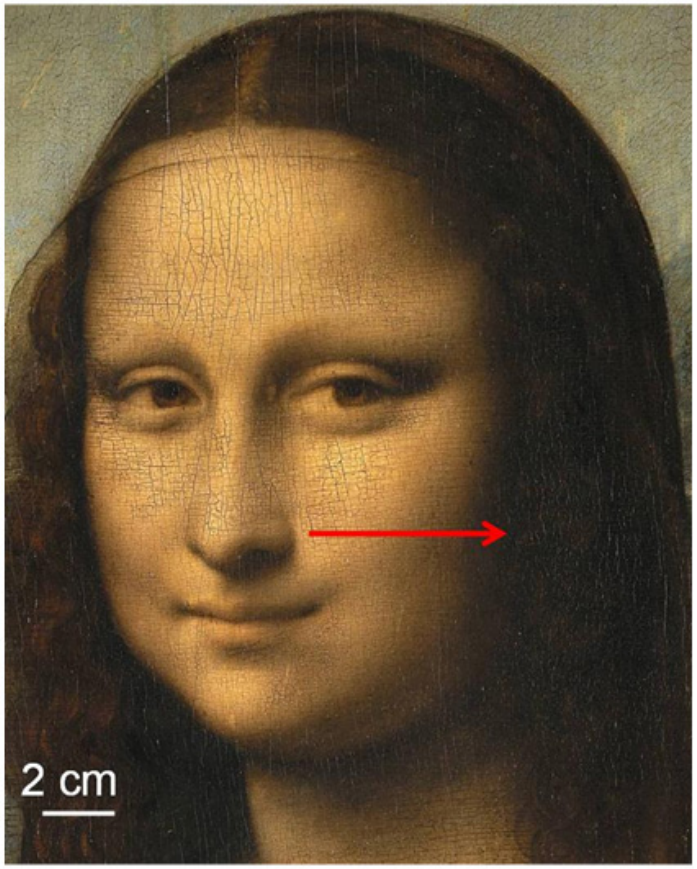

C. Fiorini, A. Gianoncelli, A. Longoni, F. Zaraga, "Determination of the thickness of coatings by means of a new XRF spectrometer ," *X-ray Spectrometry*, Vol. 31, N°1, 92.2002 ,99-

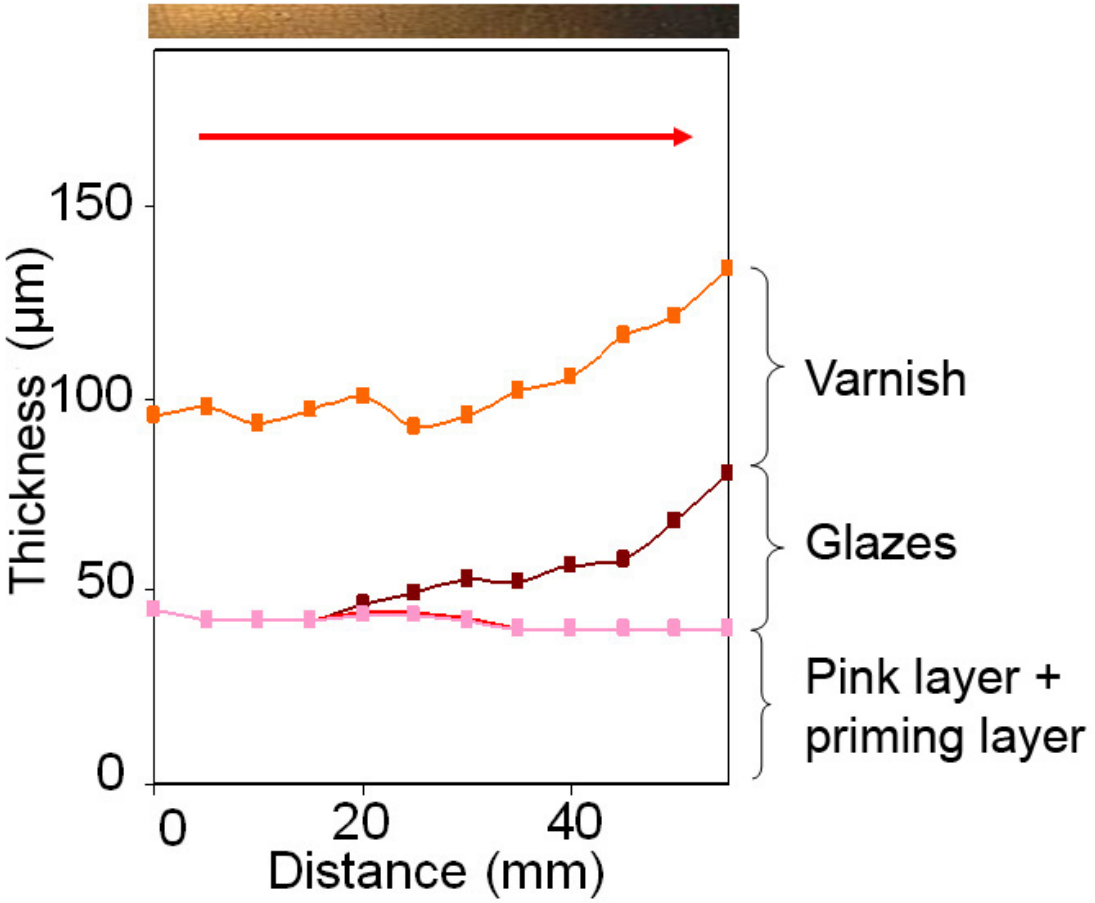
2005




L. De Viguerie, P. Walter et al. “Revealing the sfumato Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy” Angewandte Chemie, 122 (2010), 6261-6264.

- "*sfumato*": soften transitions and blend shadows like smoke
- Found the different recipes used by Da Vinci to do the shadows on the faces.
- Use of glaze layers or a very thin paint. In the case of the glazes, thin layers of 1 to 2 µm were applied to obtain a total thickness of no more than 30 to 40 micrometres.

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# X-ray diffraction

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## Energy and ‘Angle’ Dispersive XRD

- **EDXRD**

  the angle of incidence $\vartheta$ is kept fixed

  $2d*\sin\vartheta=n\lambda$

  Experimental Set-up:
  - Polychromatic source
  - ED detector

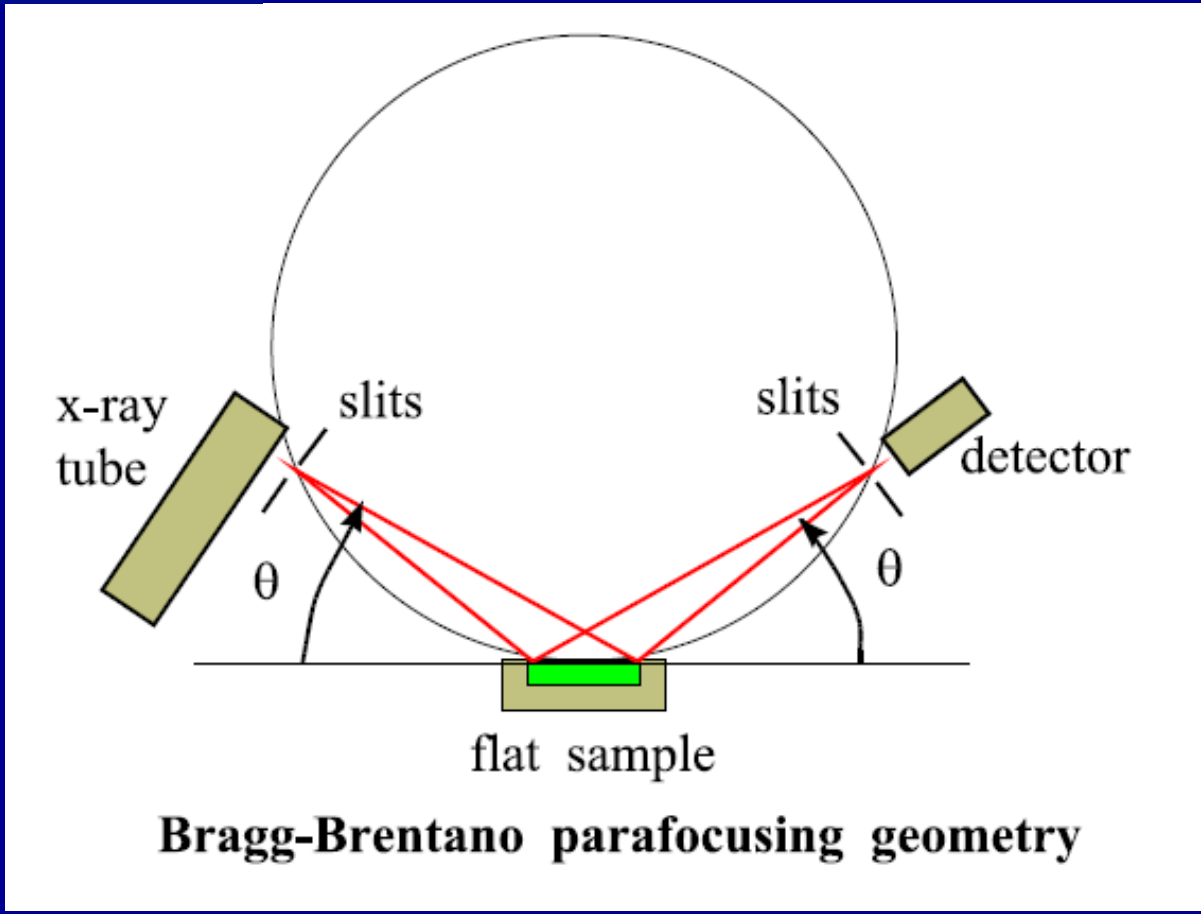
- **ADXRD**

  the wavelength $\lambda$ of the incident radiation is kept fixed

  $2d*\sin\vartheta=n\lambda$

  Experimental Set-up:
  - Goniometer
  - monochromatic source

# X-Ray Diffraction system




1D detector:
- Need of mechanical movement
- Serial detection

2D detector:
- Fixed system, easier to align
- Parallel detection

**Flat sample**
**Reflection mode**

# XRD detector: Imaging Plate

**Photostimulable phosphor powder in an organic binder (25-150µm) deposited on a flexible polymer support (250µm)**

## Advantages

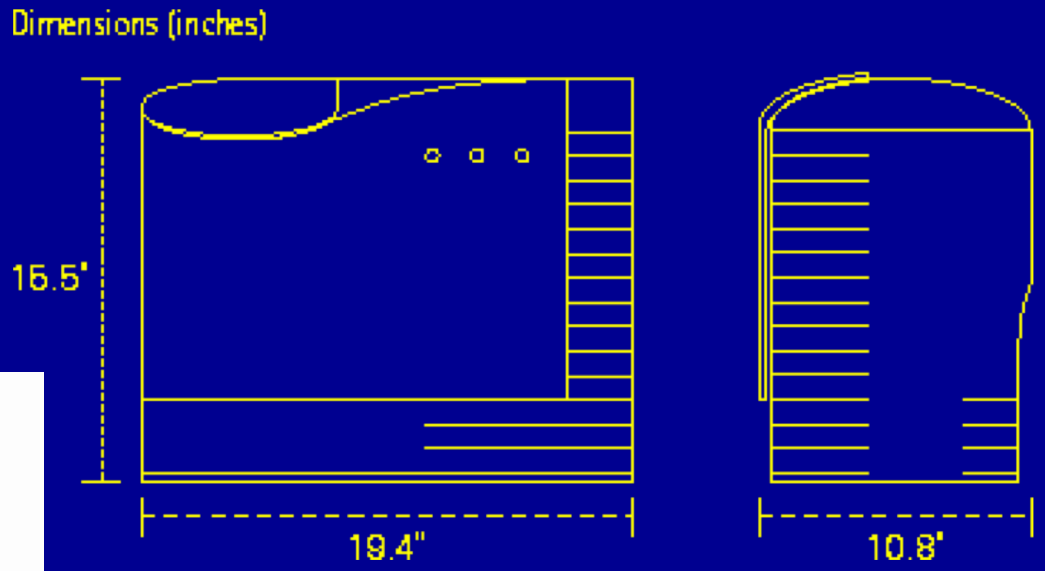
- Detector for XR, $\gamma$ radiation, $\alpha$ and $\beta$ particles, protons, electron beams
- 2D detector $\Rightarrow$ parallel detection
- Flexible mounting and wireless
- High sensitivity
- Good linearity
- High Dynamic ($10^6$ counts)
- Low noise (No dark current)

## Disadvantages

- Light sensitive: erasable with light
- No real time measure

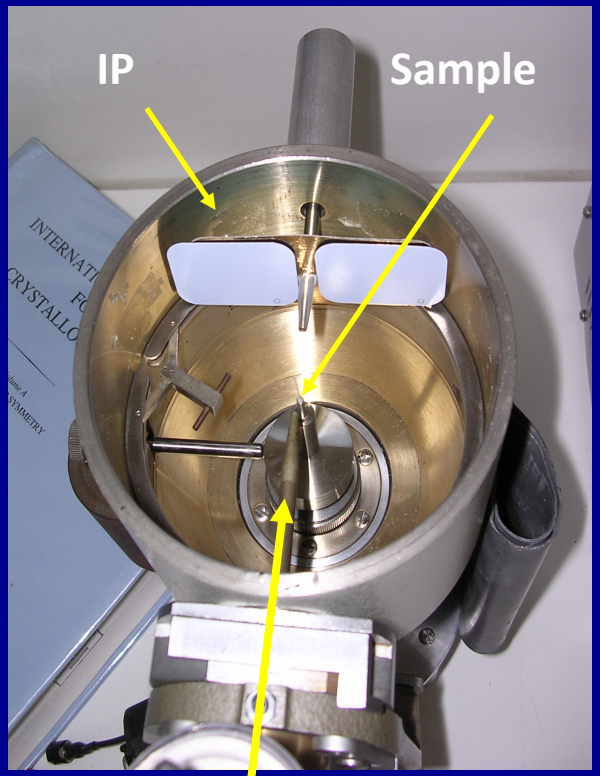
# Imaging Plate system at C2RMF

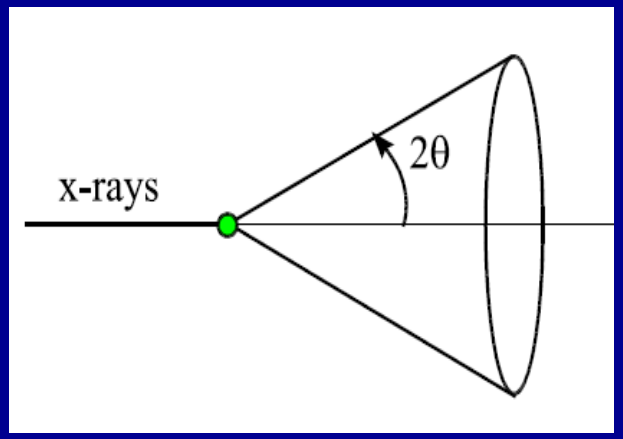
- IP scanner:
  - 10 Kg, 3 min scanning time
- Imaging plate format:
  - 15cm x 30cm or 3,1cm x 4,1 cm

