Focusing systems for X-ray micro beam generation: an overview

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Overview

- Review the most used optical systems for X-ray microprobes
- Summarize experiences in research with synchrotron radiation as well as with X-ray tube generators.
- Case studies: glazed ceramics

Overview

- The need for smaller beam spot sizes for various applications and the unique properties of X-rays have induced a remarkable and fast development in X-ray optical systems.
- These focalizing systems can be divided into three main categories:
  - Reflective
  - Diffractive
  - Refractive
- Examples of the three will be covered in this presentation, highlighting the properties that allow having spot sizes down to sub-micrometer.
- An overview of the techniques that use such optical systems will be given, emphasizing their applicability on ceramic case studies.

Reflecting optics

- Mirrors; capillaries

- This category of devices works under the principle of total-reflection. This effect happens when X-rays strike the surface at small grazing incident angles. The critical angle depends on the refraction index of the mirror material, δ:

$$\theta_c = \sqrt{2\delta}$$

Reflecting optics

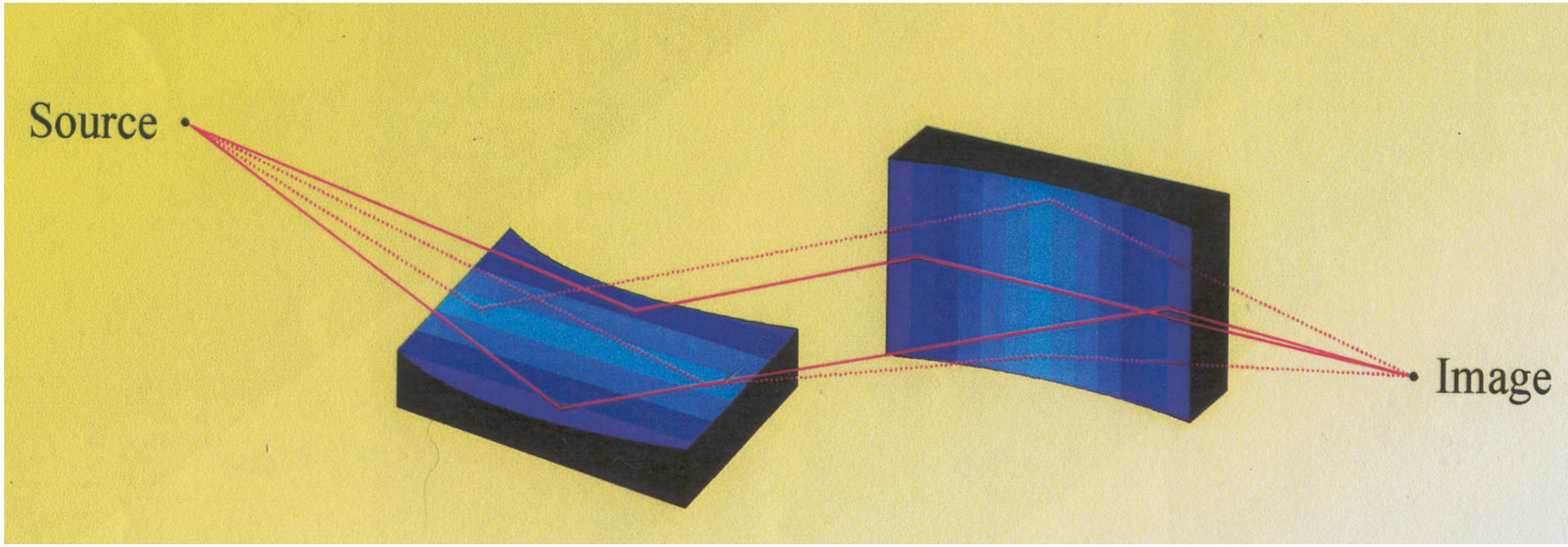
- Mirrors

  - X-ray mirrors can be composed of, gold, palladium or platinum and polished for a surface of high smoothness.

  - Mirrors used with the purpose of focusing an X-ray beam are curved into a certain shape.

  - There are several types of curved mirrors and the distinction is made on the geometry and mirror substrate. The problem of using a single curved mirror is that instead of having one point focus it produces aberration. To overcome this problem, in 1948 Kirkpatrick and Baez introduced an arrangement, which consists of two curved mirrors.

Kirkpatrick - Baez geometry



- The surface of the first mirror is aligned horizontally and the second vertically. The biggest advantage in using mirrors is achromaticity; this means that its reflectivity is basically independent of the X-ray energy for large ranges. However, a disadvantage is the difficult alignment.

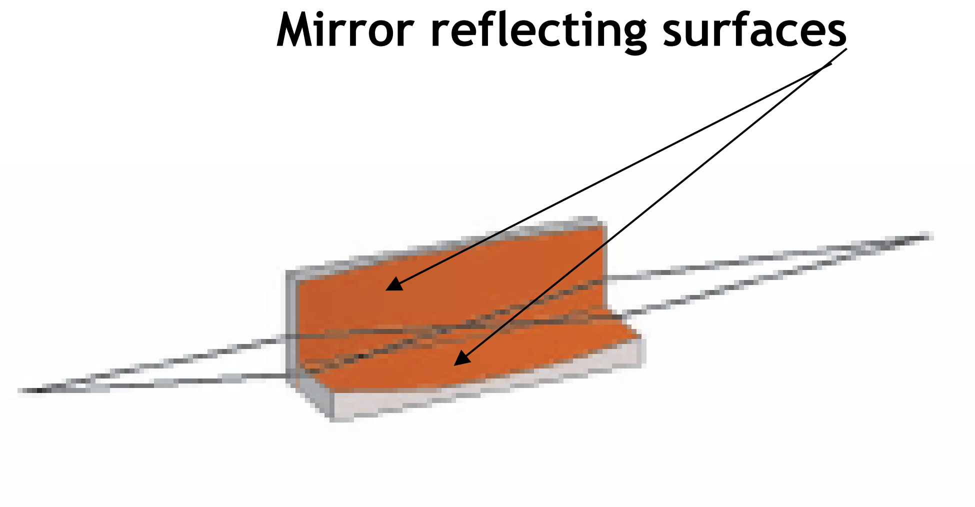
Reflecting optics

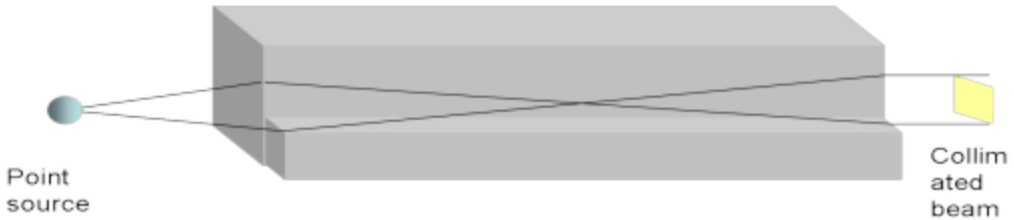
- Recent advances using these optical devices create a new arrangement of K–B mirrors called Montel (or nested) configuration, which allows the collection of larger divergences in the incident beam and focuses it to a nanometer.

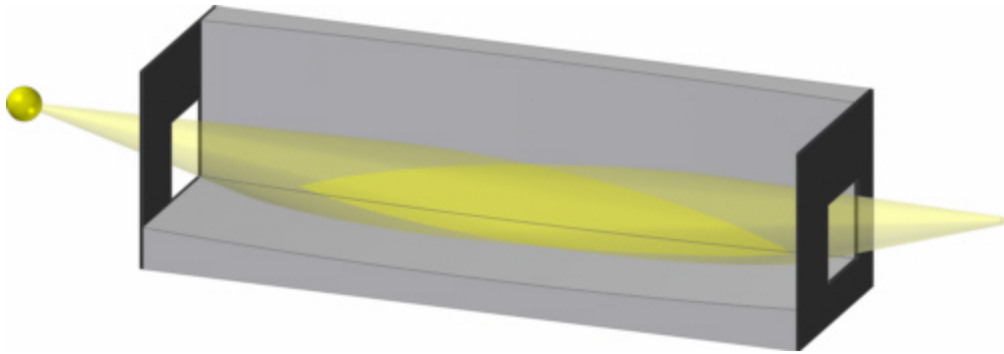
- Montel configuration consists of two mirrors' surfaces mounted side by side at a 90° angle geometry, forming a corner. The authors used a series of thin Au film stripes, as a sample, in order to measure the focal spot. The sample was scanned across the beam at a glancing angle. A doubly focused beam spot of about 150 nm, in both horizontal and vertical directions, was achieved.

- Montel's scheme overcomes the problem of different magnifications of sequential Kirkpatrick-Baez configurations, with the two mutually perpendicular mirrors. Montel optics have two optical surfaces that are coated with laterally graded multilayers (two Göbel Mirrors).

Montel configuration







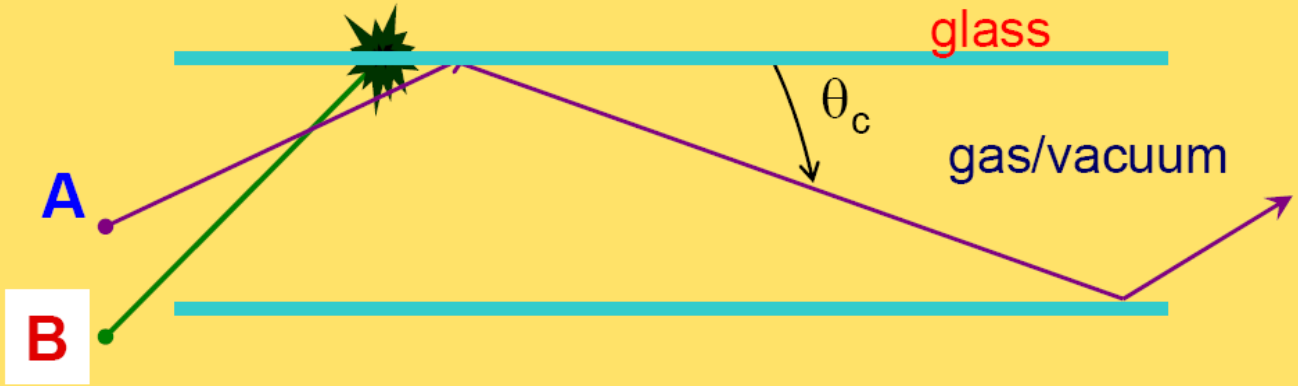
Capillaries

- Capillaries are hollow glass tubes bent into certain shapes to provide focalization. In capillaries the X-rays undergo multiple total reflections, as long as the incident angle at each reflection is less than a critical angle.

$$\theta_c = (mrad) \approx \frac{30}{E(keV)}$$

Total-Reflection

Total External Reflection



Incident photon "**A**" angle ≤ critical angle (θ_c)

Incident photon "**B**" angle > critical angle (θ_c)

<u>for silicate glass:</u>

$$\theta_c\,(mrad) \cong \frac{30}{energy(keV)}$$

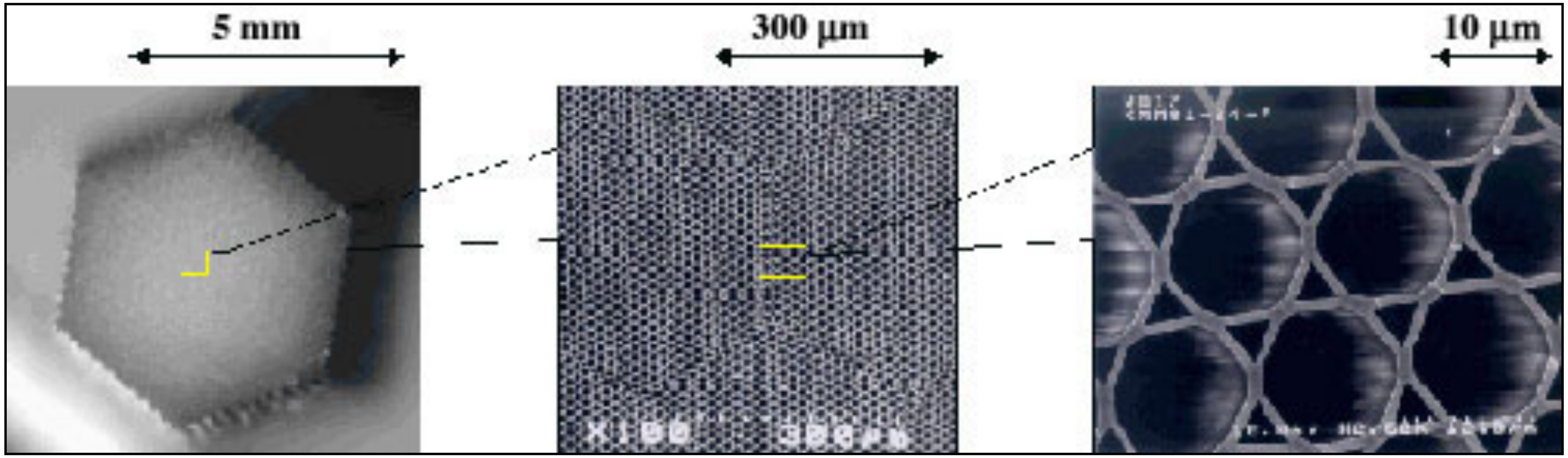
At Cu Kα (8.0 keV)

θc ≈ 3.8 mrad. or 0.22º

At Mo Kα (17.4 keV)

θc ≈ 1.7 mrad. or 0.10º

polycapillary lens

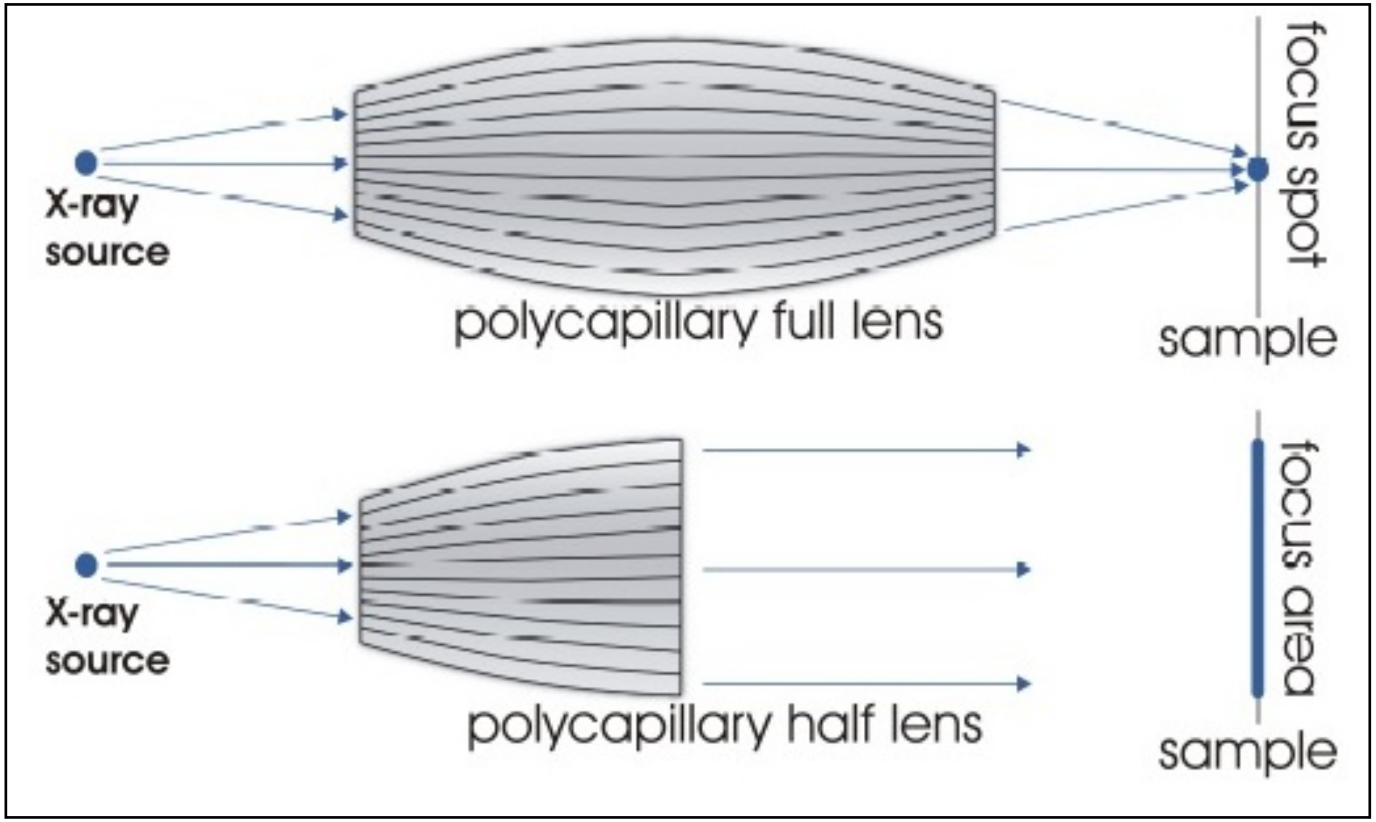


The polycapillary lens consists of over 100 000 monocapillary tubes, which focus the X-ray beam through total-reflection on the inner walls of the individual capillaries to a focal point of about 50 –100 µm diameter.

With this sub-millimetre X-ray beam it is straightforward to perform individual measurements on adjacent materials.

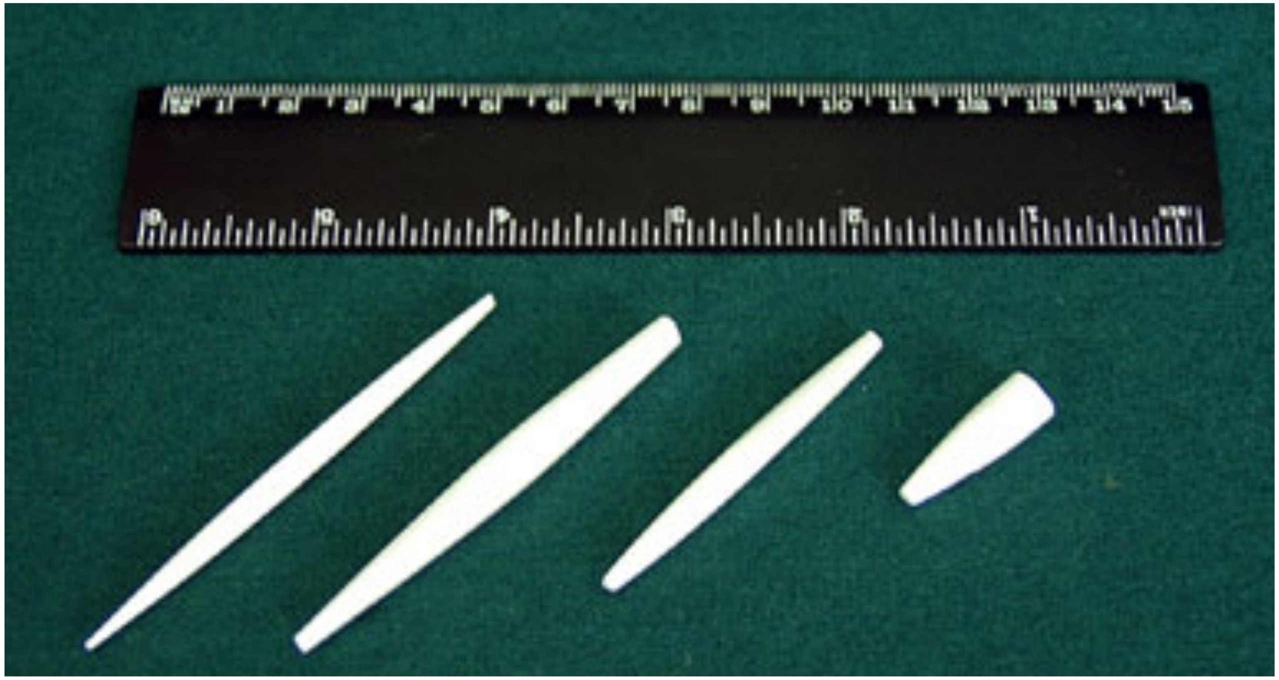
Optics for µ-X-ray Spectrometry

Polycapillary

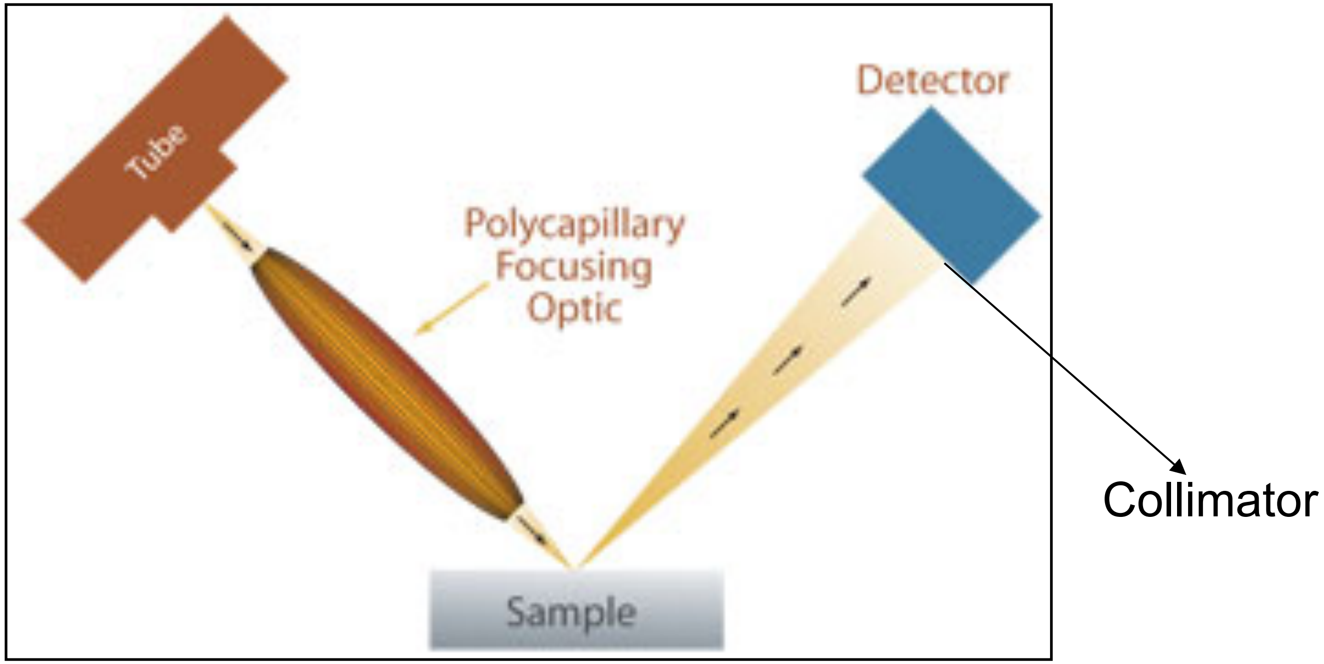


Optics for μ-X-ray Spectrometry

Polycapillaries



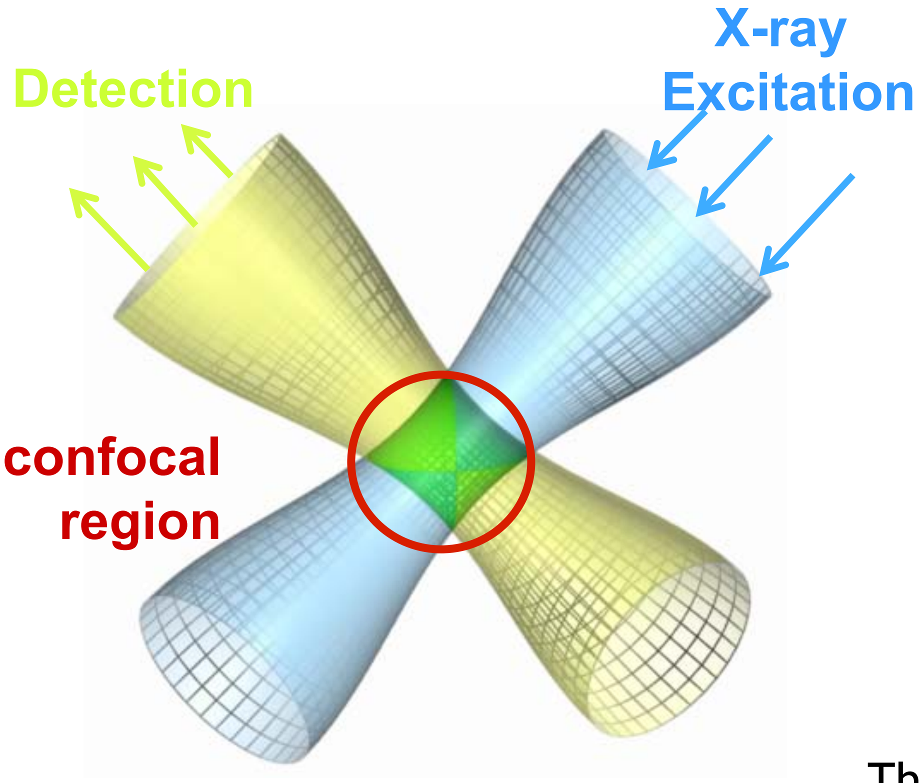
µ-X-ray Fluorescence



µ beam size (10-100 µm) «» µ analysis

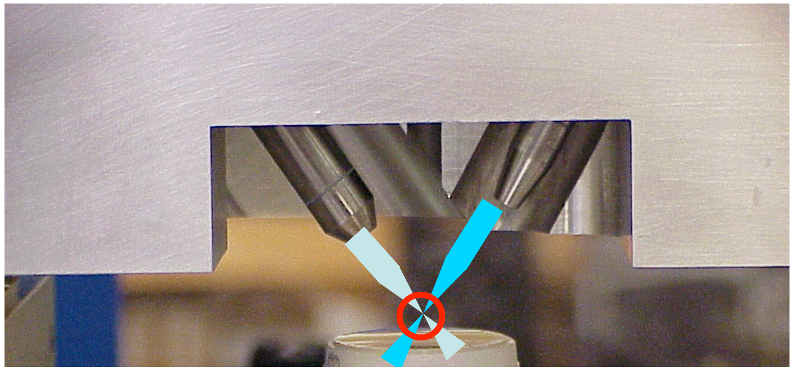
Confocal technique

Confocal μ-XRF



Two polycapillaries

Confocal region: overlap the two focal spots



The overlapping of the two focal spots selects a micro-volume, allowing 3D analysis