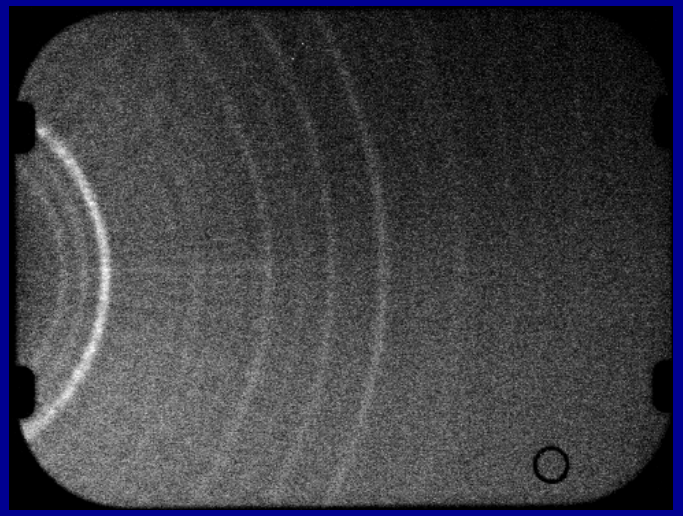


# XRD in Transmission: sample

- Source: Mo Tube (30 kV, 215 µA)
- Sample: quartz capillary
- Acquisition time: 3h15

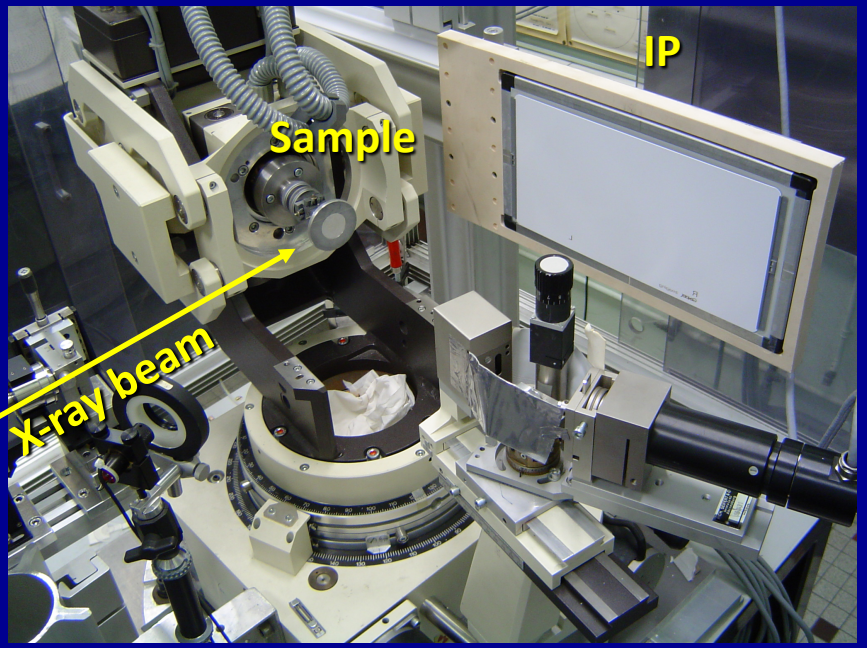


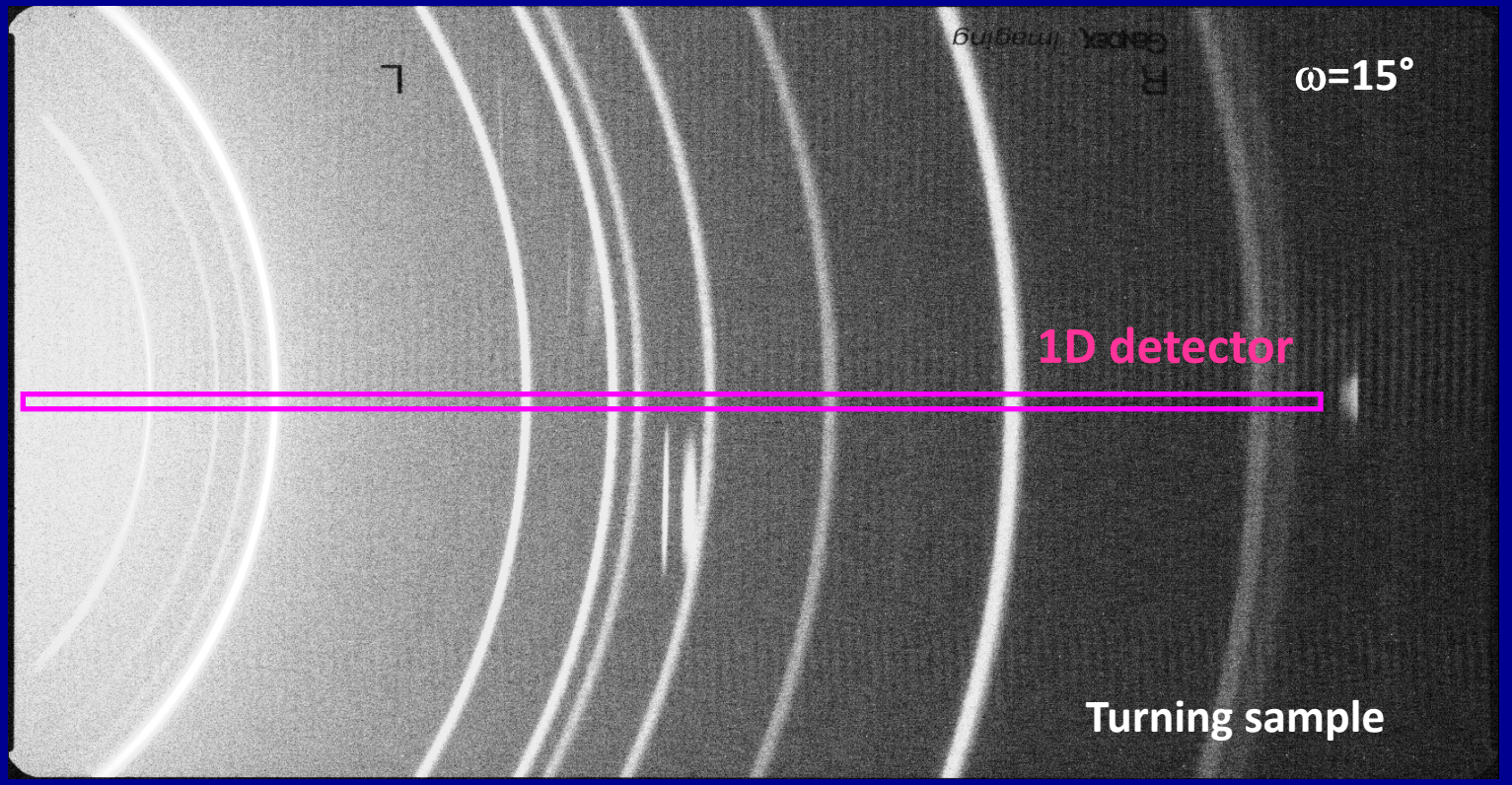
# XRD in Reflection: in situ

- Experimental Set-up:
  - source: Cu Tube Philips, 2200 W (50 kV, 40 mA)
  - x-ray beam size ~ 2mm$^2$
  - detector: IP
  - sample: quartz, $CaCO_3$, hematite
  - measurement time: 15-30 min



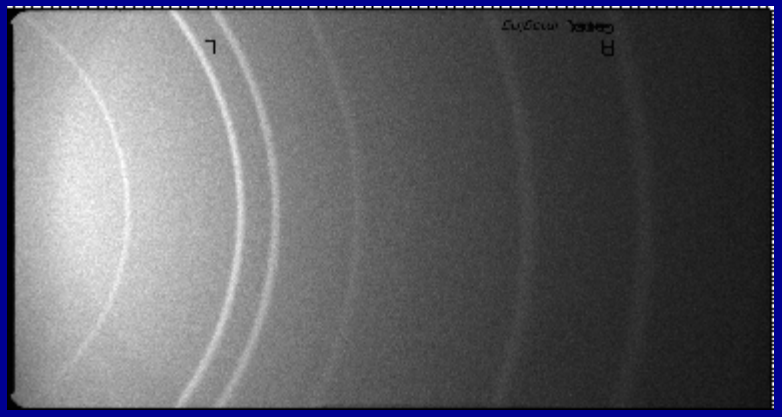
# in Reflection Mode

**Quartz sample** (in powder)
15 min measurement time



# n Reflection Mode

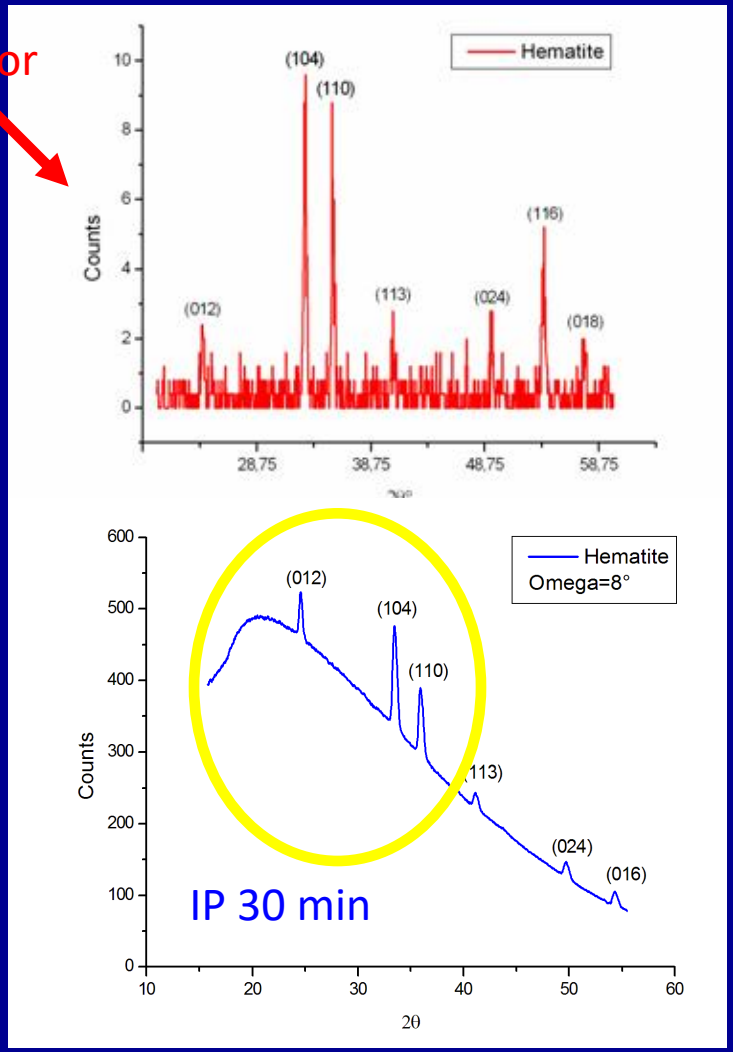
**Hematite ($Fe_2O_3$)**



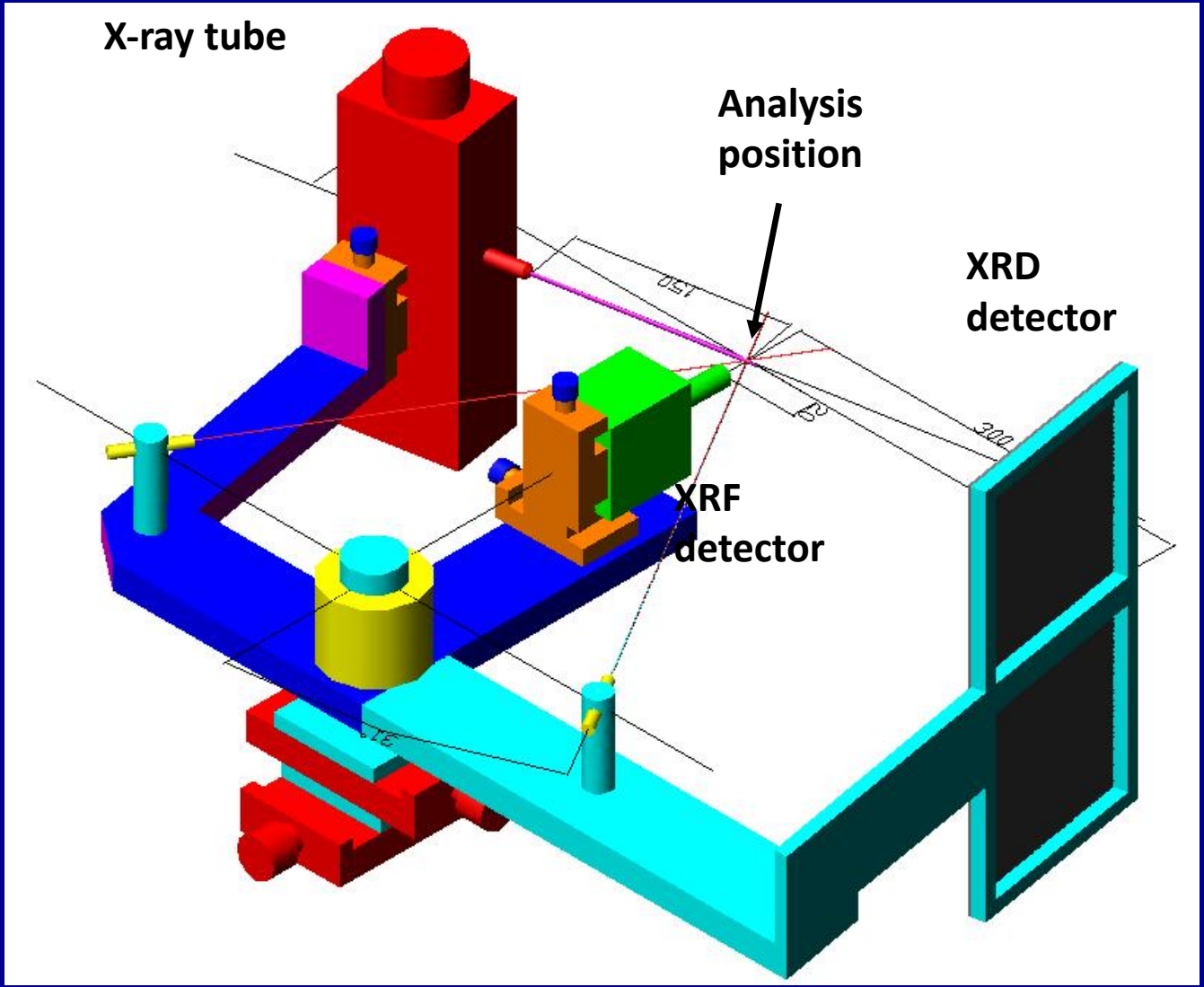
The X-ray Fluorescence of Fe is not negligible

Need of a monochromator system

Scintillator
32 min



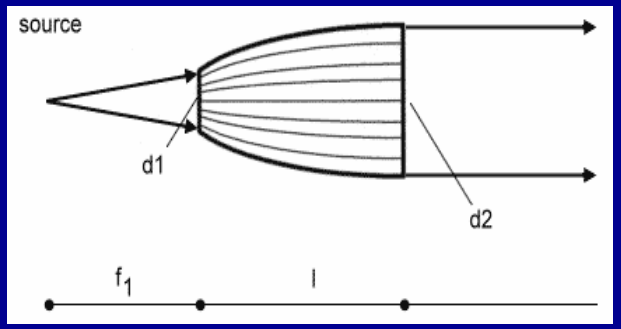
# The XRF and XRD system



# X-ray Source

## Both for XRF and XRD

- Cu anode X-ray Tube
- Polycapillary optics: high intensity Semilens for quasi parallel beam (divergence < 10 mrad)





- Φ=5 mm
  (with slits of 4mm x 75-100-200-500µm)

- Air cooled
- High voltage: max 50 kV
- Tube current: max 800µA
- Electrical power: max 30 W

- Weight: ~ 4 Kg x-ray tube
  8 Kg Power Supply

- Possibility of working at 10° incidence on the sample with a working distance of 20-30 cm

- Ni filter to cut Cu $K_\beta$ for X-ray diffraction

# The XRF and XRD system

- X-ray Tube power supply:
  - 8 Kg, 30W max
- SDD power supply and electronics
  - 2 kg

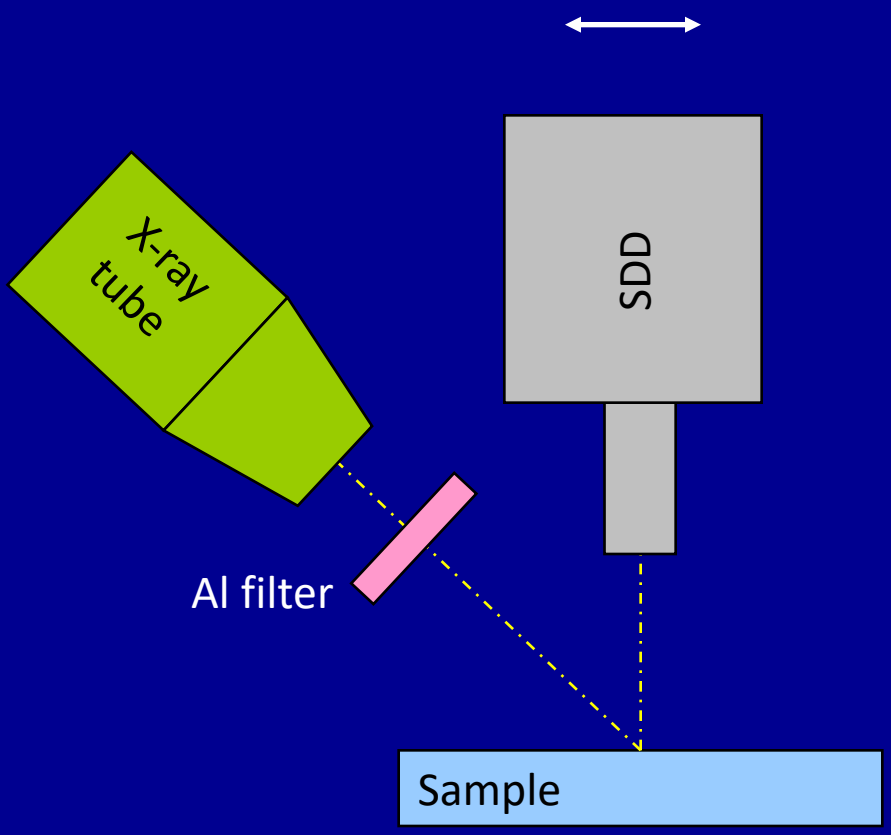

60 cm

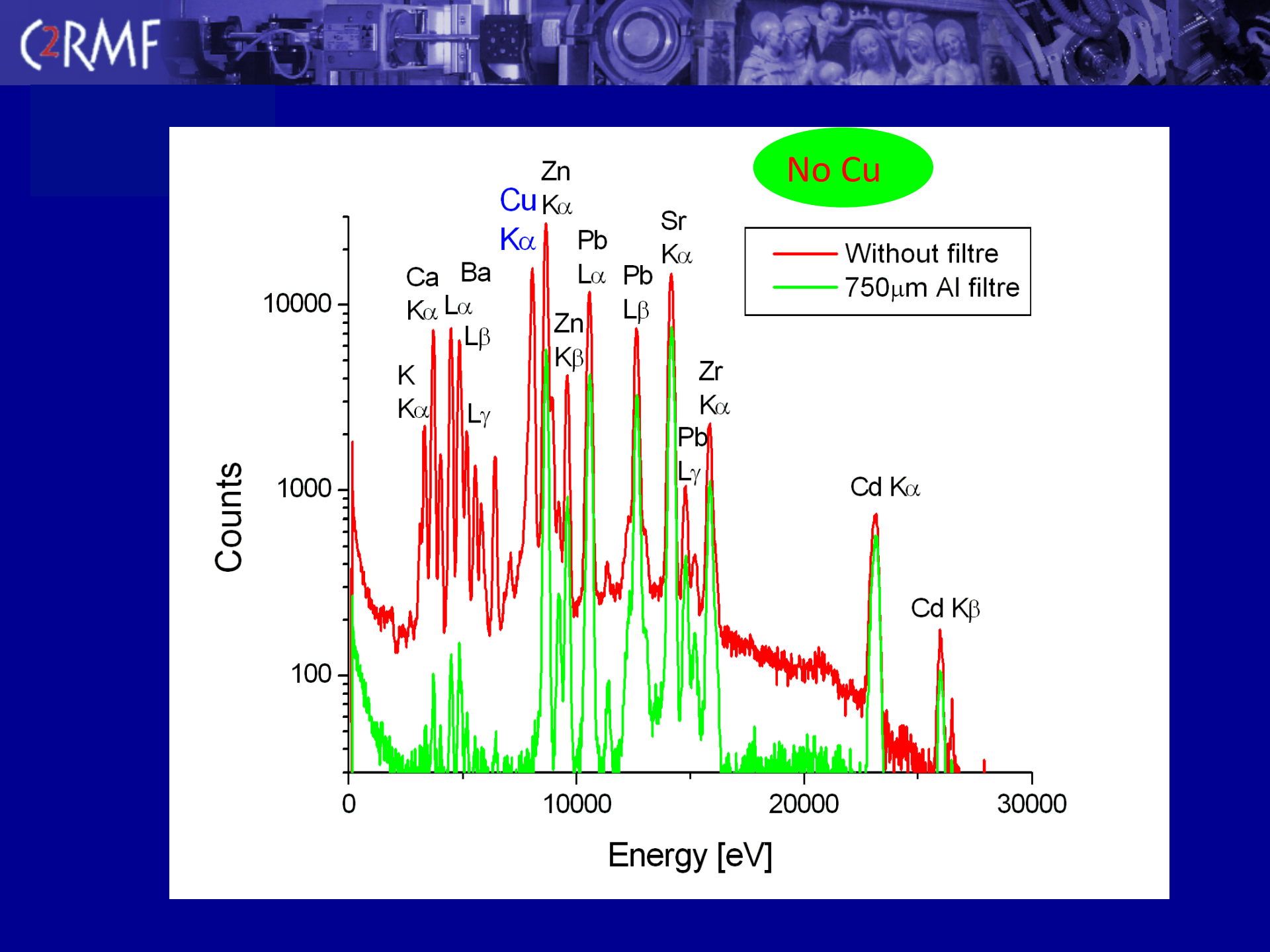
- IP scanner:
  - 10 Kg, 3 min scanning time
- Imaging plate format:
  - 15cm x 30cm or 3,1cm x 4,1 cm

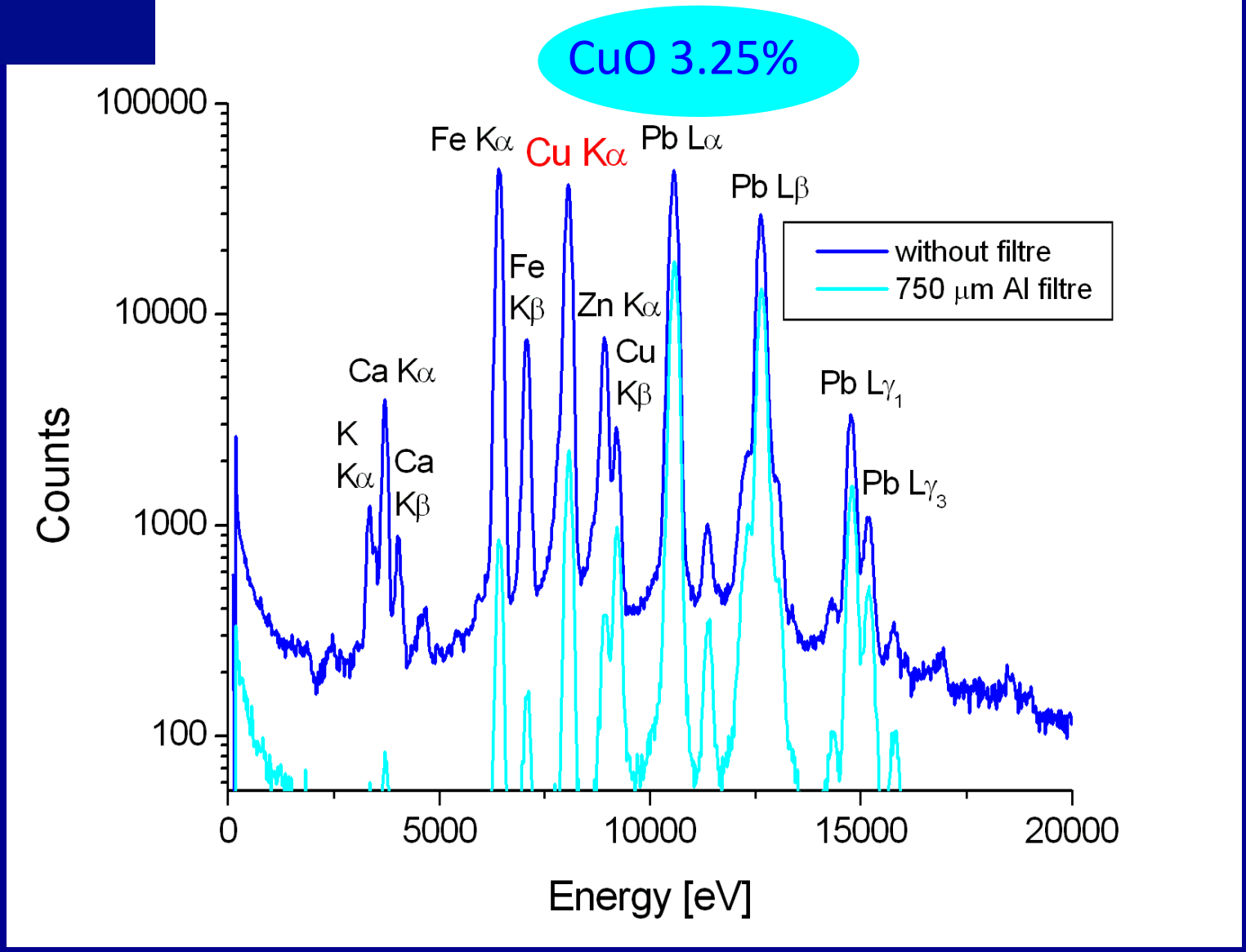
# X-ray Fluorescence System

- X-ray with Cu anode
- SDD detector
- Al filter

| | Nist 1412 | Bgira4 |
|---|---|---|
| $SiO_2$ | 42.38 | 42.00 |
| $Al_2O_3$ | 7.52 | 3.58 |
| $Fe_2O_3$ | 0.031 | 3.01 |
| MgO | 4.69 | 1.50 |
| CaO | 4.53 | 4.07 |
| $NaO_2$ | 4.69 | 5.00 |
| $K_2O$ | 4.14 | 3.87 |
| $SO_3$ | | 0.26 |
| PbO | 4.4 | 30.40 |
| $SnO_2$ | | 3.02 |
| CuO | | 3.25 |
| SrO | 4.55 | |
| $LiO_2$ | 4.53 | |
| BaO | 4.67 | |
| ZnO | 4.48 | |
| CdO | 4.38 | |




No Cu
Without filtre
750μm Al filtre
Counts
Energy [eV]
10000
1000
100
0
10000
20000
30000
K Kα
Ca Kα
Ba Lα
Lβ
Lγ
Cu Kα
Zn Kα
Zn Kβ
Pb Lα
Pb Lβ
Sr Kα
Pb Lγ
Zr Kα
Cd Kα
Cd Kβ


CuO 3.25%
Counts
Energy [eV]
100000
10000
1000
100
0
5000
10000
15000
20000
Fe Kα
Cu Kα
Pb Lα
Pb Lβ
Fe
Kβ
Zn Kα
Cu
Kβ
Ca Kα
K
Kα
Ca
Kβ
Pb Lγ1
Pb Lγ3
without filtre
750 μm Al filtre

# XRD system: 2D detection by IP

- XRD detector: Imaging Plate
- IP format: 15cm x 30cm

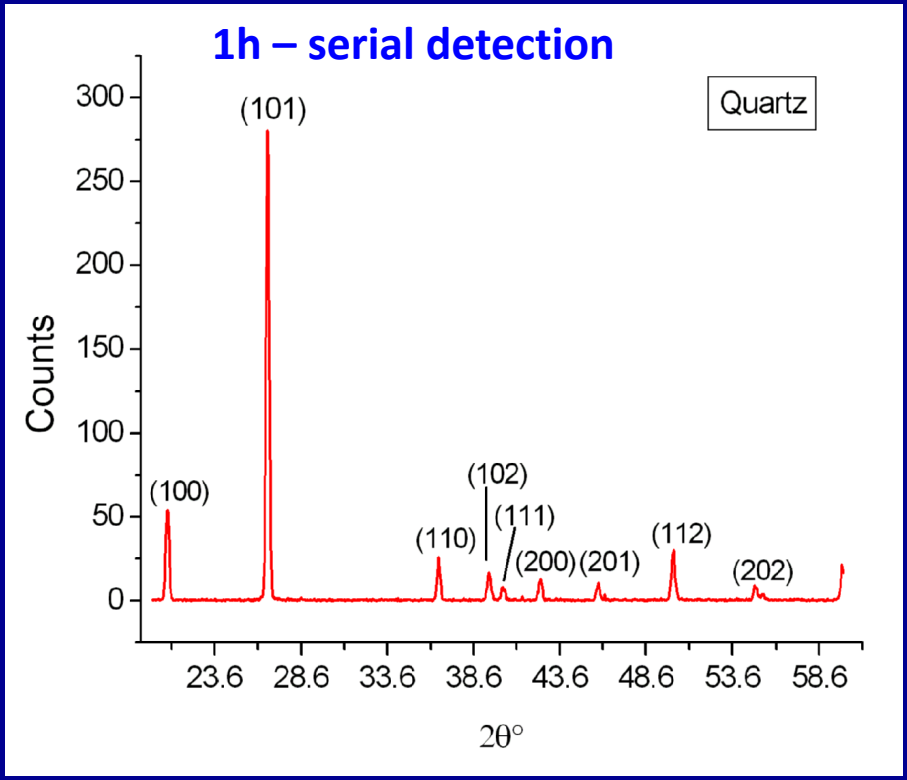
- IP scanner:
  10 Kg, 3 min scanning time