Multilayers Curved Crystals

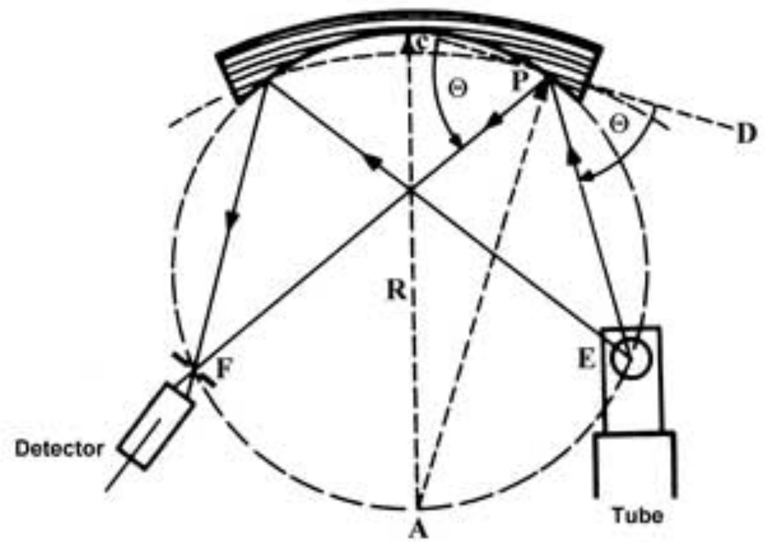
- Multilayers are also included in the reflecting optics group. They use the effect of Bragg-reflection to reflect X-rays.

- A multilayer consists of consecutive alternative high and low Z material layers.

Its periodic arrangement enhances the reflectivity due to the constrictive interference of the multiple reflections that take place at each surface. Different types of crystal curvature are used for focusing.

The most commonly used is the Johansson type.

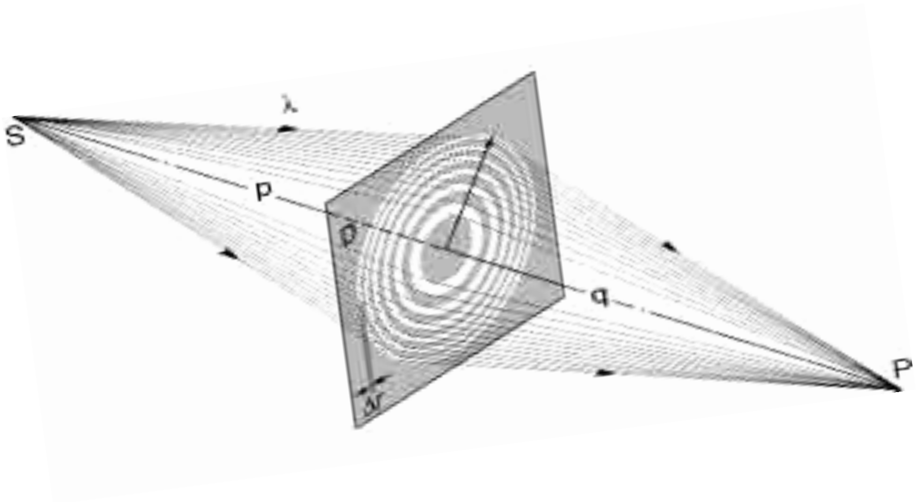
$n\lambda = 2d \sin\theta$ **Bragg's equation**

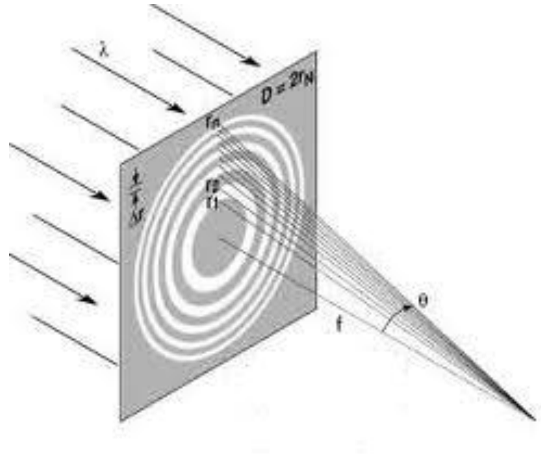


Johansson wavelength spectrometer

Diffracting optics: Fresnel zone plates

- Fresnel zone plates (FZP): concentric rings (called Fresnel zones) alternatively of transparent and opaque materials. These rings are seen as a diffracting grating that causes the incident beam to diffract. To focus the beam in a small spot, the width of the rings d_n has to be in a way that only those X-rays can pass the FZP who contribute constructively at the focal point.





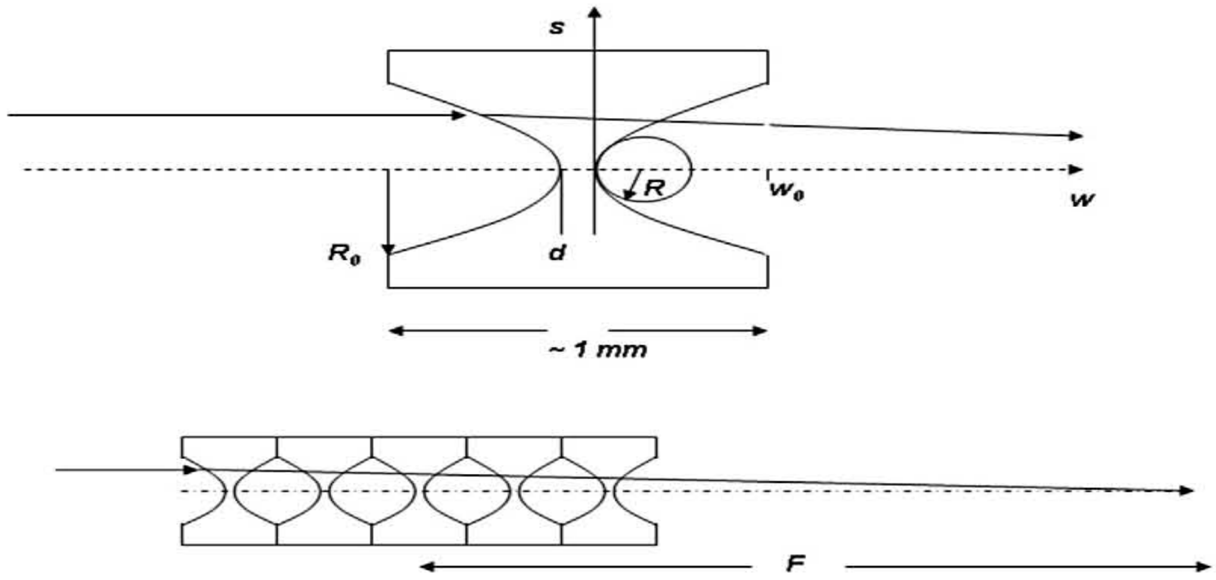
Focusing X-rays with a diffracting zone plate

Refractive optics: Compound Refractive Lenses (CRL)

X-rays are guided by refraction at surfaces between different materials (Snell's law).

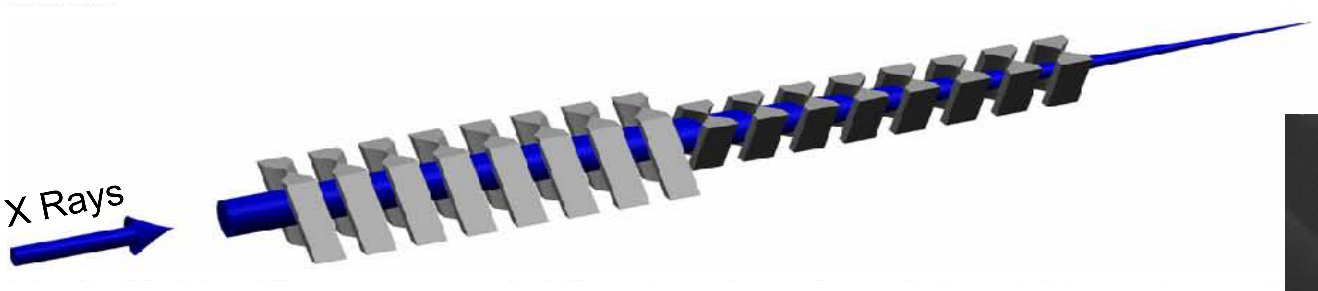
For **X-rays** the difference of the refractive index to one is called **index decrement** δ .

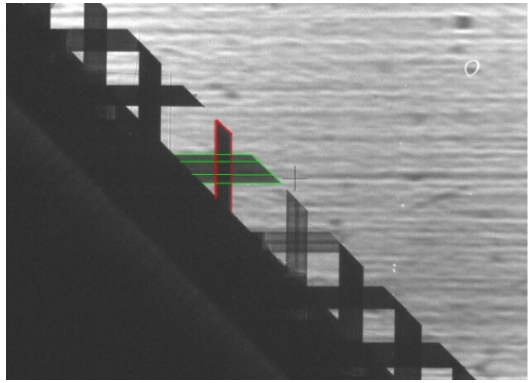
Since $10^{-7}<\delta<10^{-5}$, several well aligned lens elements with **very small radii of curvature** (strong curvature) are needed to form a refractive X-ray lens with a focal length in the range below a meter.



http://www.x-ray-optics.com/index.php?option=com_content&view=article&id=46&Itemid=54&lang=en

Compound Refractive Lenses (CRL)





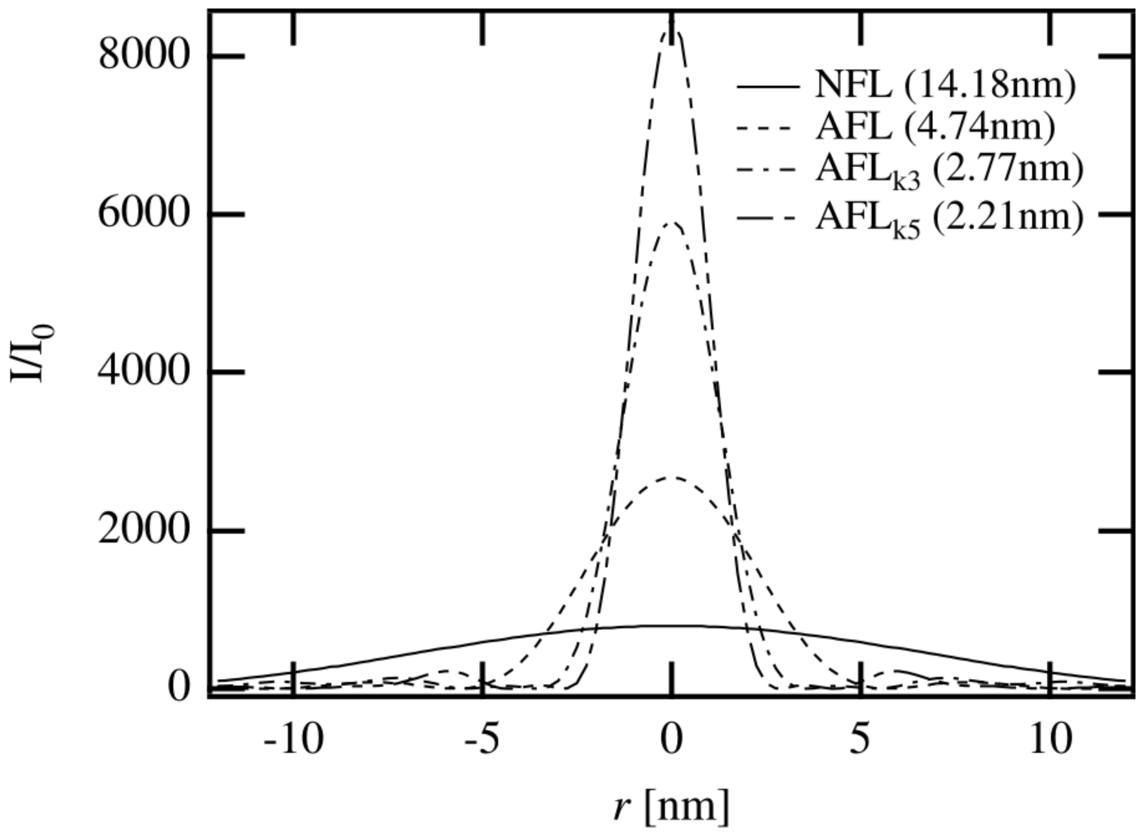
Focusing in the region of some 100 nm possible;

Composed by light elements to provoke little absorption of the radiation;

Focusing of X Rays ranges from 5-200 keV possible;

The energy bandwidth of these lenses is very small and the incident beam needs to be paralel: only provided by synchrotron.