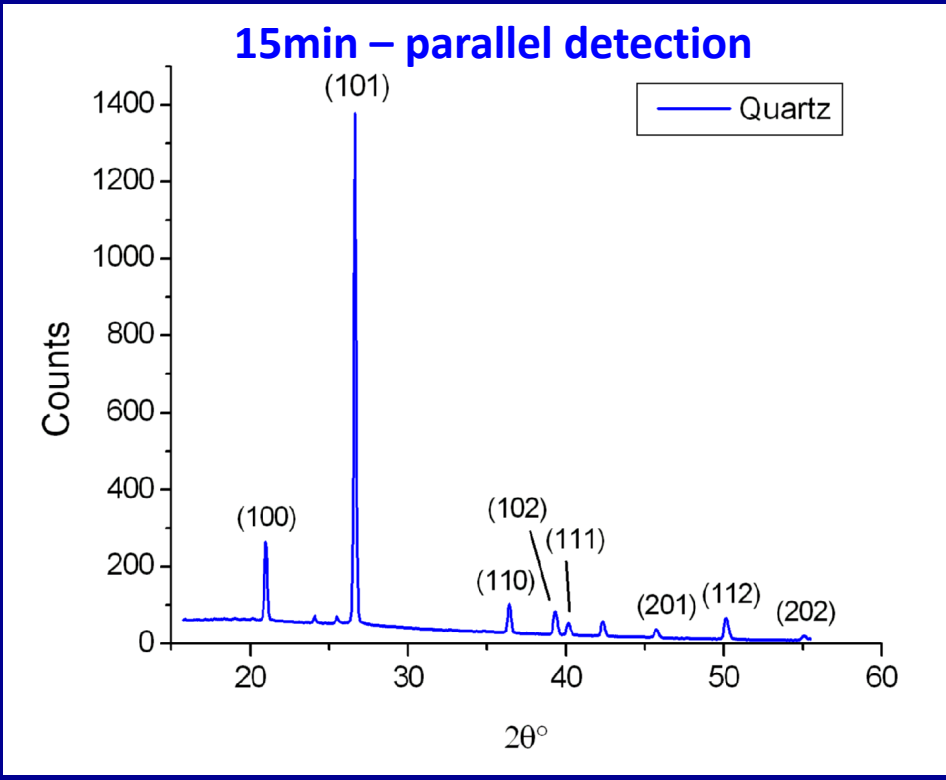
**Scintillator detector**

$\vartheta$-$2\vartheta$ geometry

**Imaging Plate**

Perpendicular to incident X-ray beam



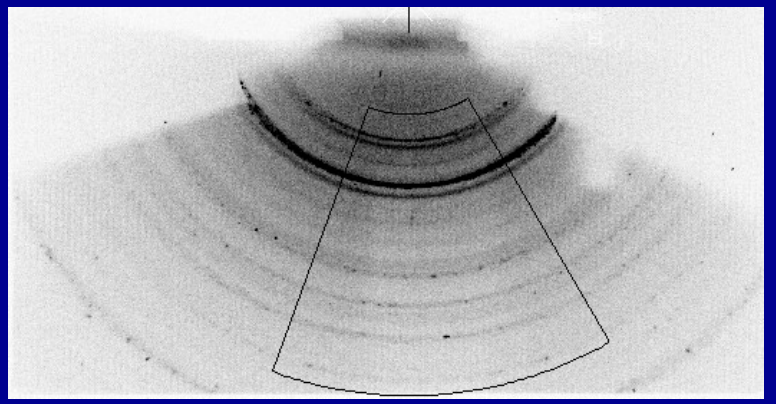
# Quartz in terra cotta

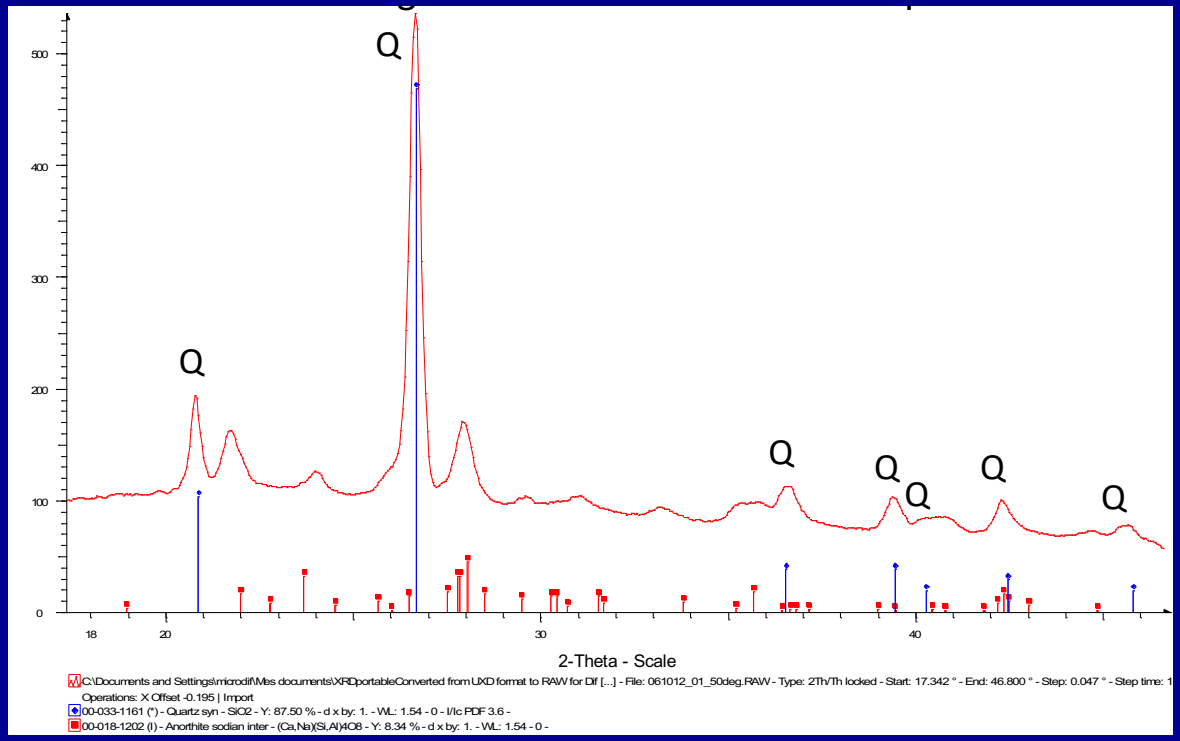
- 40 kV, 700µA, 15 µm Ni filter, ω=10°
- 4mm x 0.5mm beam size