Compound Refractive Lenses (CRL)



Beam profiles at the focal position obtained by wave propagation for:

. NFL (nanofocusing refractive X-ray lenses)
. AFL (adiabatically focusing lenses), and two kinoform AFLs with three (AFLk3) and five (AFLk5) segments, respectively.

The intensity is normalized to the incident on the lens.
For the AFL with one segment, more than 90% of the transmitted radiation is focused. The segment boundaries of the kinoform lens introduce disturbances in the wave field. As a consequence, only about 51% of the transmitted radiation is focused.

Case study

XRF elemental study in glazed ceramics

Ceramics

- We can group ceramics in categories that rely on the chemical composition, firing process or superficial treatment

- The major division is made between glazed and not glazed bodies. This is based on the composition and firing temperature of the ceramic body

- The most common glazes on decorative ancient ceramics are based on tin-lead;

Samples

Ceramic fragments (XVI-XVIII centuries) from two production centers in Portugal (**Coimbra** and **Lisbon**);

Coimbra: faiences and tiles

Lisbon: tiles

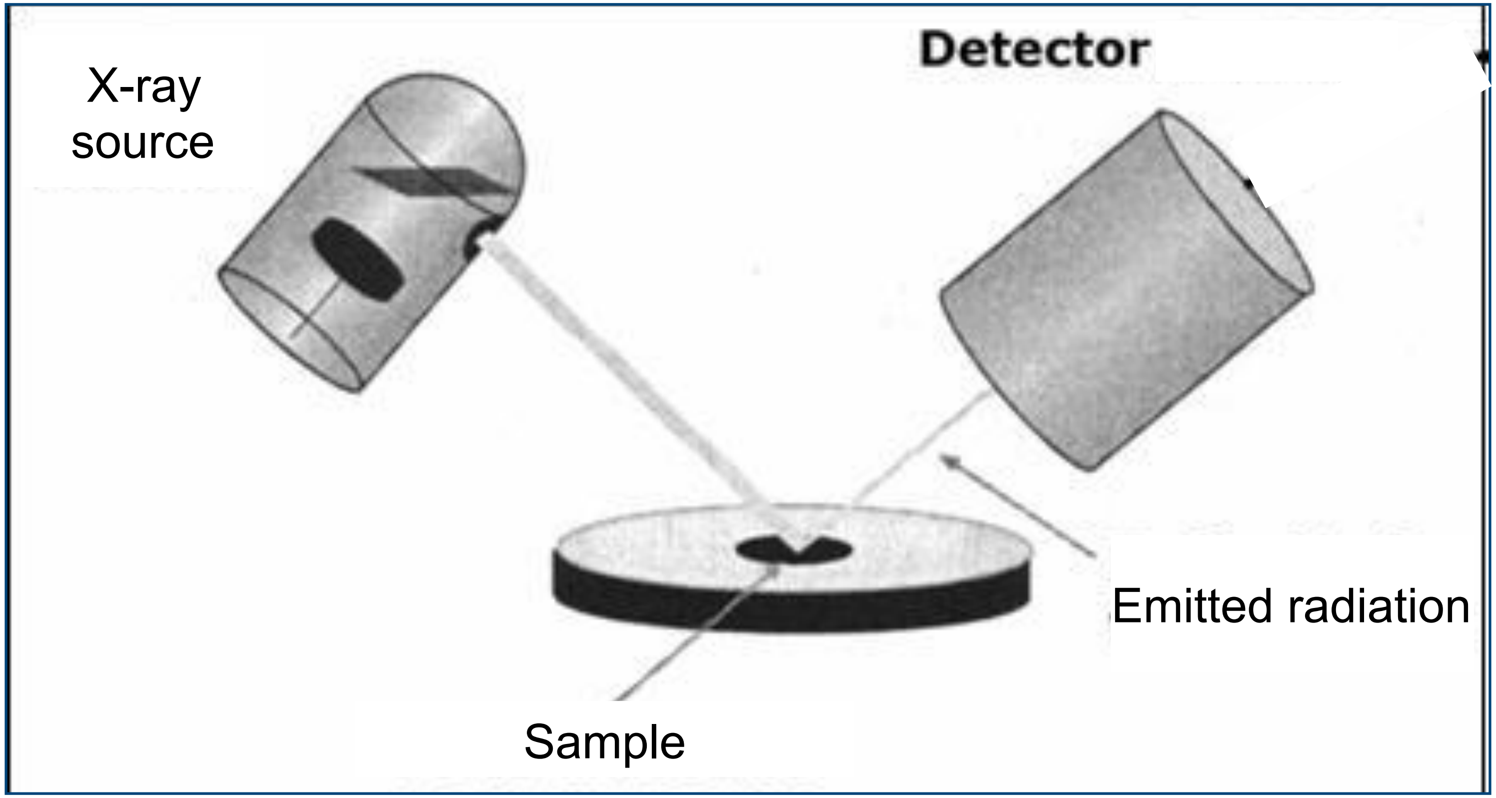
- **Faiences** → glaze thickness up to 200 μm
- **Tiles** → glaze thickness up to 400 μm

The thickness of the system color + glaze can go up to 250 μm for faiences and up to 500 μm for tiles.

In general they are polychrome lead-based glazed ceramics.




X-ray fluorescence technique



X-ray fluorescence technique

- XRF is a surface analysis technique for high elements (Z>13) and the X ray beam is totally absorbed in the glaze layer without reaching the ceramic body. This is a big advantage for these kind of pieces since the major differences between different production centres relay on the glaze and pigment constitution;

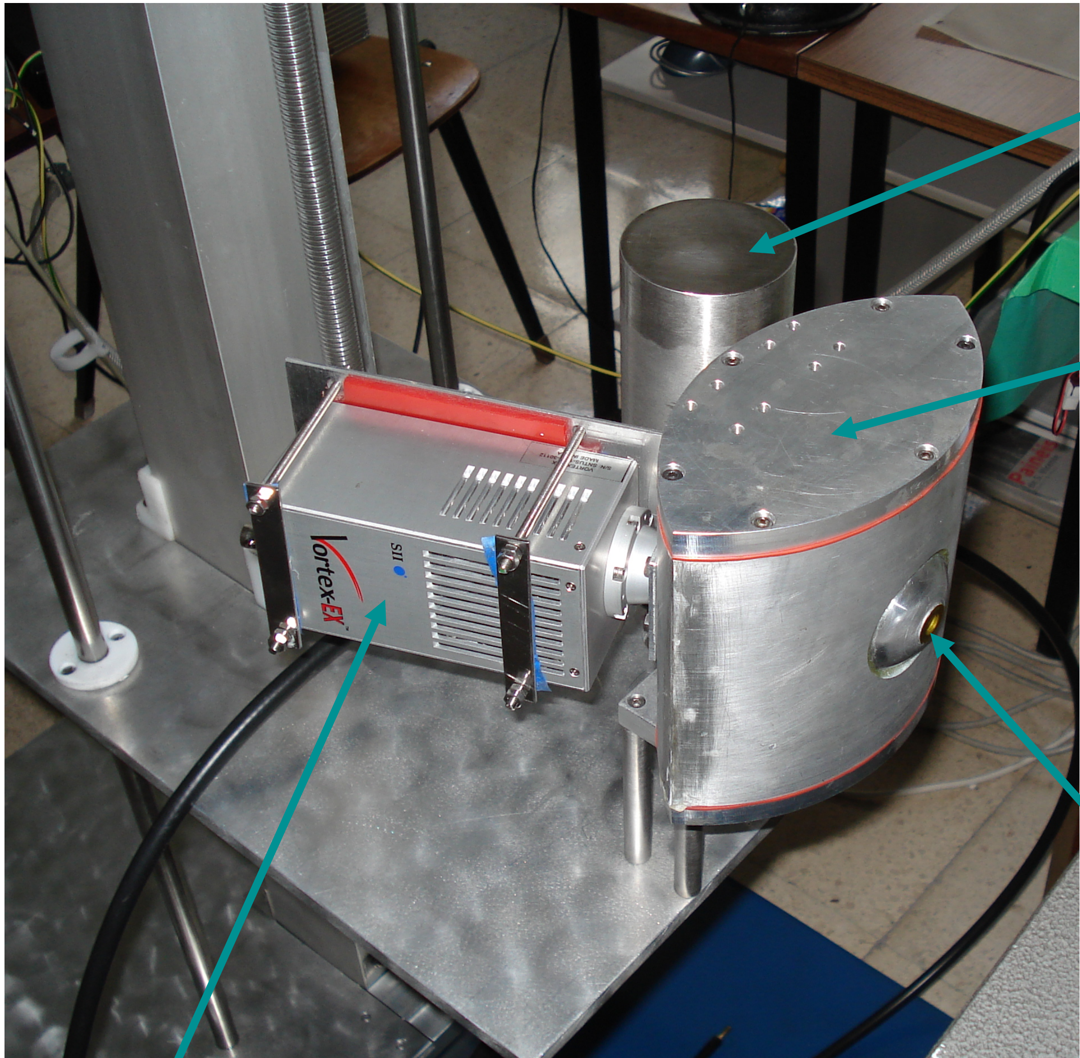
- Non destructive technique and allows μ-X ray beams:

  - Detailed study of small areas of the pieces, in small details of the pigments very close to each other.

  - These details are the “finger-print” of the ceramics

    - ***In situ* analysis of museum pieces**

μ-EDXRF setup (portable)