⇓

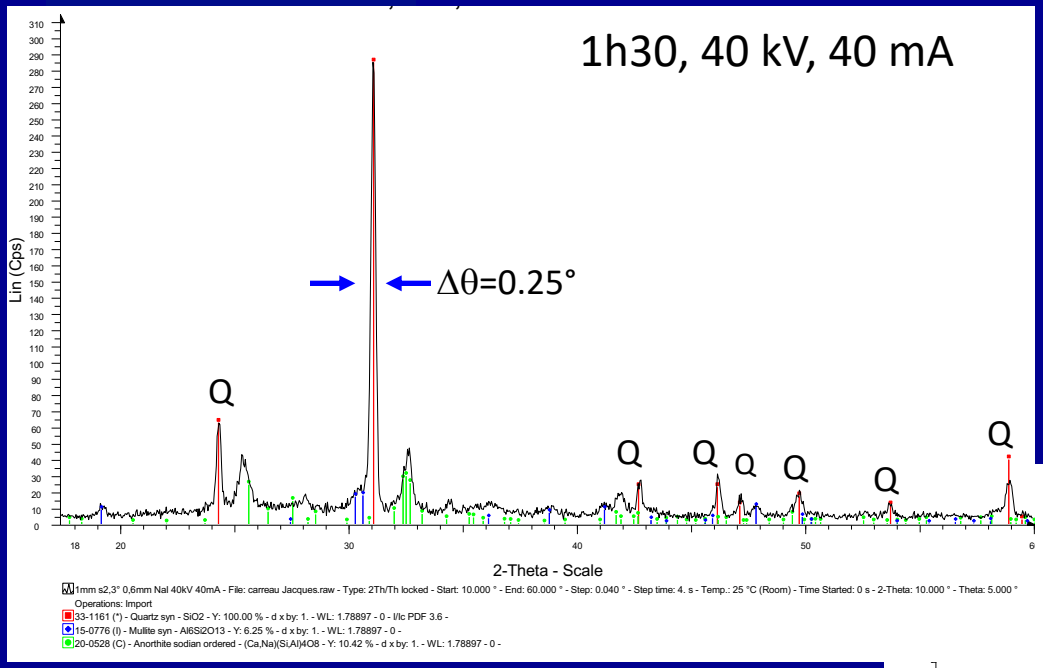
4mm x 3mm spot size on the sample

- quartz sample (tile)
- 5 minute acquisition time
- Integration over 50°



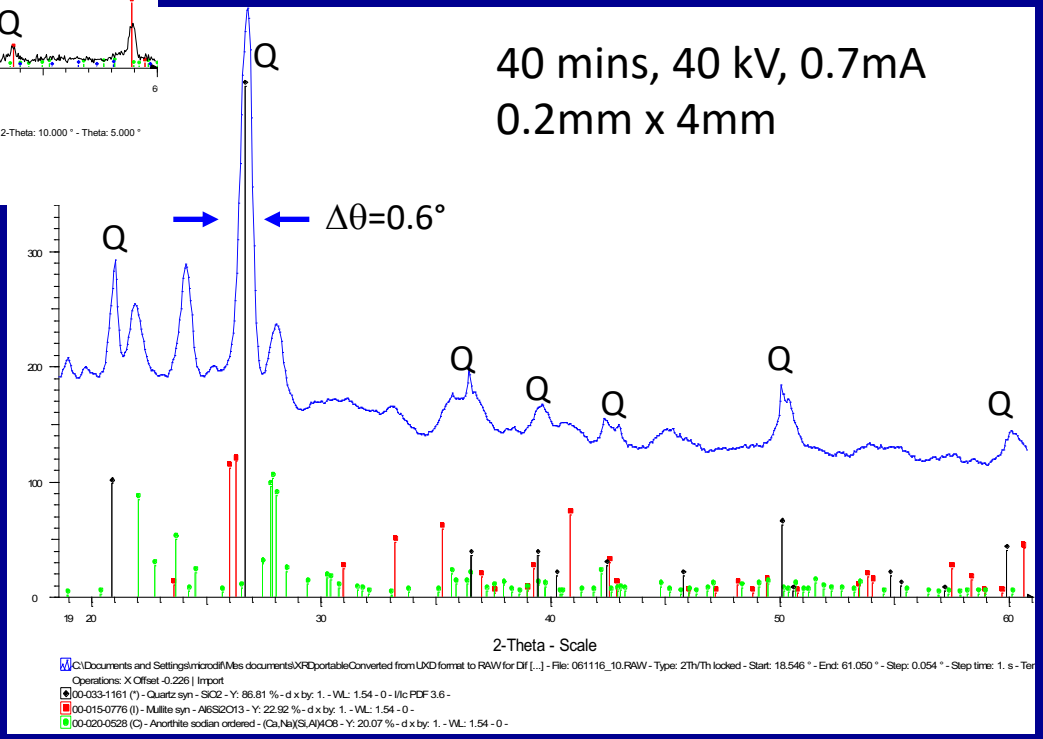


# Quartz in terra cotta: comparison



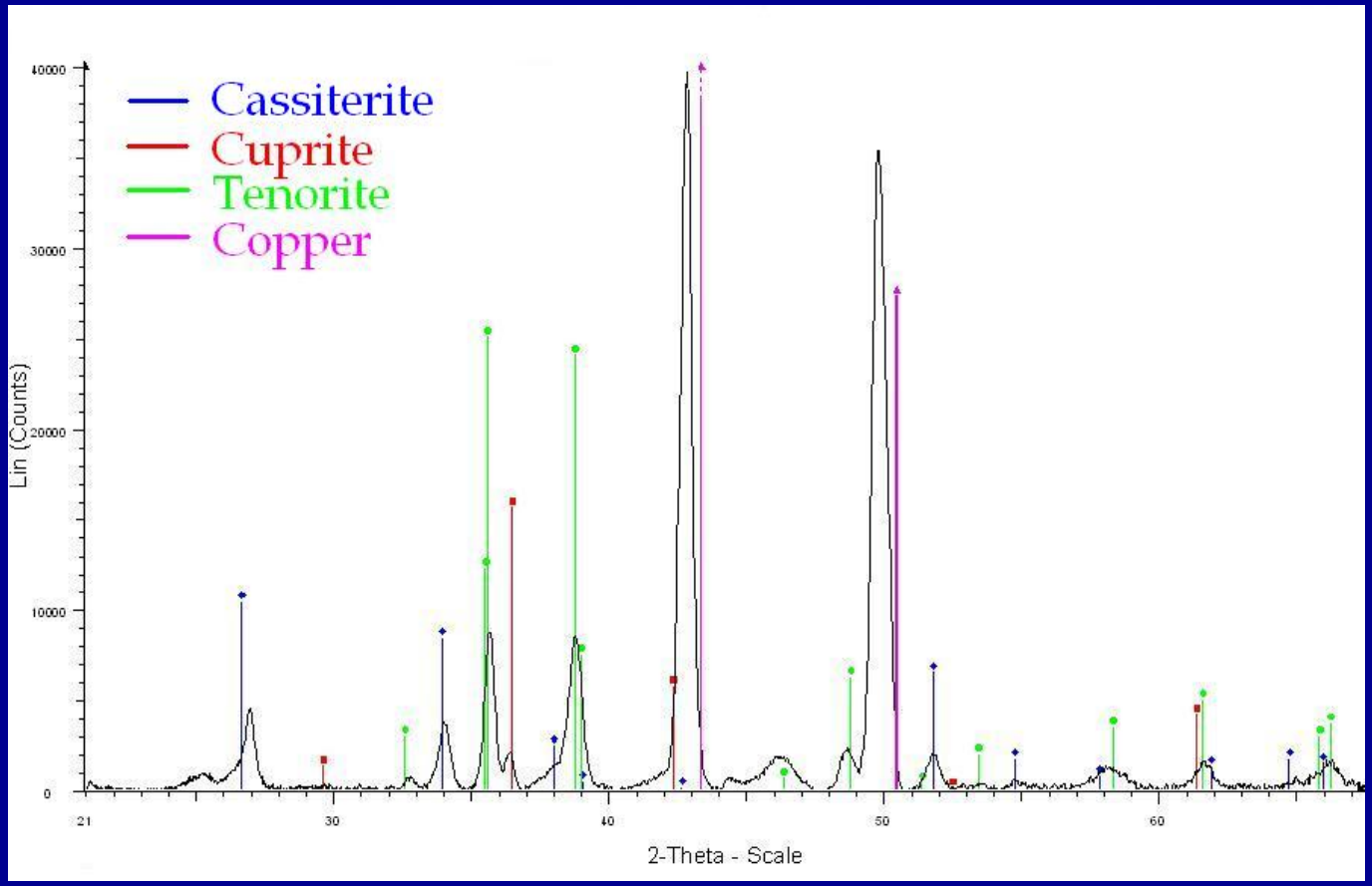

Bruker D5000

Portable XRD-XRF



# Bronze (Cu with 10% Sn)

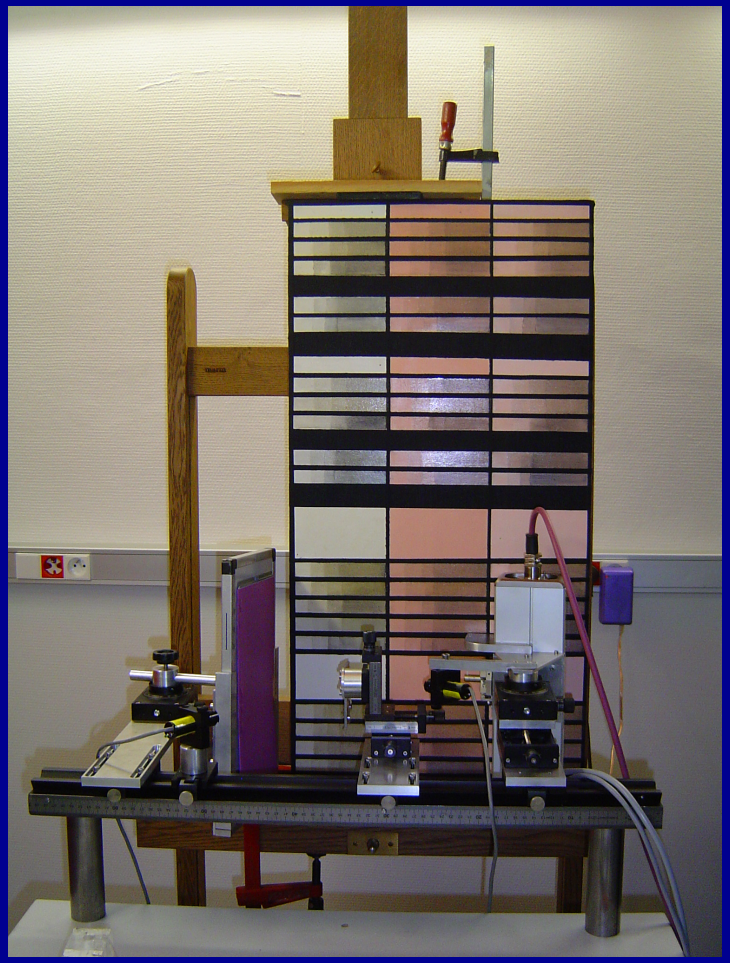
covered with an oxide layer of about 0.5 µm (30 min at 600°C in air)

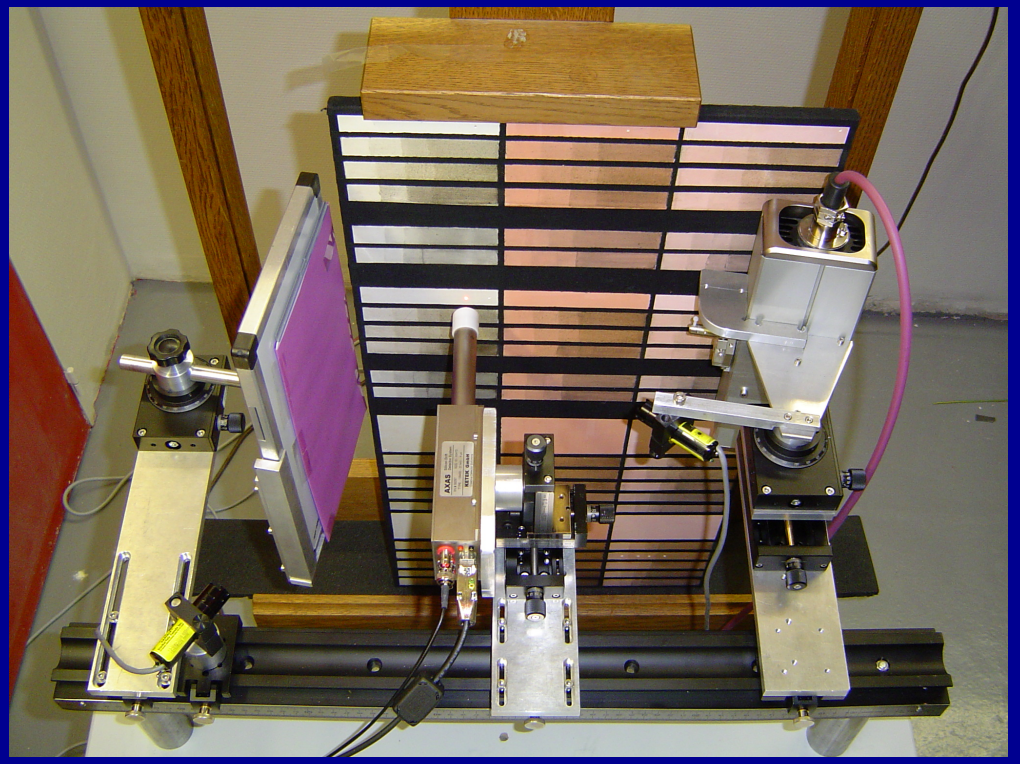



XRD: $SnO_2$, CuO, $Cu_2O$, Cu

XRF: Sn, Cu

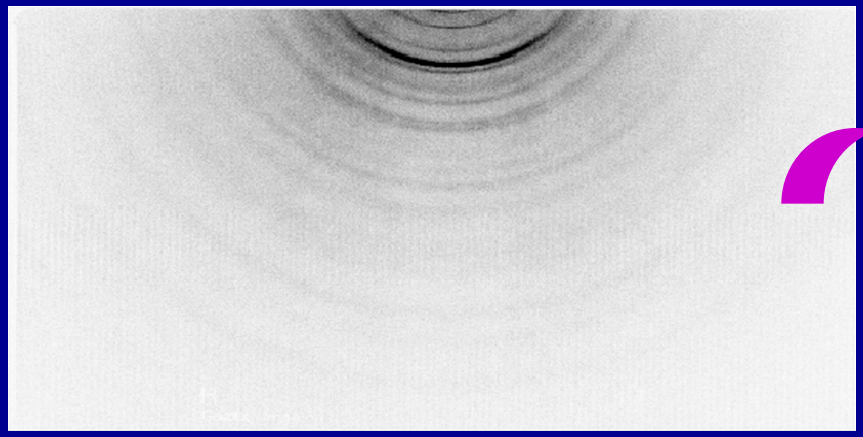
# XRD on painting

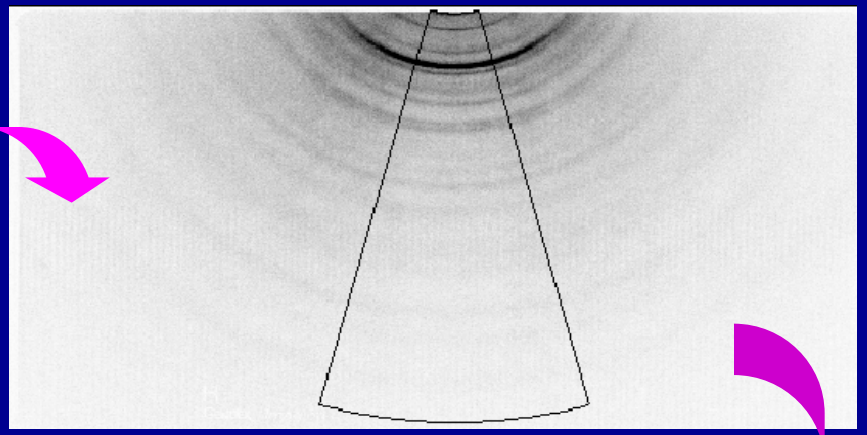


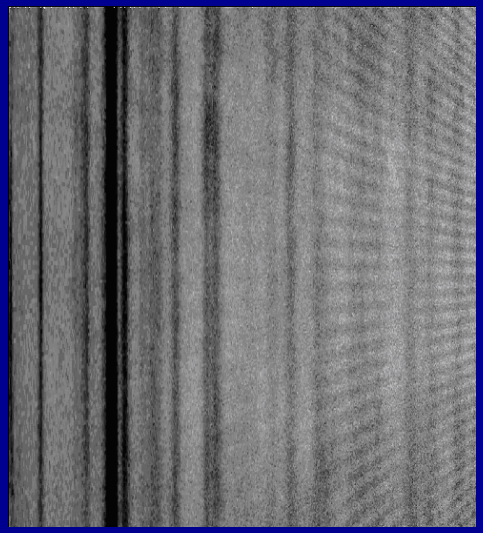


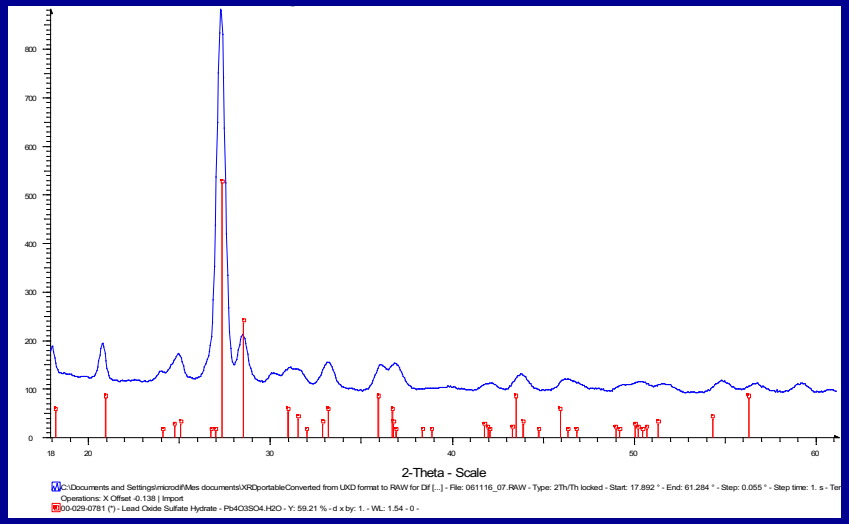
A. Gianoncelli , J. Castaing, L. Ortega, E. Doorhyée, J. Salomon, P. Walter, J.-L. Hodeau, P. Bordet “A portable instrument for in situ determination of the chemical and phase composition of cultural heritage objects” X-ray spectrometry , vol. 37 (2008) 418 – 423.