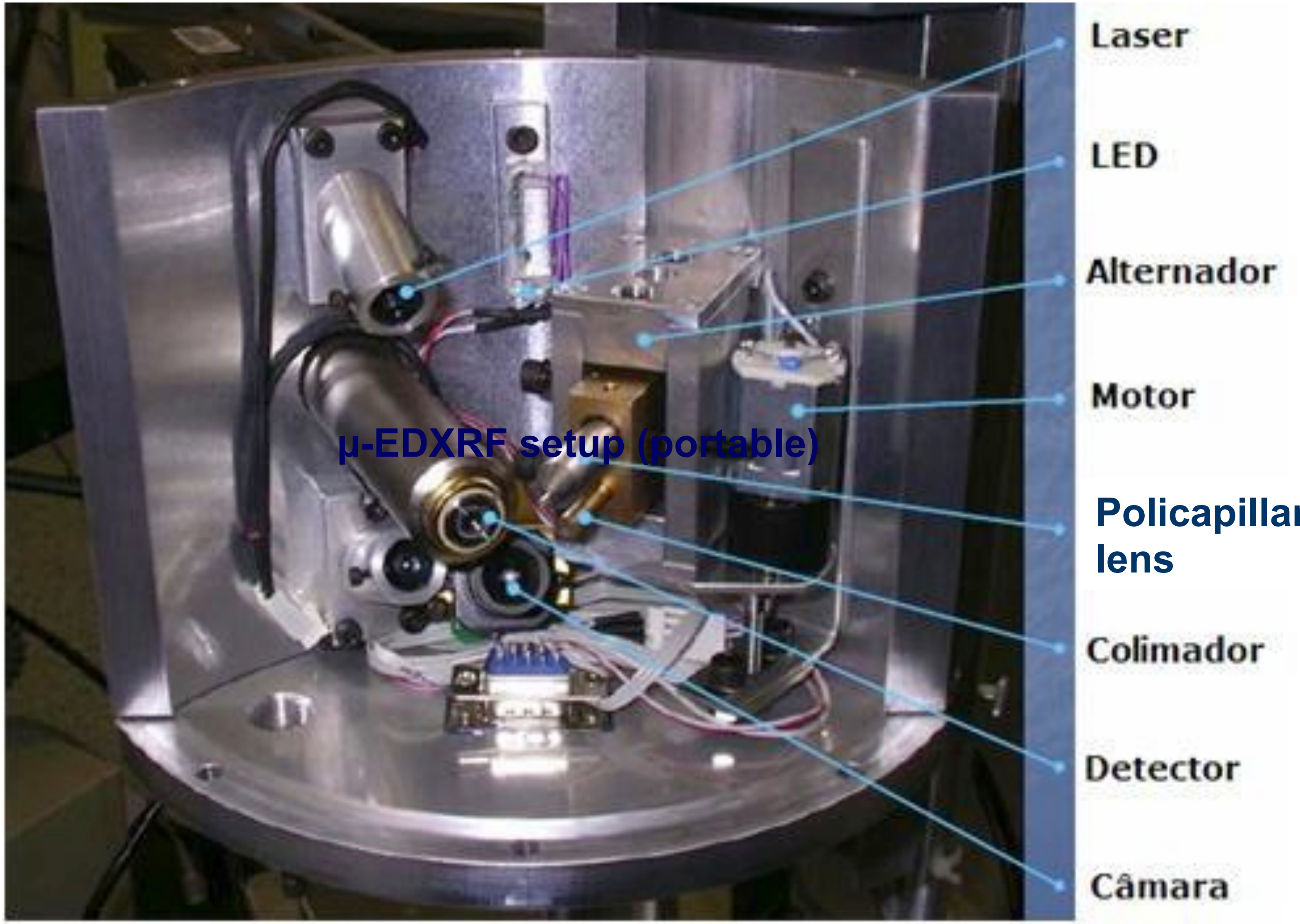
X Ray Source

Vacuum Chamber

Kapton window – Sample positioning

SDD Detector

Policapillary experimental setup

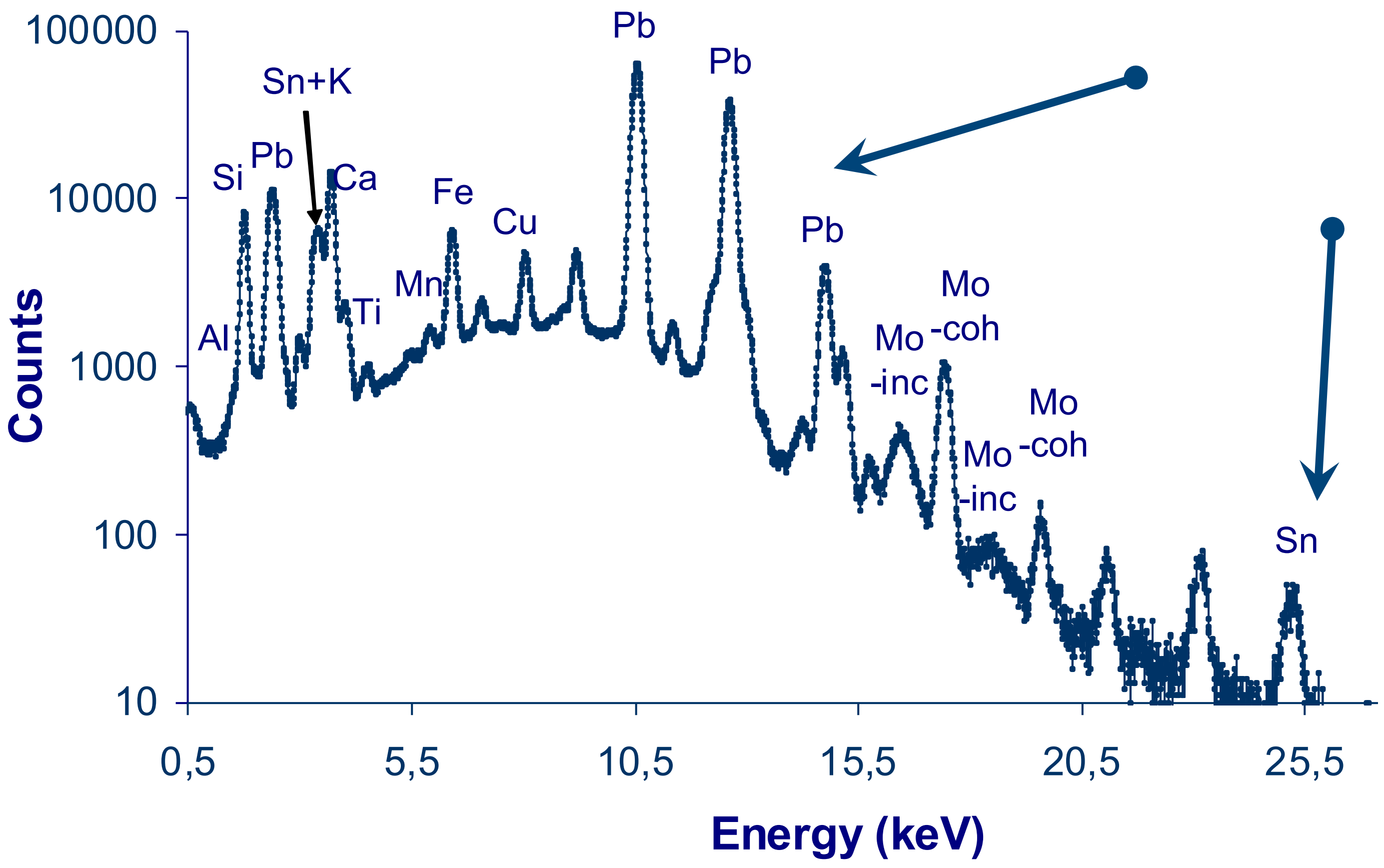


Policapillary: ~ 90 µm
Colimador: ~ 1.2 mm


Vortex-EX

RESULTS: conventional μ-XRF

- **Glaze: it is similar in all analysed samples. Lead-tin type**



See: A.Guilherme et al. “Chemical and mineralogical characterization on glazes of ceramics from Coimbra (Portugal) from XVI-XIX centuries” Anal. Bioanal. Chem. 2009. 395(7): 2051-2059

μ-XRF Results

Colours:

The blue: mainly due to the presence of **Co**.

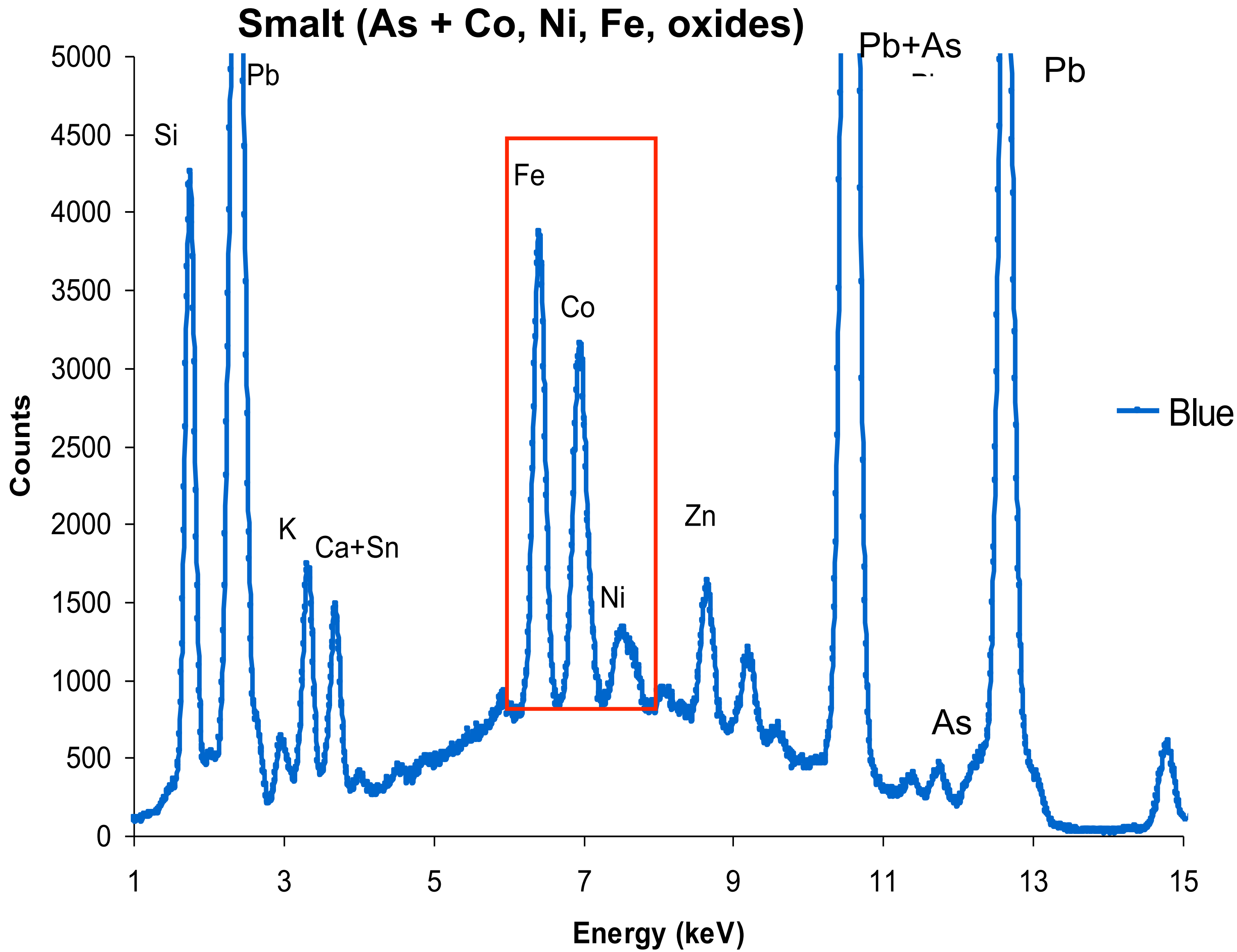
(previous works have shown that the pigment comes from a source of

Smalt

Fe-Co-Ni-As are found in every spectra.

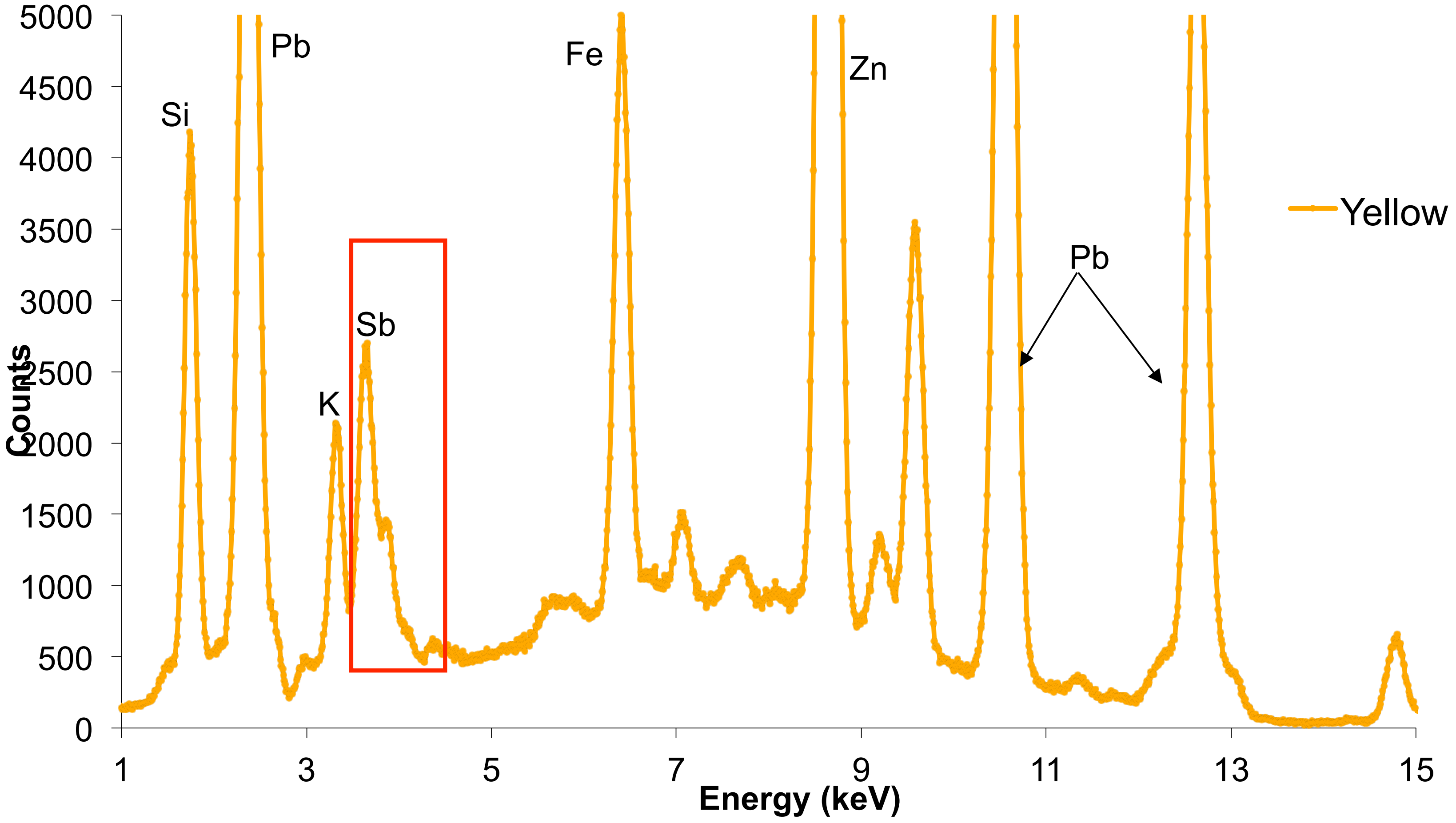
[1] *A.Guilherme et al., X-ray fluorescence (conventional and 3D) and scanning electron microscopy for the investigation of Portuguese polychrome glazed ceramics. Spectrochmica Acta B, (2011) 65(5), 297-307.*