# Pigments: lead white







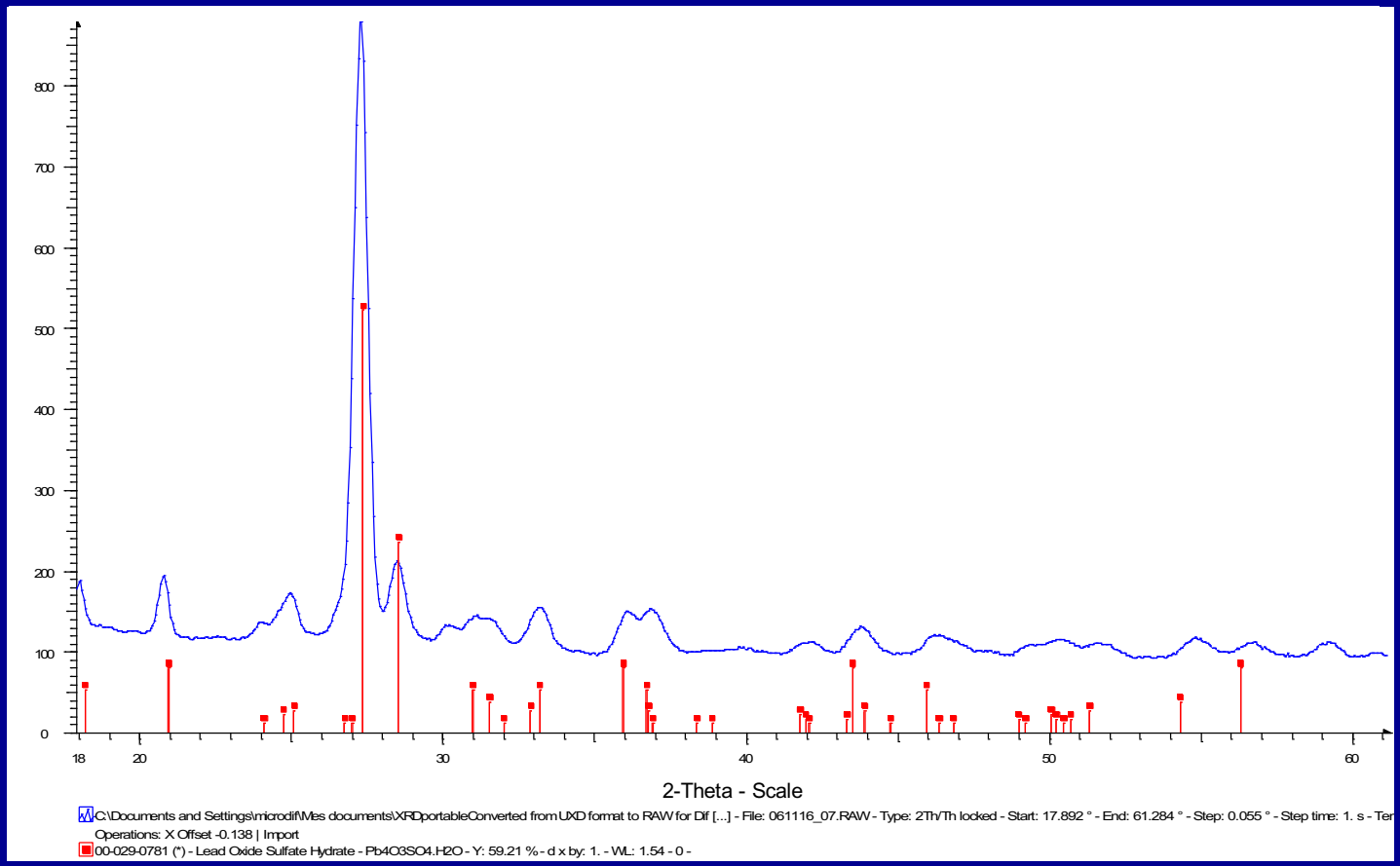


# Pigments: lead white

- 40 kV, 700µA, 15 µm Ni filter

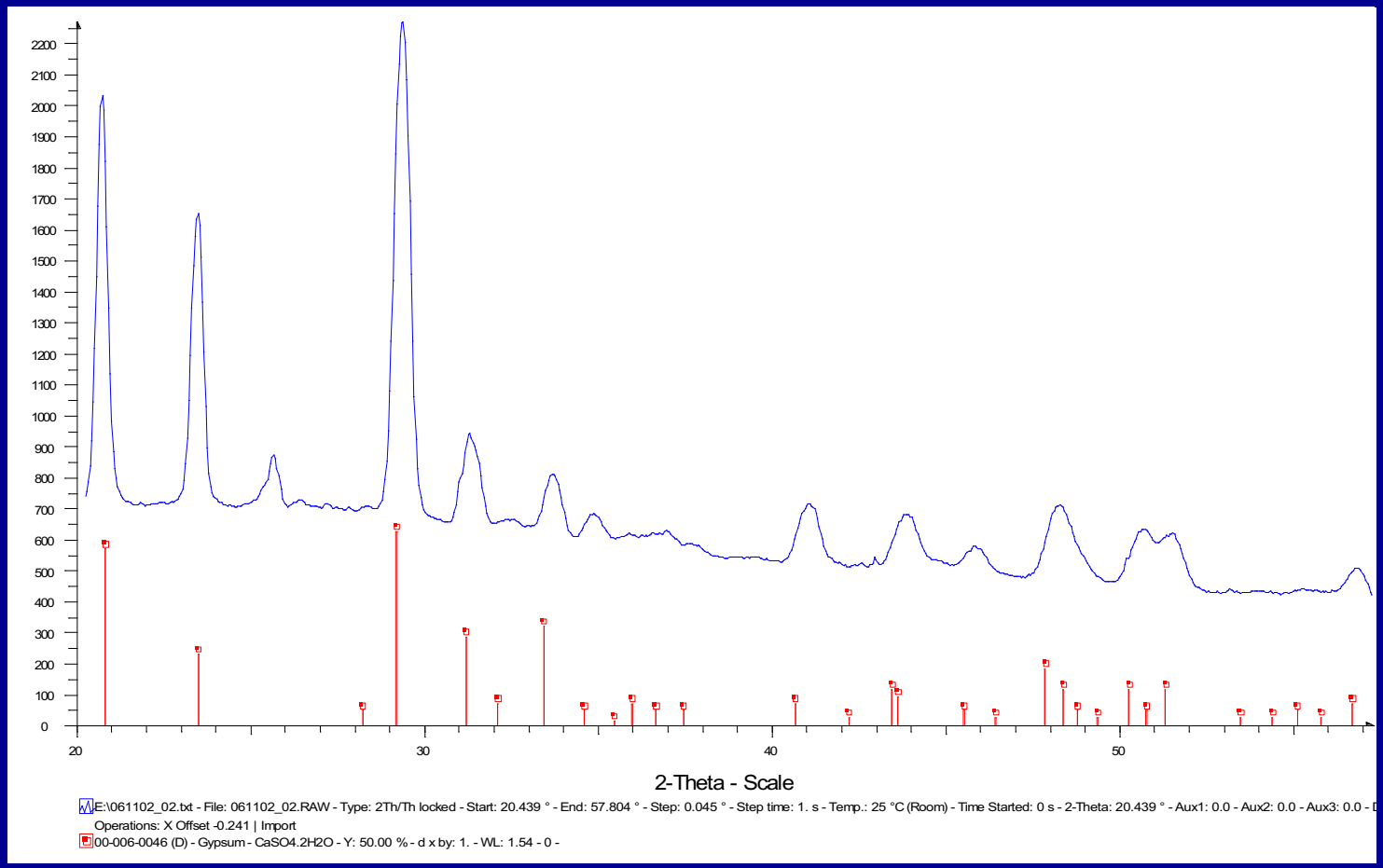
- Lead white (test painting)
- 30 minute acquisition time
- Integration over 30°

| | |
|---|---|
| Lead White | 20-30µm |
| Preparation (gypsum) | 300µm |



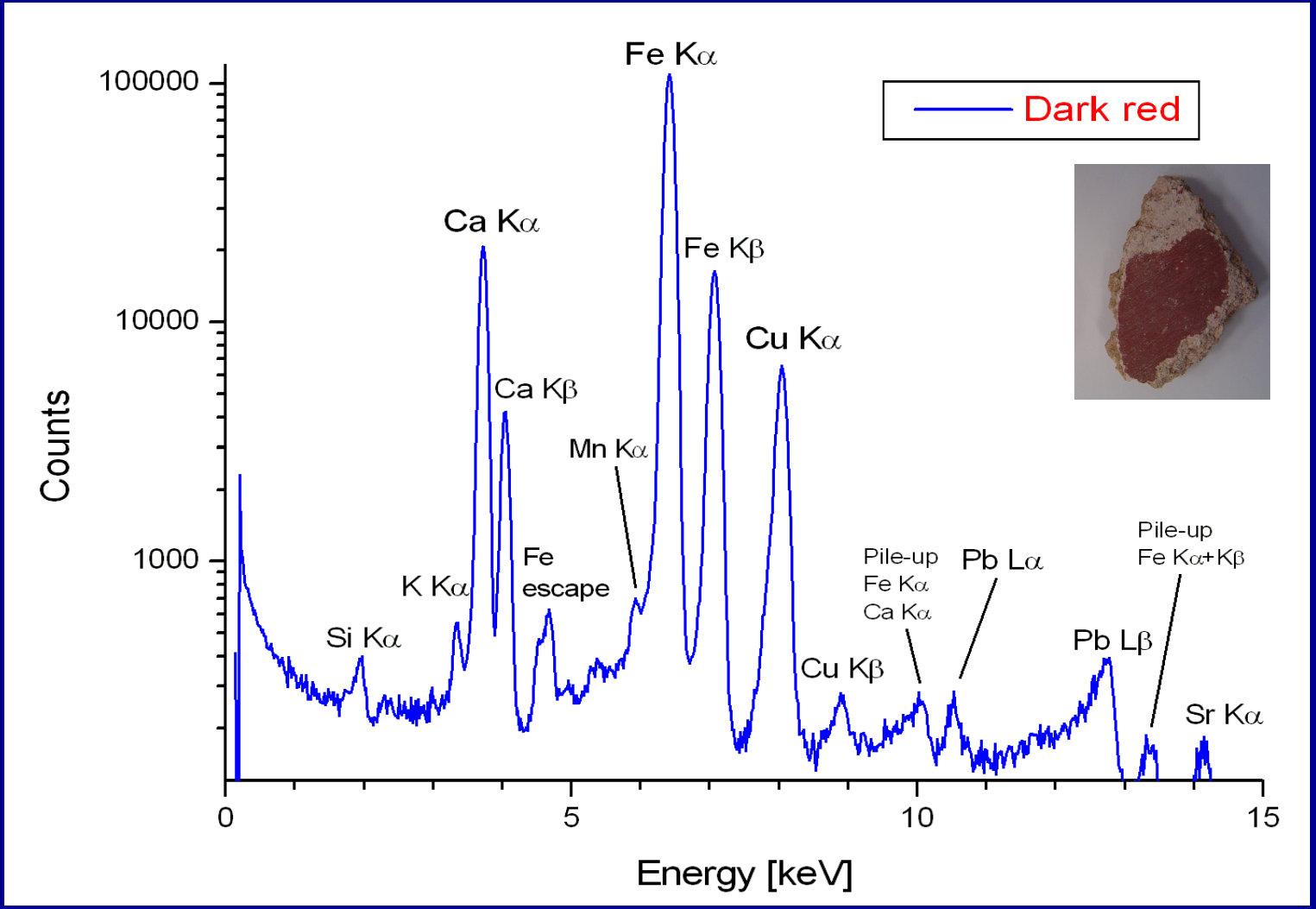
# Pigments

- 40 kV, 700µA, 15 µm Ni filter, slit: 4mm x 0.5mm
- Gypsum (test painting), canvas preparation, 300 µm thickness
- 30 minute acquisition time, Integration over 30°



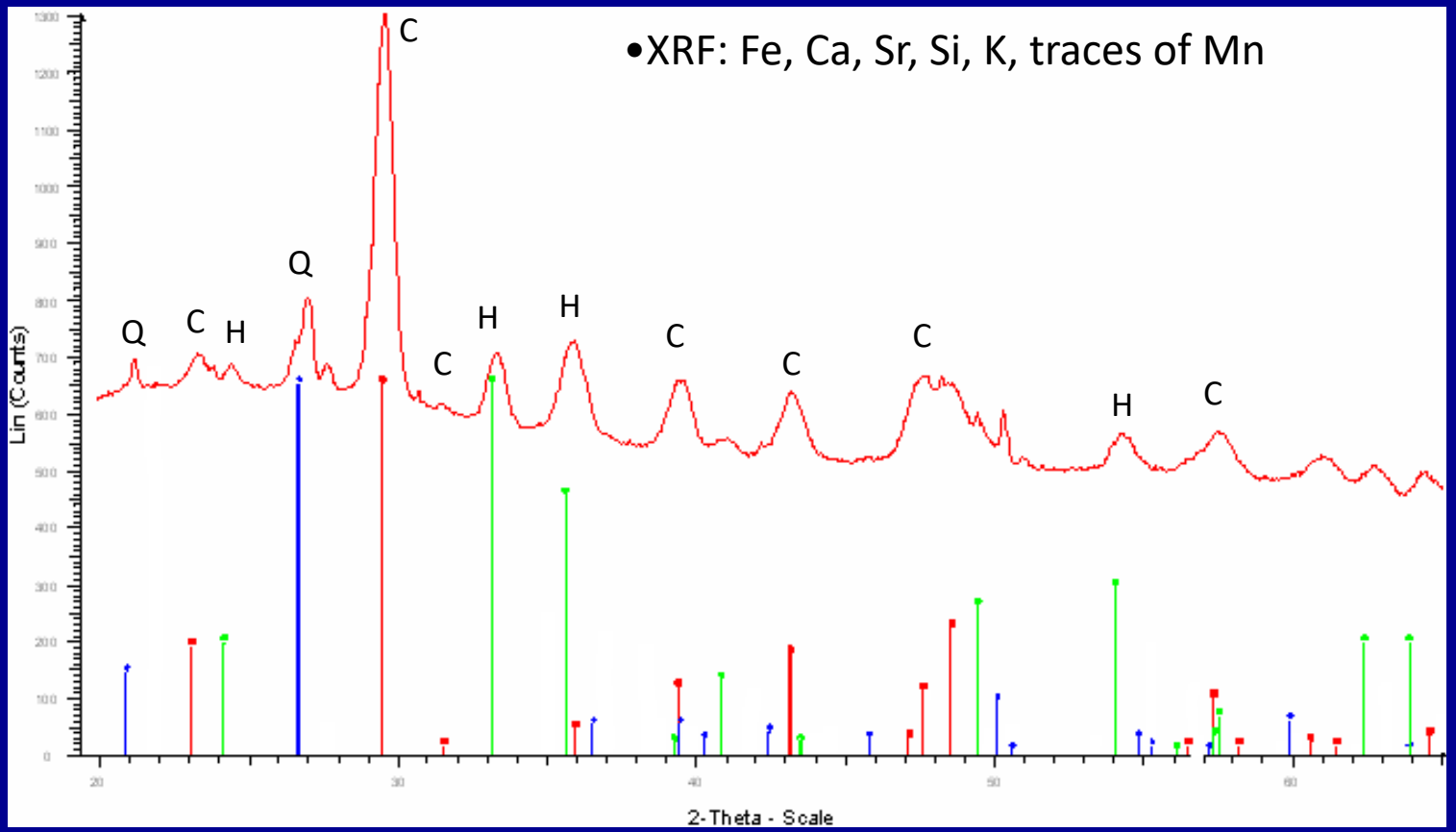
# XRF: Mural paintings

300 sec, with Ni filtre



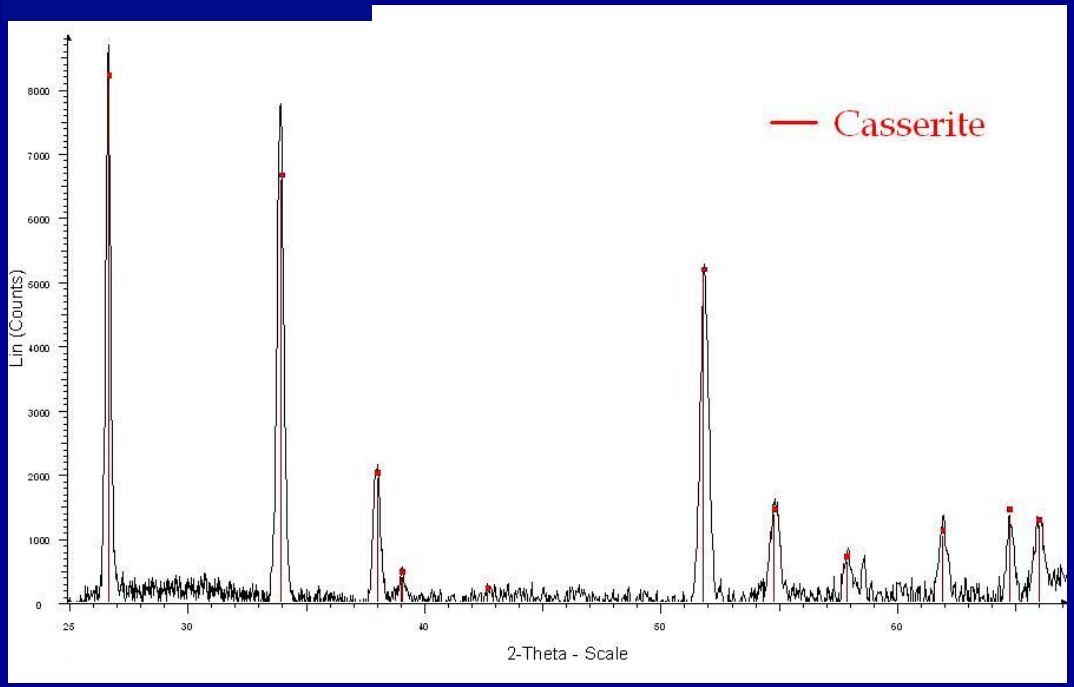
# XRD Mural paintings: dark red

- 40 kV, 700µA, 15 µm Ni filtre
- 5mm x 0.2mm beam size
- 40 minute acquisition time
- Integration over 30°



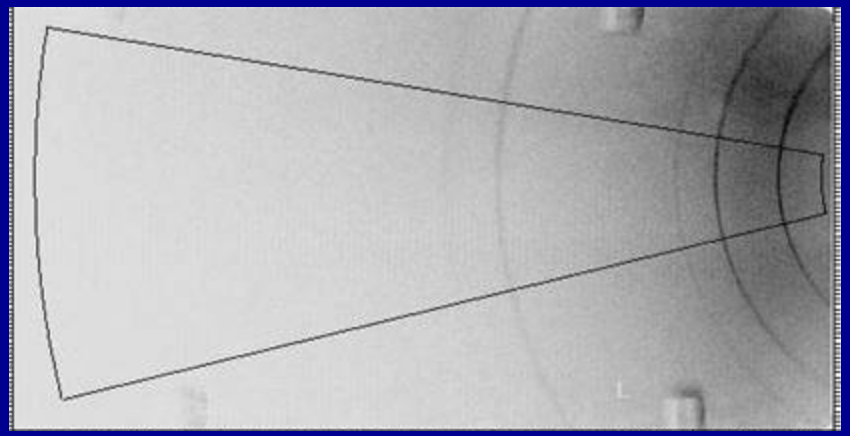

A. Gianoncelli , J. Castaing, L. Ortega, E. Doorhyée, J. Salomon, P. Walter, J.-L. Hodeau, P. Bordet “A portable instrument for in situ determination of the chemical and phase composition of cultural heritage objects” X-ray spectrometry , vol. 37 (2008) 418 – 423.