Blue colour


Smalt (As + Co, Ni, Fe, oxides)
Counts
Energy (keV)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1
3
5
7
9
11
13
15
Si
Pb
K
Ca+Sn
Fe
Co
Ni
Zn
Pb+As
As
Pb
Blue

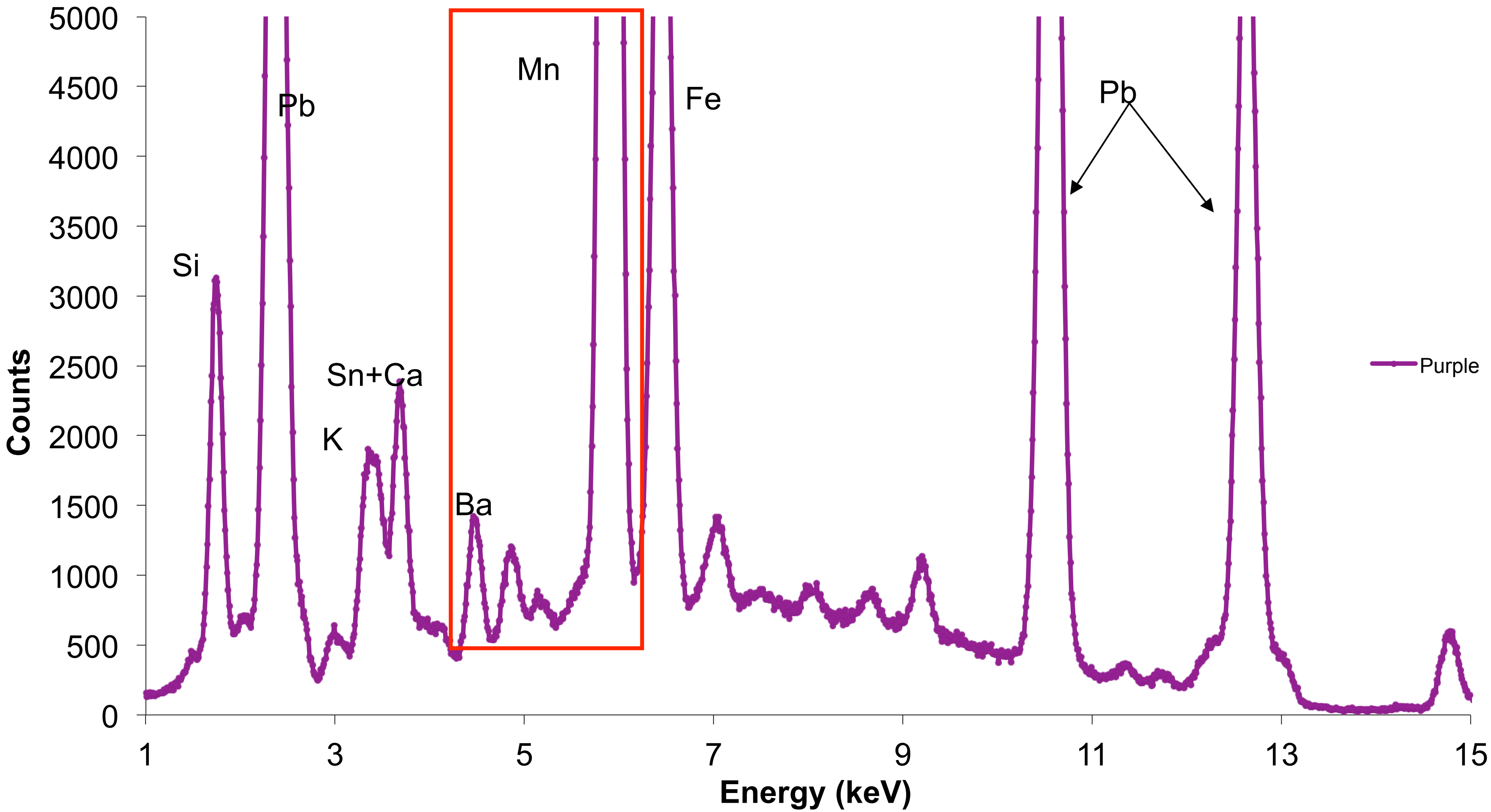
Yellow

The yellow: a compound with **Sb** and **Pb** (Naples' Yellow: $Pb_2Sb_2O_7$)
Sb-Lα and **Pb-Lα** were monitored.



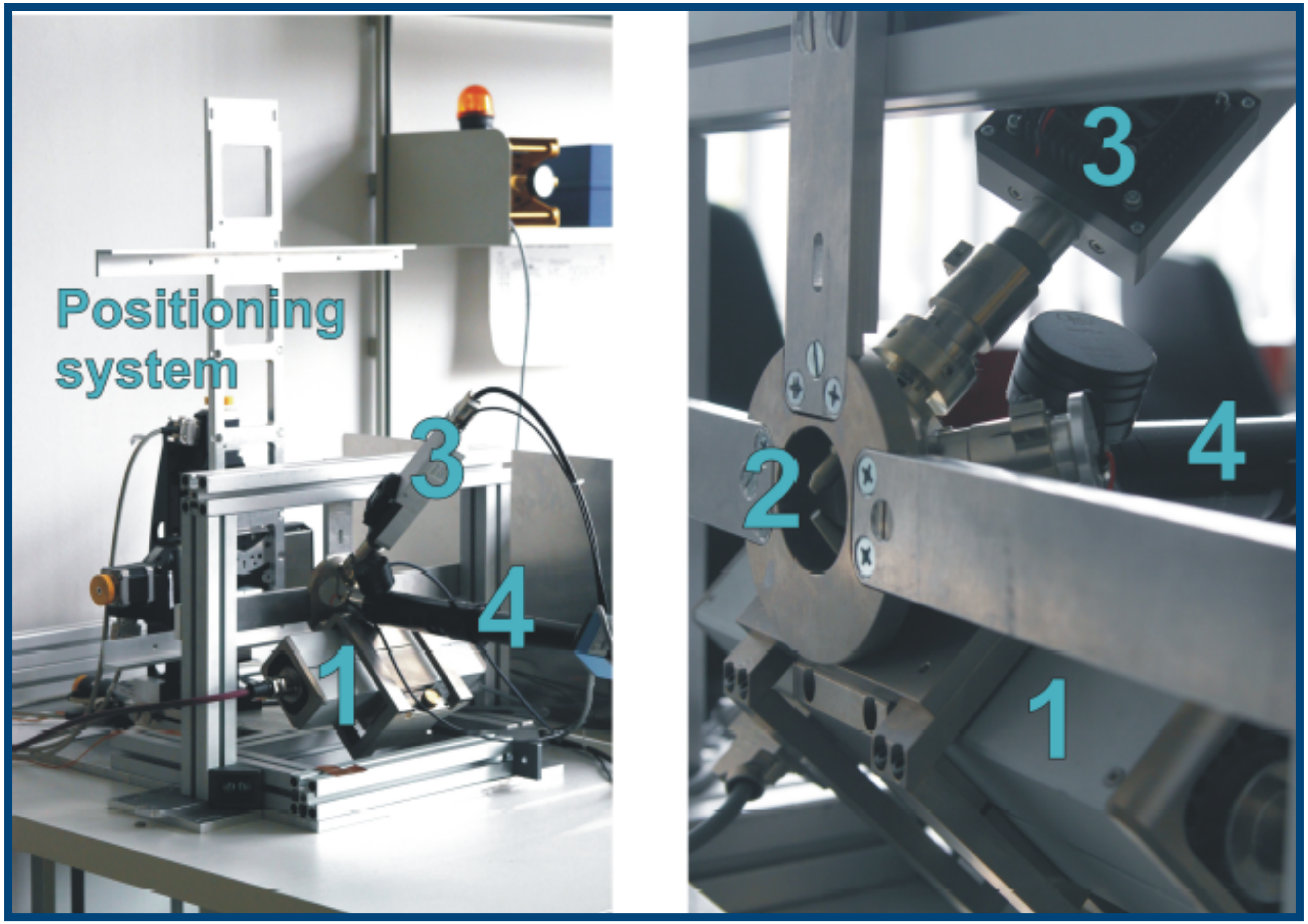
Purple

Psilomelane Barium Manganese Oxide Hydroxide also known as black hematite $[(Ba,H_2O)_2Mn_5O_{10}]$



Confocal technique

Experimental set up: 3D μ-XRF



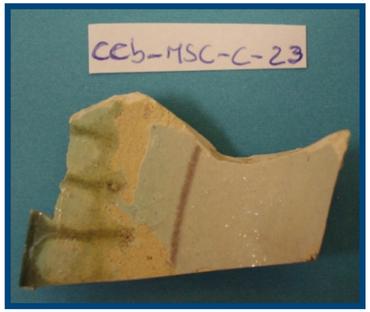
1 – X Ray tube;

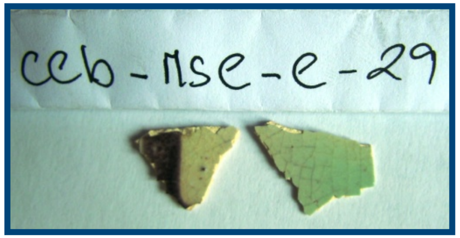
2 –Polycapoillary lenses

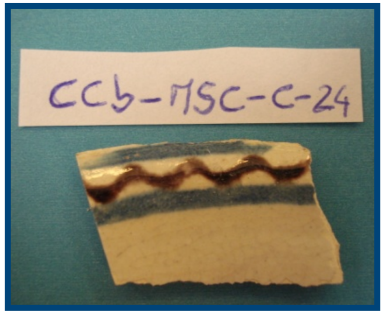
3 – Detector SDD
4 – Microscope with camera
5 – Positioning system

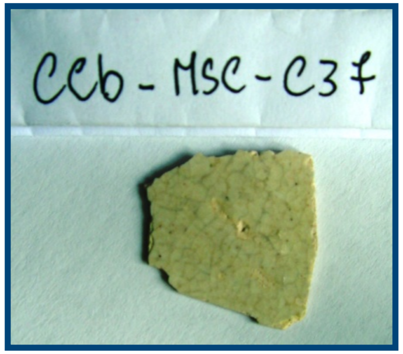
Glazed ceramic: small pieces of identified samples

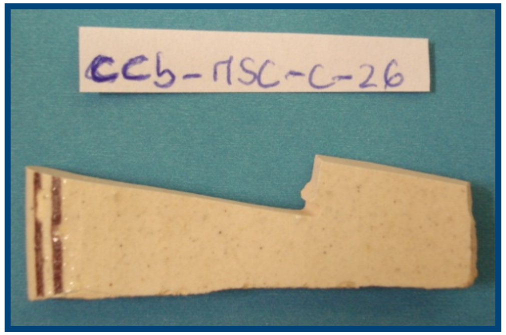
Coimbra



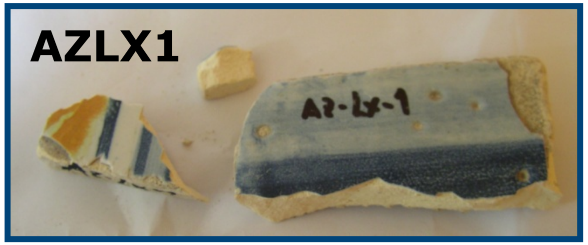


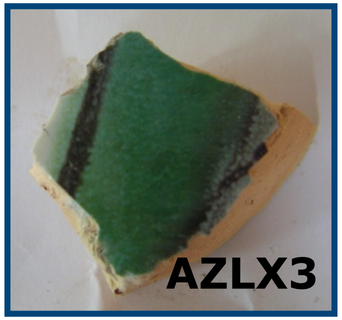






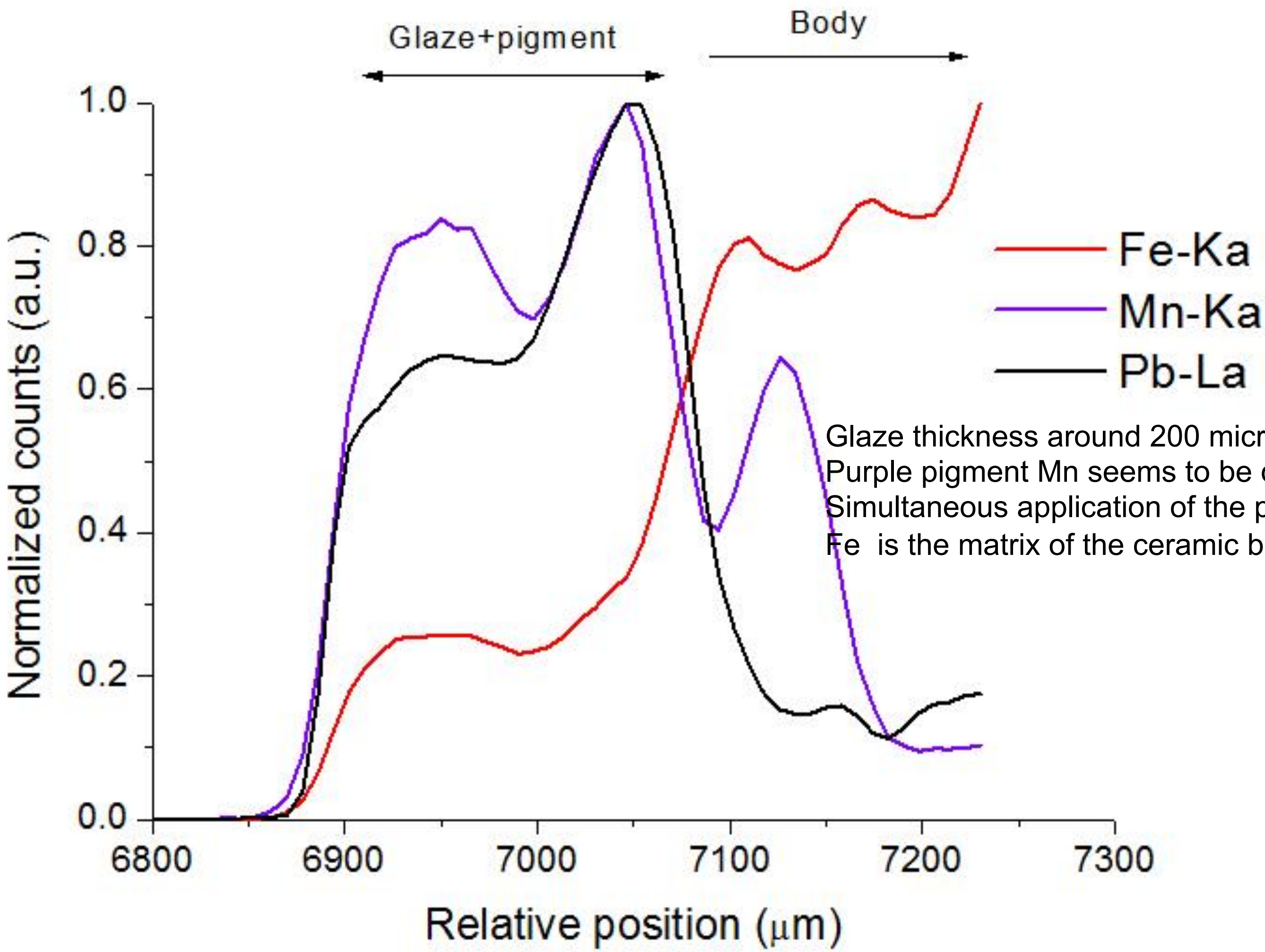
Lisbon



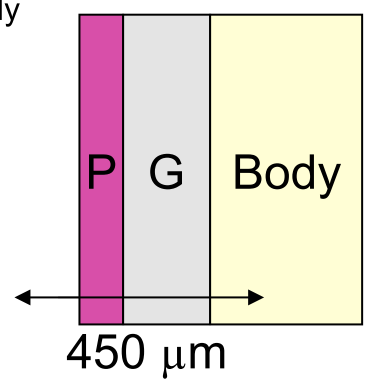


RESULTS: 3D μ-XRF

- **Lateral scans: perpendicular to the cross section of the sample.**



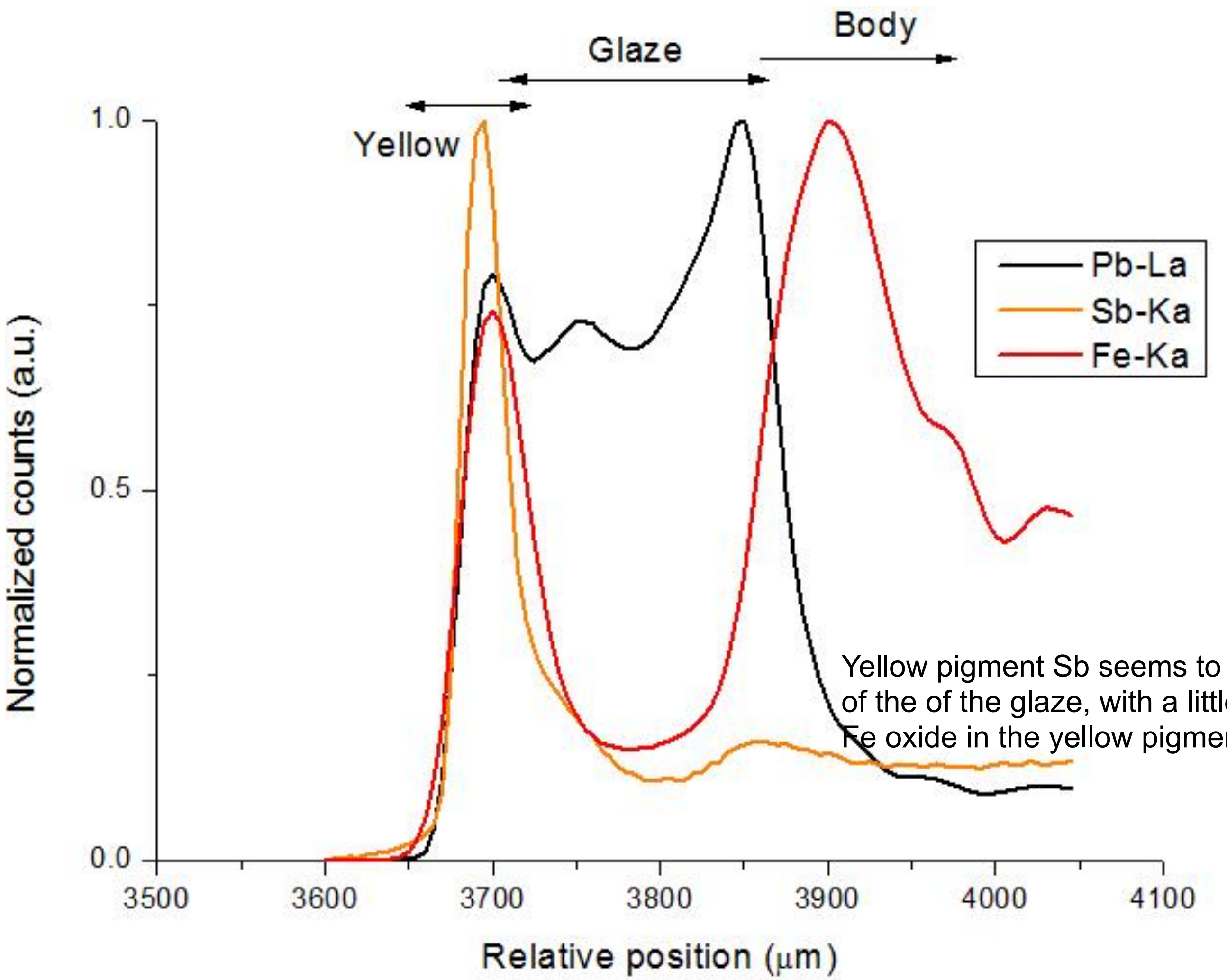
Glaze thickness around 200 microns corresponding to Pb distributior
Purple pigment Mn seems to be diffused into the glassy matrix
Simultaneous application of the pigment and glaze: One firing proces
Fe is the matrix of the ceramic body

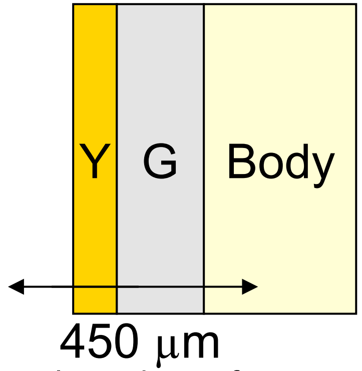


PURPLE

YELLOW: 3D µ-XRF

- **Lateral scans**

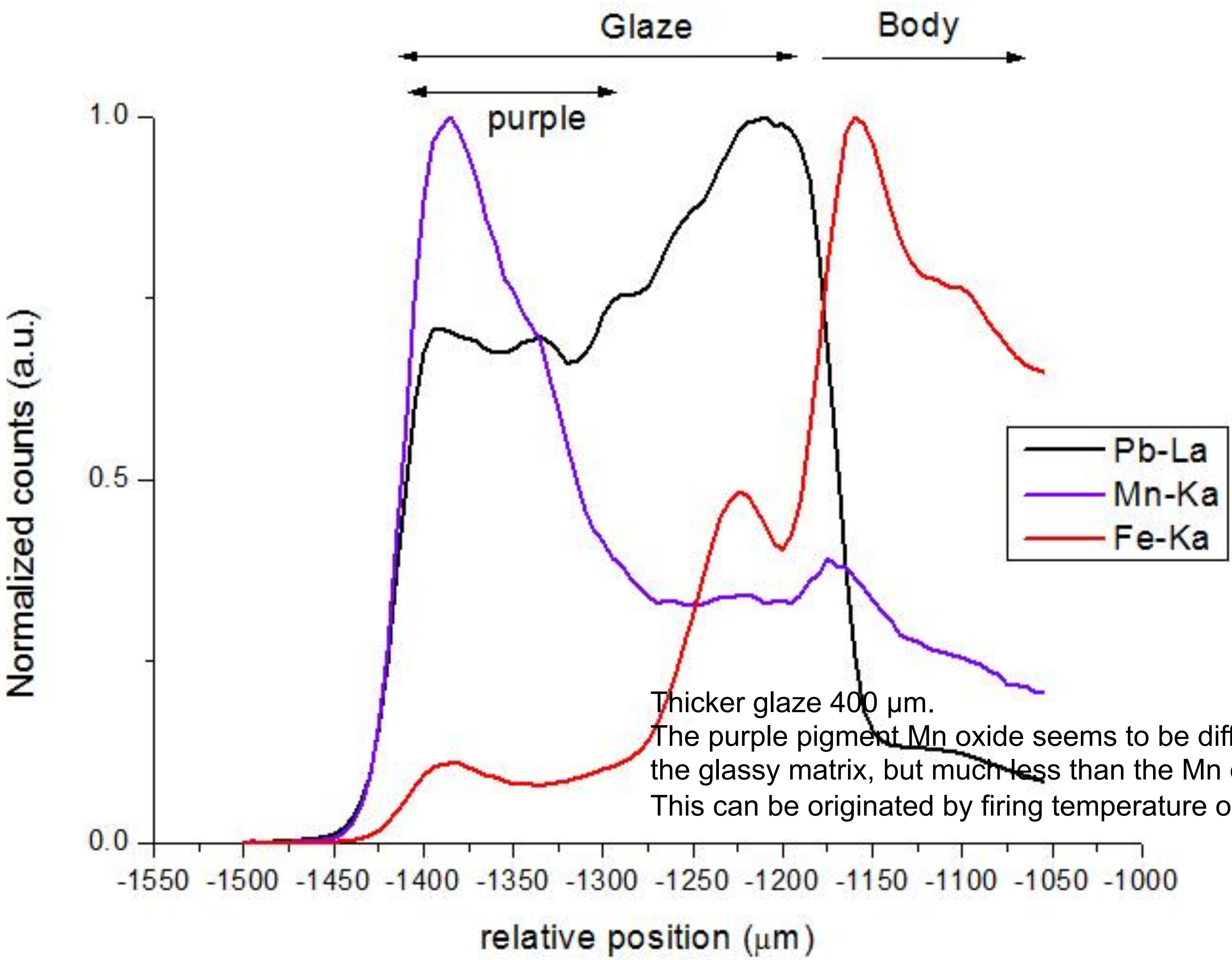




Yellow pigment Sb seems to remain mostly on the surface of the of the glaze, with a little diffusion into the glaze.
Fe oxide in the yellow pigment and again existing in the ceramic body