# Della Robbia shard




blue glaze: only
Cassiterite ($SnO_2$) is observed

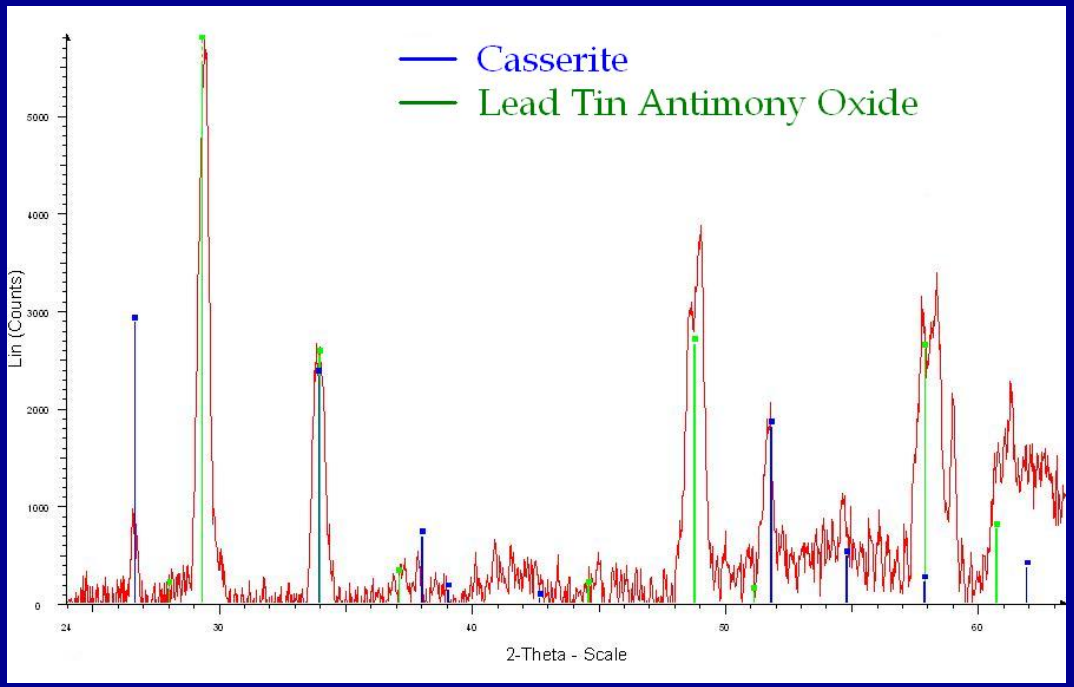
From XRF:
Si, Pb, K, Ca, Fe, Co, Ni, Sn, traces of Cu



A. Gianoncelli, L. Ortega, J. Castaing, E. Dooryhée, J. Salomon, J.-L. Hodeau, P. Walter, P. Bordet, "A portable XRF-XRD instrument for in-situ analysis of Cultural Heritage objects " proceedings of Conservation Science 2007, 10-11 May 2007, Milan, Italy

# Della Robbia shard

Green glaze: Cassiterite and Lead Tin Antimony Oxide



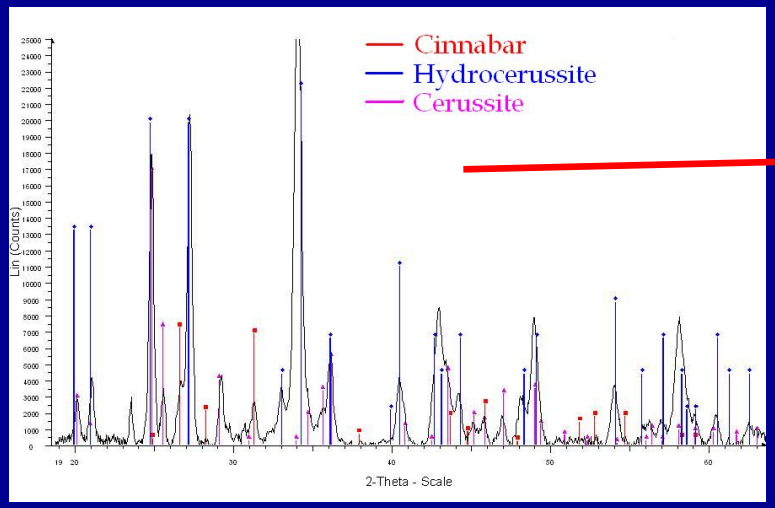

From XRF:

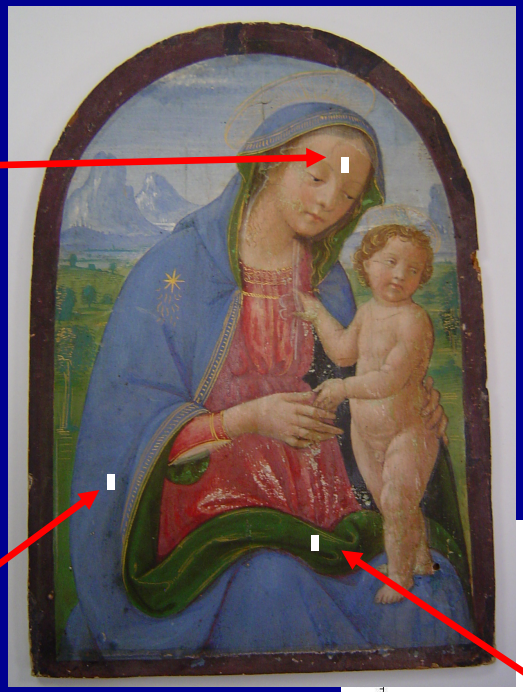
Si, Pb, K, Ca, Fe, Cu, Sn, Sb, As and traces of Zn

A. Gianoncelli , J. Castaing, L. Ortega, E. Doorhyée, J. Salomon, P. Walter, J.-L. Hodeau, P. Bordet “A portable instrument for in situ determination of the chemical and phase composition of cultural heritage objects” X-ray spectrometry , vol. 37 (2008) 418 – 423.

# Painting by Mainardi

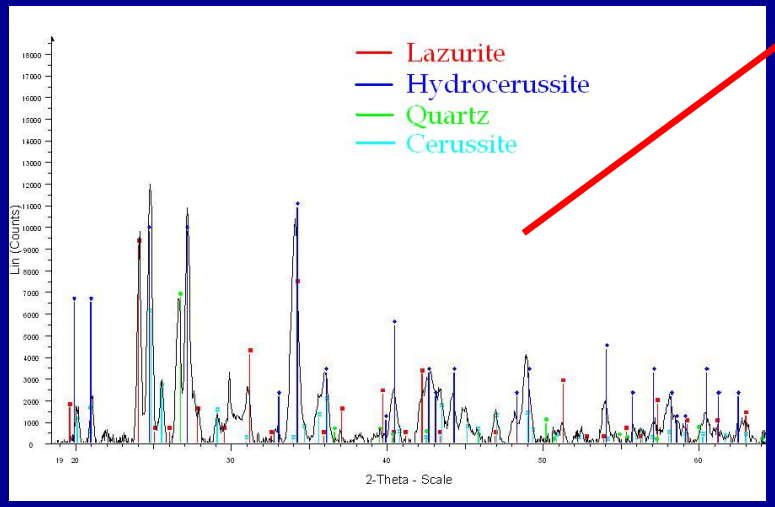
XRF: Pb, Hg, Fe, Ca and traces of Mn, Ti



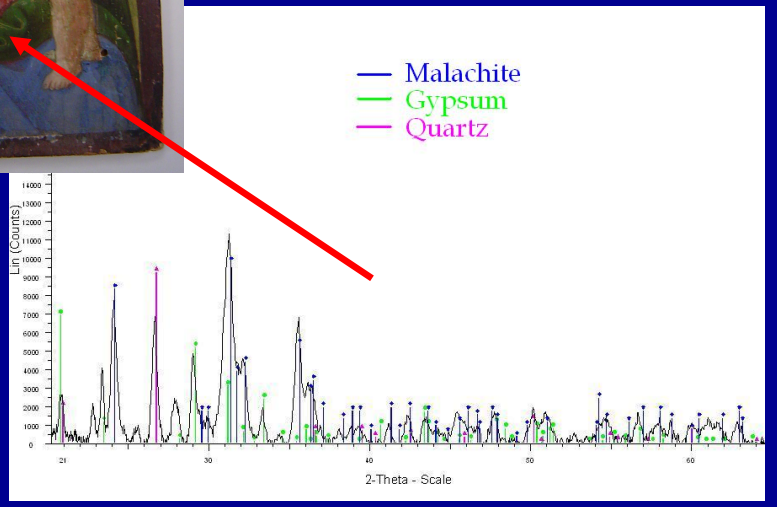



Lazurite:
$(Na,Ca)_8[(S,Cl,SO_4,OH)_2|(Al_6Si_6O_{24})]$

Malachite:
copper carbonate hydroxide mineral,
$Cu_2Co_3(OH)_2$




XRF: Pb, Cu, Fe, Ca & traces of K, Ba, Mn




XRF: Cu, Pb, Fe, Ca, K, Mn & trace of Ba

# C2RMF – CNRS UMR 171

Palais du Louvre - Porte des Lions - 14 quai F. Mitterand, 75001 Paris

*J. Castaing, M. Menu, P. Walter, J. Salomon, T. Guillou, B. Moignard, L. Pichon*

In collaboration with:

L. Ortega, E. Dooryhée, P. Bordet, J.L. Hodeau

(Institut Néel, CNRS & Université Joseph Fourier, Grenoble, France)

CENTRE DE RECHERCHE ET DE RESTAURATION DES MUSÉES DE FRANCE

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Access, Research and Technology for the conservation of the European Cultural Heritage

Nuclear Instruments and Methods in Physics Research A 711 (2013) 106–110

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Technical Notes

# The ICTP-Elettra X-ray laboratory for cultural heritage and archaeology

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ABSTRACT

A set of portable/transportable X-ray analytical instruments based on radiography, microtomography, fluorescence and diffraction have been built and are being operated at the Multidisciplinary Laboratory (MLAB) of the 'Abdus Salam' International Centre for Theoretical Physics (ICTP) in collaboration with Elettra-Sincrotrone Trieste. This is part of a project funded by the Region Friuli Venezia Giulia (Italy) and the ICTP, which aims to develop innovative X-ray analytical tools for noninvasive studies of cultural heritage objects and palaeontological remains. The X-ray instruments at MLAB are also used for hands-on training activities involving students and scientists from developing countries. The MLAB analytical tools complement the microtomography instruments available at Elettra-Sincrotrone Trieste. Examples of our first studies in archaeological and palaeontological applications are presented here.



Research article

X-RAY SPECTROMETRY

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# Energy dispersive X-ray diffraction and fluorescence portable system for cultural heritage applications†

**Ariadna Mendoza Cuevas,[a,b]* Federico Bernardini,[a,c] Alessandra Gianoncelli[d] and Claudio Tuniz[a,c]**

**A portable X-ray diffraction (XRD) and X-ray fluorescence (XRF) system, based on energy dispersive detection in reflection geometry, has been developed for the non-invasive study of cultural heritage materials. This analytical system is an open-work platform based on a low-power miniaturized X-ray tube (Ag anode), a single Si-drift detector, and a set of collimators that have been mounted on a compact and versatile manual or motorized stage, which allows independent and precise angular positioning of both source and detector and the study of complex geometry objects. The design of two instruments and experimental setups, and their advantages are discussed. The XRF and XRD analytical performance has been tested through the analysis of standard reference materials and some applications, including provenance study of obsidian and 'green stone' artifacts, identification of pigments in a model of fresco painting, and chemical element analysis of bones. The main advantages of portable energy dispersive X-ray diffraction systems compared with commonly used angle dispersive X-ray diffraction (ADXRD) instruments are shorter measurement times and compactness. Moreover, optimum XRF spectra can be collected because a polychromatic beam is used instead of a (quasi) monochromatic beam as in an angle dispersive X-ray diffraction-X-ray fluorescence portable system. Results demonstrate that it is possible to identify the main crystalline phases in a measurement time of 100 s–600 s and the system is sensible enough for answering common questions, as the ones presented, in the cultural heritage field.** 

Elettra Sincrotrone Trieste

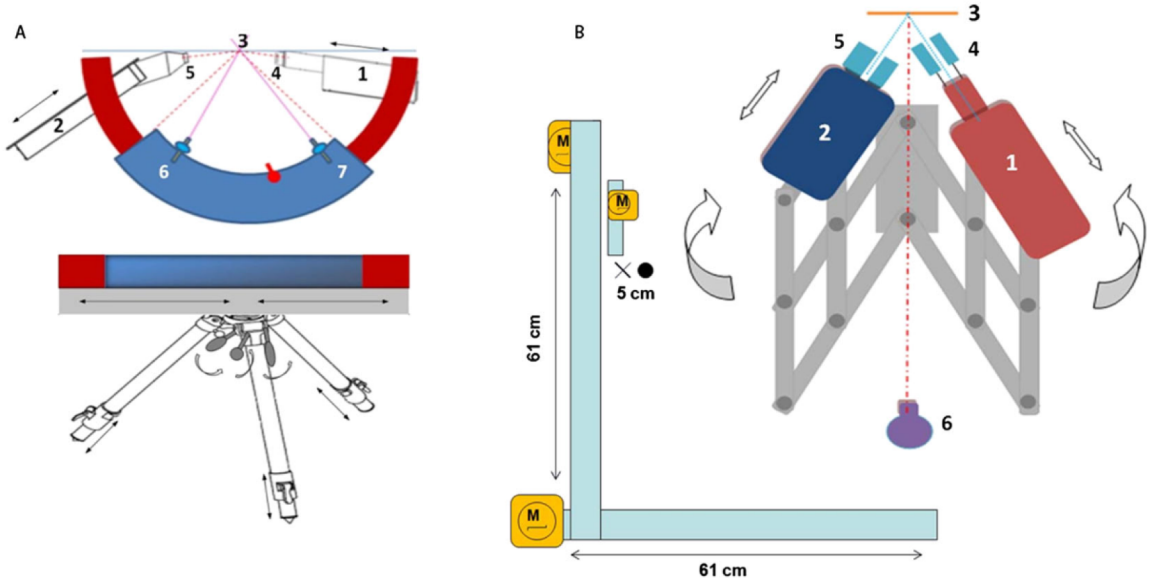


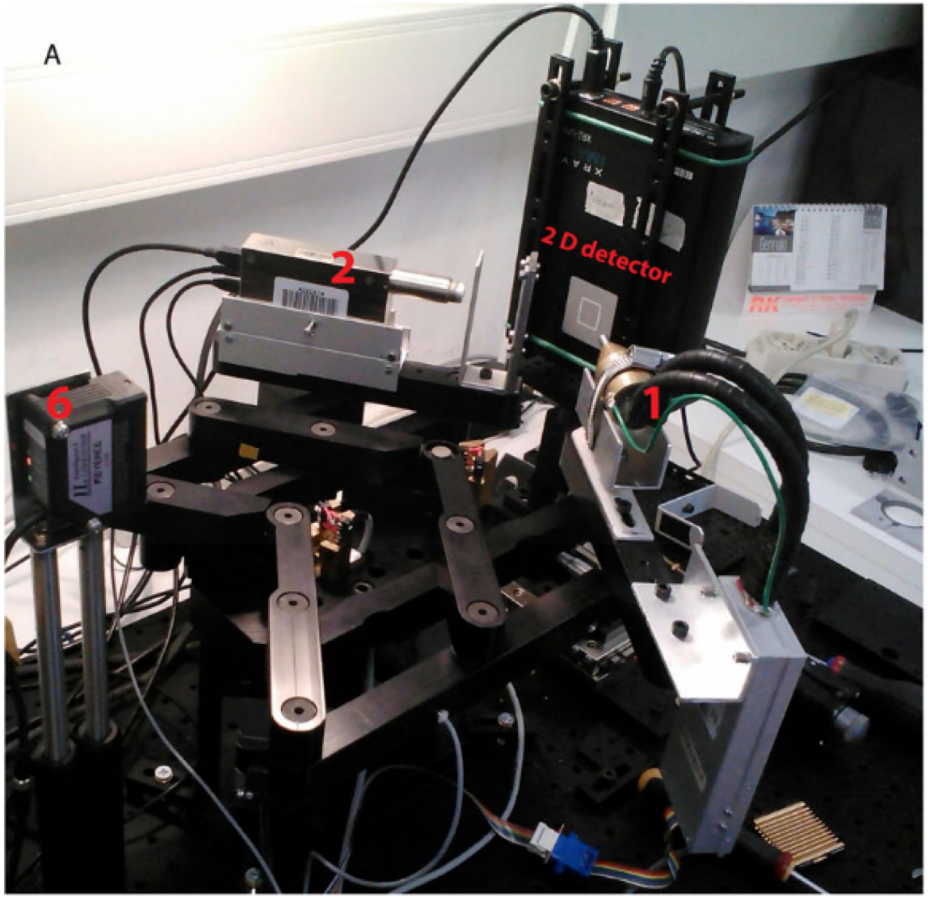

**Figure 1.** Schematic drawing of the measurement head and its support for the first (A) and second Portable ED XRD-XRF system prototypes (B): X-ray tube (1), detector (2), collimators (4 and 5), and lasers (6 and 7). EDXRD, energy dispersive X-ray diffraction

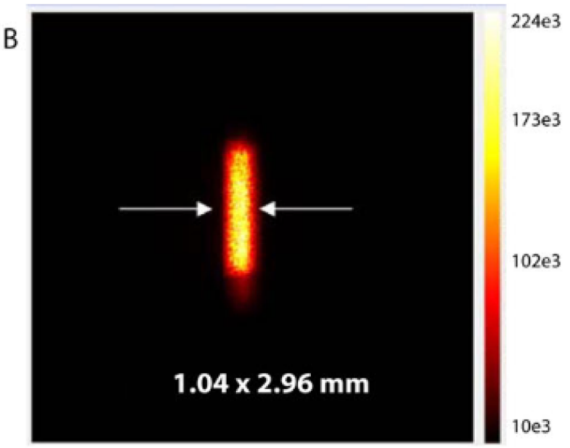
**Table 1.** Portable EDX XRF-XRD systems specifications

| Main features and parameters | First prototype | Second prototype (motorized) |
|---|---|---|
| X-ray tube anode (minimum–maximum voltage, maximum current, anode spot) | Ag (10–40 kV, 100 μA, 2 mm) | Ag (10–50 kV, 200 μA, 400 μm) |
| Weight (g) | 360 | 500 |
| Maximum energy range | Polychromatic beam (0–40 kV) | Polychromatic beam (0–50 keV) |
| Output power (W) | 8 | 10 |
| Beam size (source slit collimator) | 1.2, 0.8 mm (selective slit collimator) | 0–0.5 mm (variable slit collimator) |
| Detector (energy range, Mn −kα FWHM resolution, active area, Be window) | Si-drift (1–120 keV, 125 eV, 27 $mm^2$, 500 μm) | Si-drift (0.5–120 keV, 136 eV, 9 $mm^2$, 450 μm) |
| Detector slit collimation | 0.6 × 3.8 mm | 0–1 × 0–4 mm variable slit collimation |
| Weight (g) | 190 | 190 |
| Goniometer type (minimum step) | Reflecting manual goniometer/ED detector (0.25) | Reflecting automated goniometer/ED detector (0.003) |
| 2 scan range (2 = $_1$ + $_2$) | 3–85° ($_1$ = $_2$ = ) | 0–73° |
| | 0–90°(independently $_1$ and $_2$) | 0–90° (independently $_1$ and $_2$) |
| Measurement head weight | 6 kg (goniometer can be lighter) | 7 kg (goniometer can be lighter) |
| | | 0.4 kg (X-ray tube power supply and controller) |
| Total weight | 9.82 kg (measurement head + tripod) + notebook | 7 kg (associate electronic of motors) |
| | | 14.4 kg (measurement head + associate electronic) + PC |

ED, energy dispersive; EDX, energy dispersive X-ray; FWHM, full width at half maximum; XRD, X-ray diffraction; XRF, X-ray fluorescence

Elettra Sincrotrone Trieste



Elettra Sincrotrone Trieste

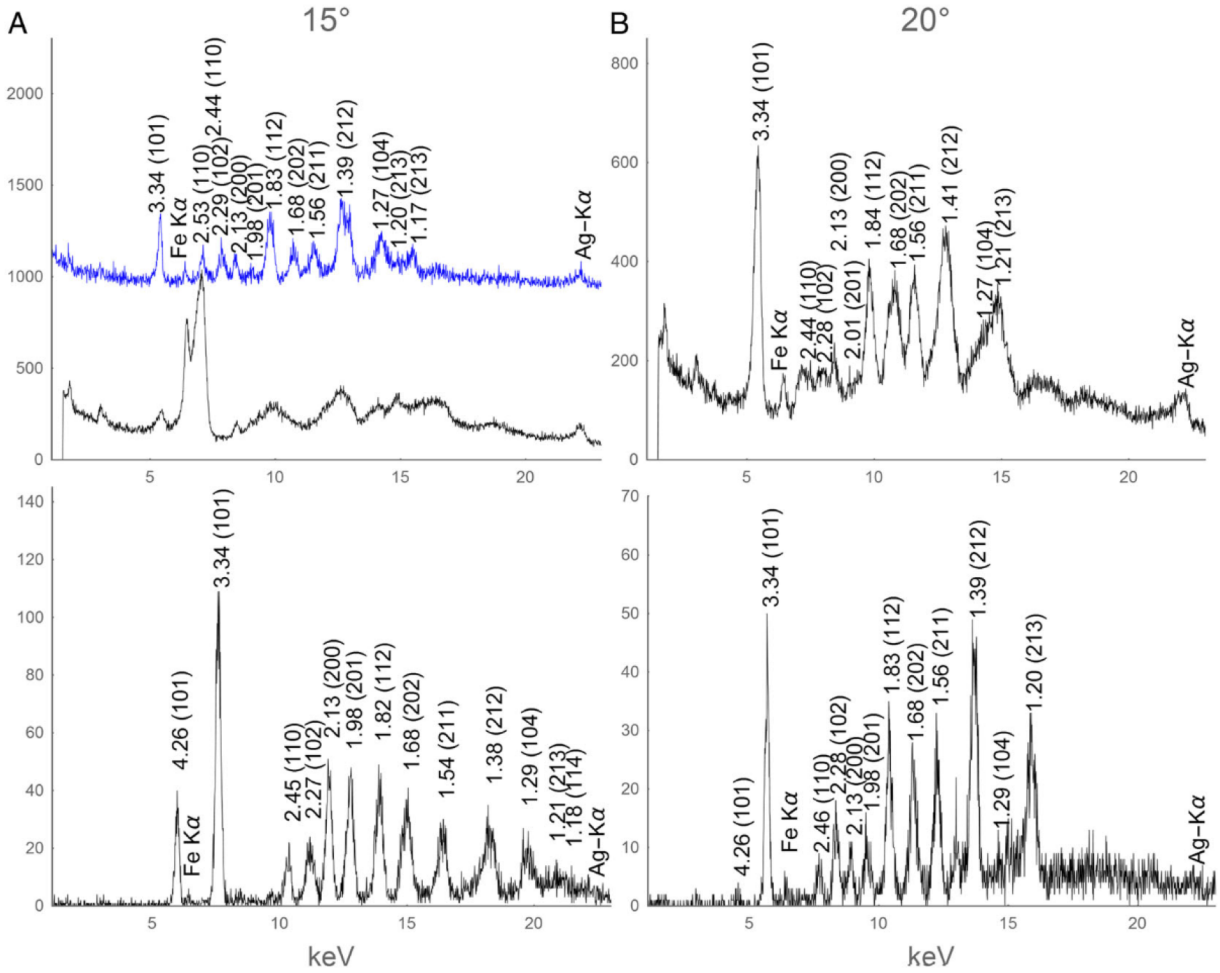



**Figure 3.** The EDXRD diffractogram of quartz acquired with the first (A) and the second (B) prototypes acquired for 400 s (28 kV, 142 μA) and 300 s (28 kV, 300 s), respectively at two different scattering angles (15° and 20°). Values of dobs and reflection index for each peak are indicated. EDXRD, energy dispersive X-ray diffraction

Elettra Sincrotrone Trieste

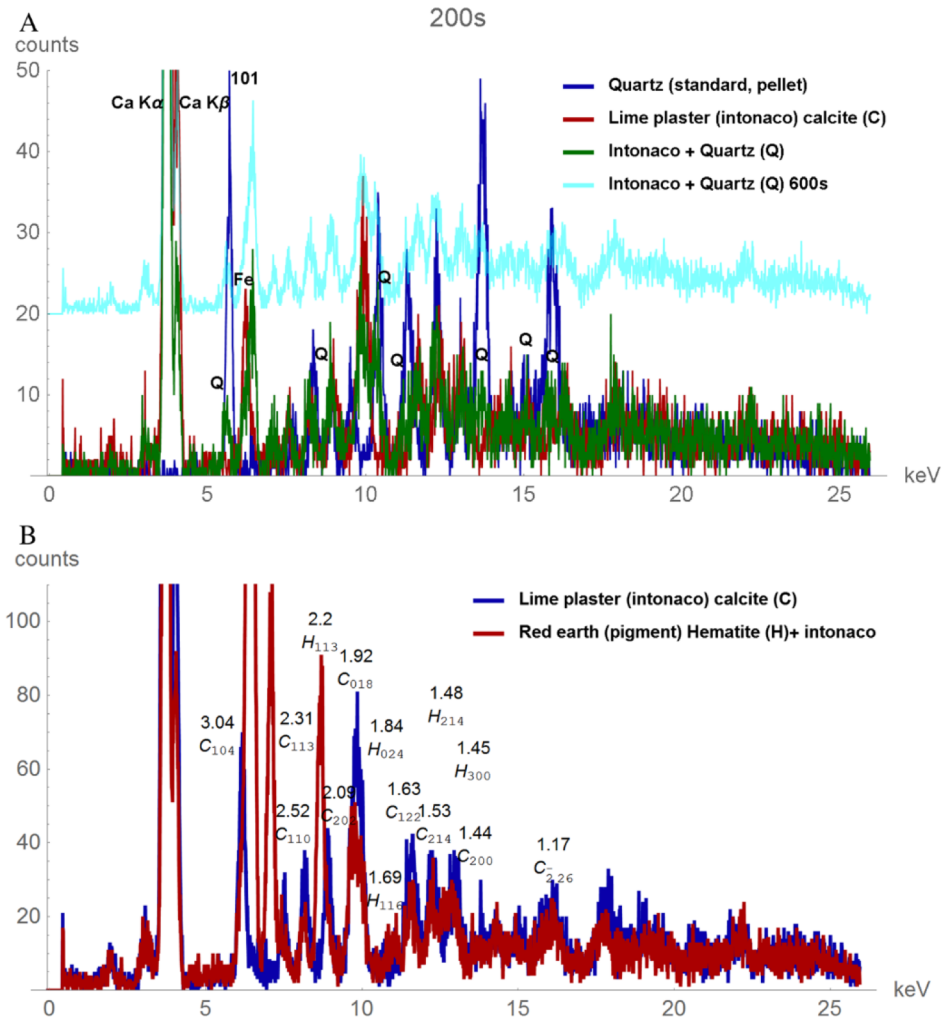



**Figure 7.** The XRD-XRF spectra of a quartz layer (A) and a hematite layer (B) on calcite (*intonaco*) of the modeled fresco in XRD mode compared with quartz-powdered standard and calcite layer spectra. Values of $d_{obs}$ and reflection index for each peak are indicated. XRD, X-ray diffraction; XRF, X-ray fluorescence

Elettra Sincrotrone Trieste

# Conclusions and perspectives

- **Conclusions**:

  - The developed instrumentations proved to be satisfactory in terms of performances with their pros and cons

  - The use of two complementary techniques is helpful: it provides useful information about the analysed sample, helping to better understand its nature and its state of conservation.

- **Further improvements**:

  - XRF signal may affect XRD diagrams: A system of selective filtering is in development and lead to a patent

  - Scanning system to perform not only punctual analysis, but mapping as well