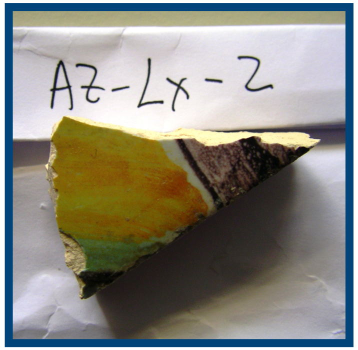
PURPLE: 3D µ-XRF

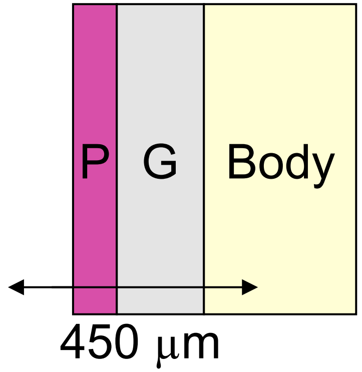
- **Lateral scans**



Thicker glaze 400 µm.
The purple pigment Mn oxide seems to be diffused into the glassy matrix, but much less than the Mn of the sample from Coimbra.
This can be originated by firing temperature or the viscosity of the glaze is higher

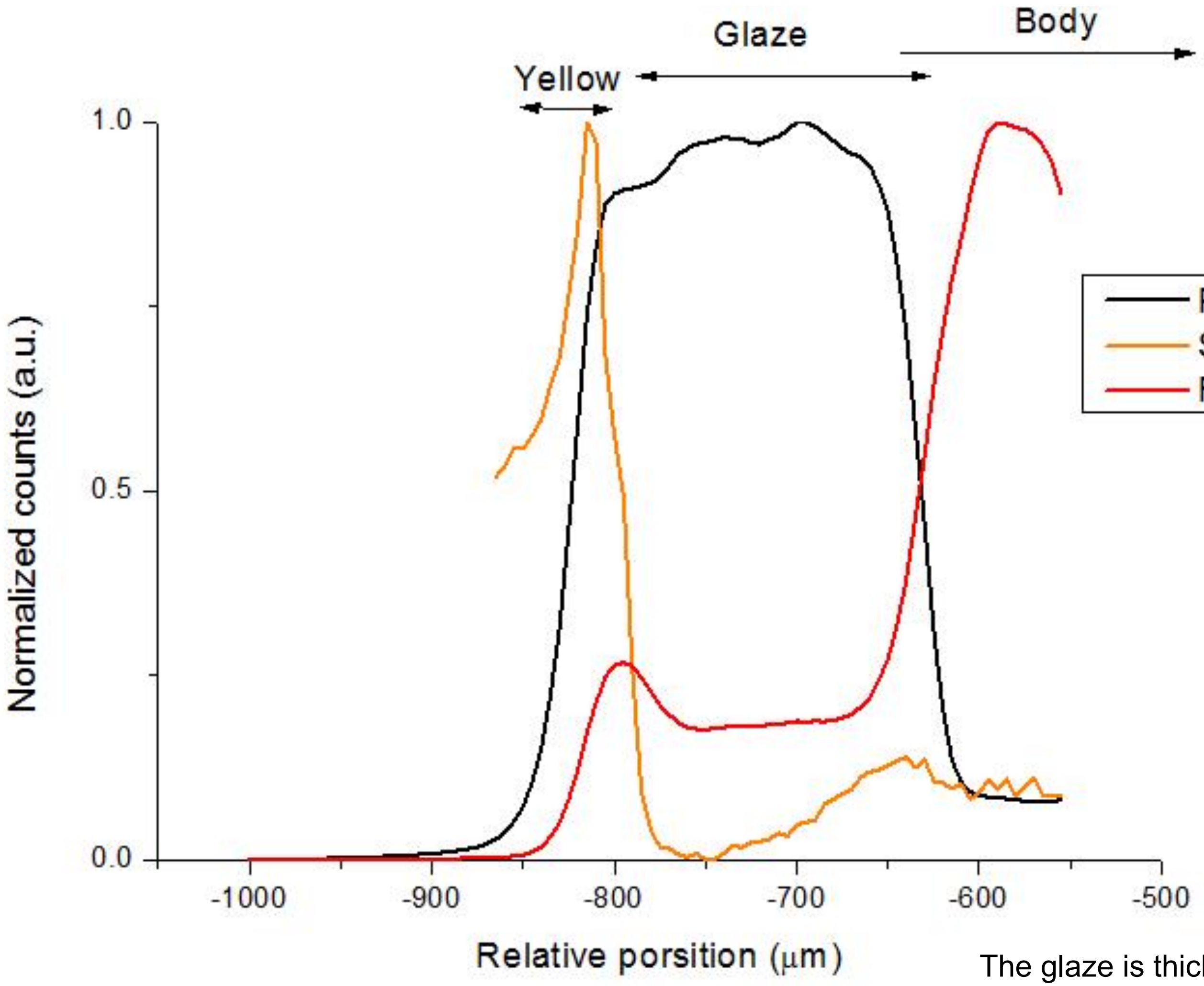
Lisbon



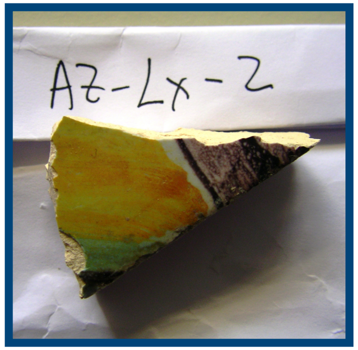


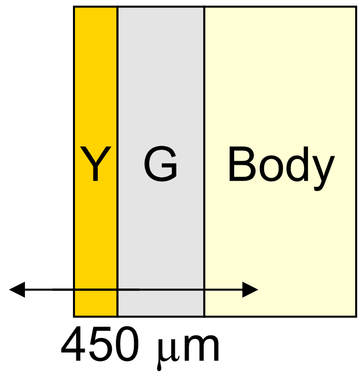
YELLOW: 3D µ-XRF

• **Lateral scans**



Lisbon





The glaze is thicker than in Coimbra samples.
The yellow pigment Sb is less diffused than in the case of the yellow from Coimbra samples

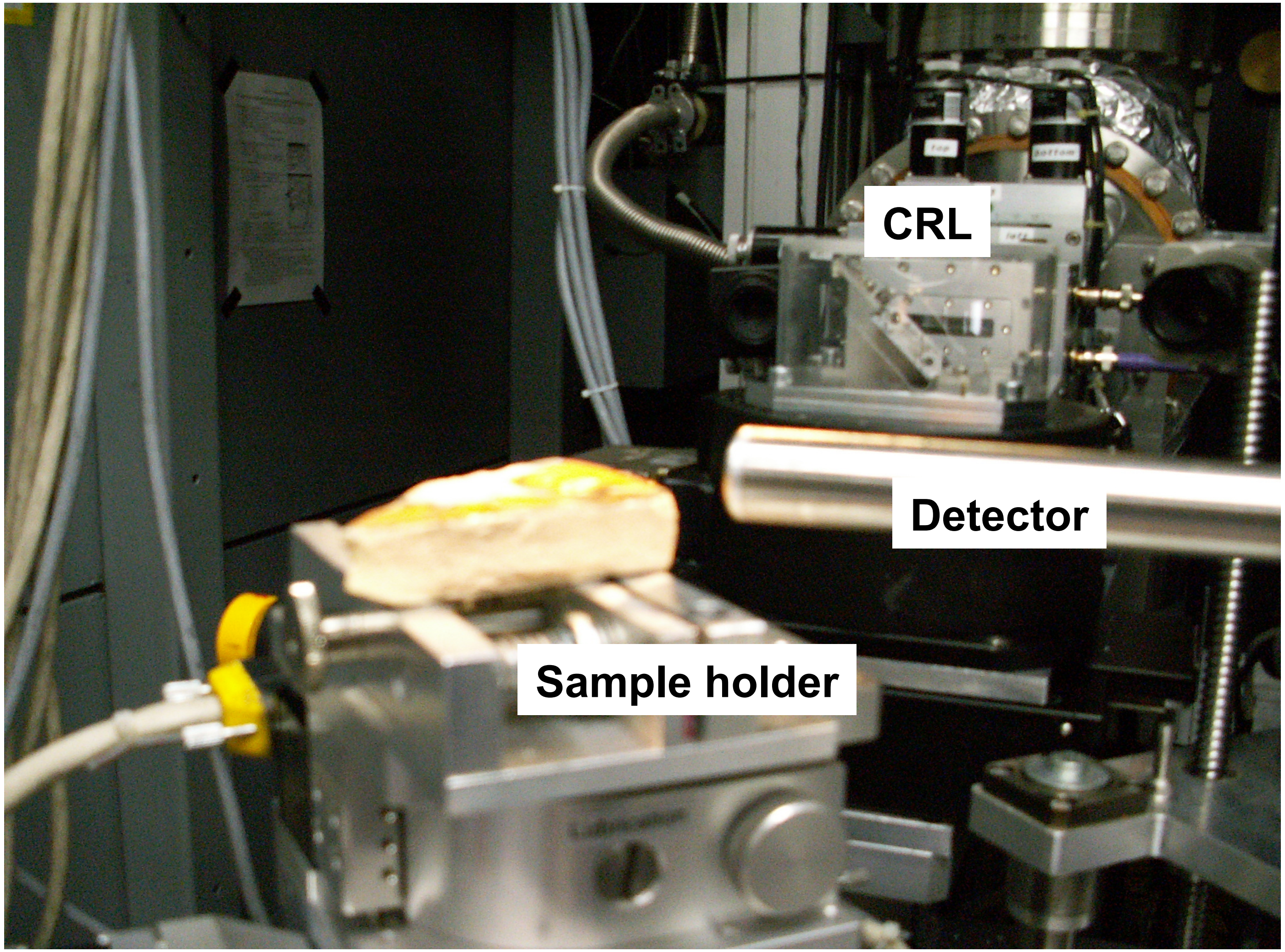
Compound Refractive Lens

With this CRL, a beam spot of 1 μm diameter is obtained

Methodology: With this beam it will be possible to monitor the elements that characterize both the pigments and the glaze, and the diffusion ability of the pigment throughout the glaze can be checked.

- Cross-section scans were performed along the surface decoration, glaze and body.
- From each spectrum the ROI of certain elements was evaluated along the scan.

μ-X Ray Fluorescence CRL

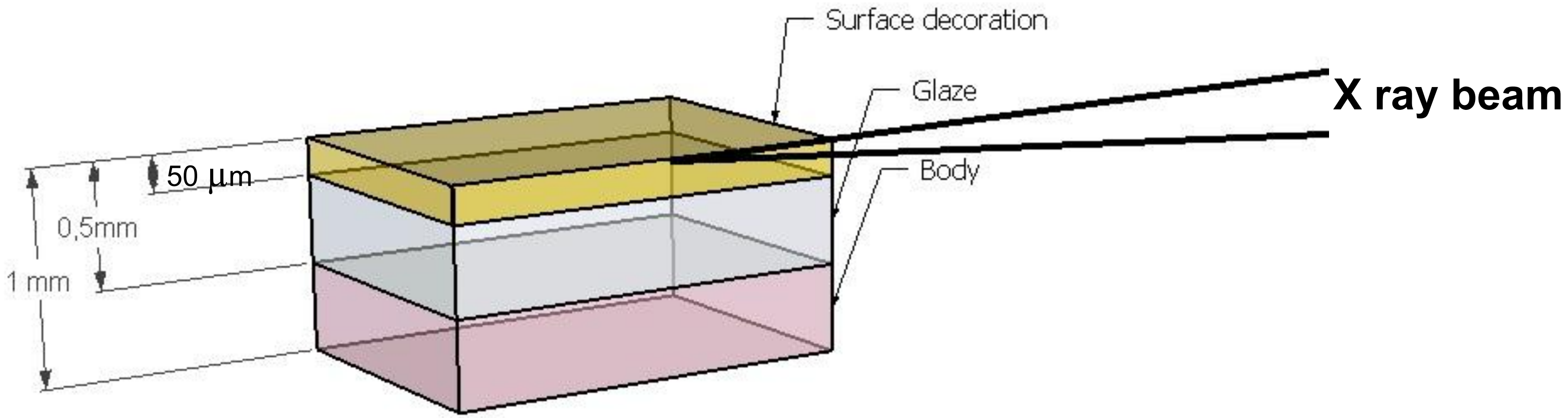


μXRF setup @BAM*line*

µ-X Ray Fluorescence scans

The scans were performed on the cross-section of each sample, following the order color-glaze-body, in steps of 1 µm

60 s per step



The pigments diffusion

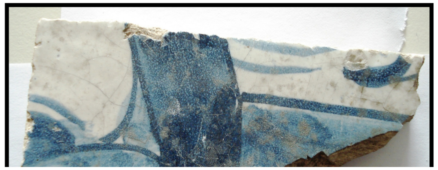
The diffusion ability of the pigments throughout the glaze varies according to:

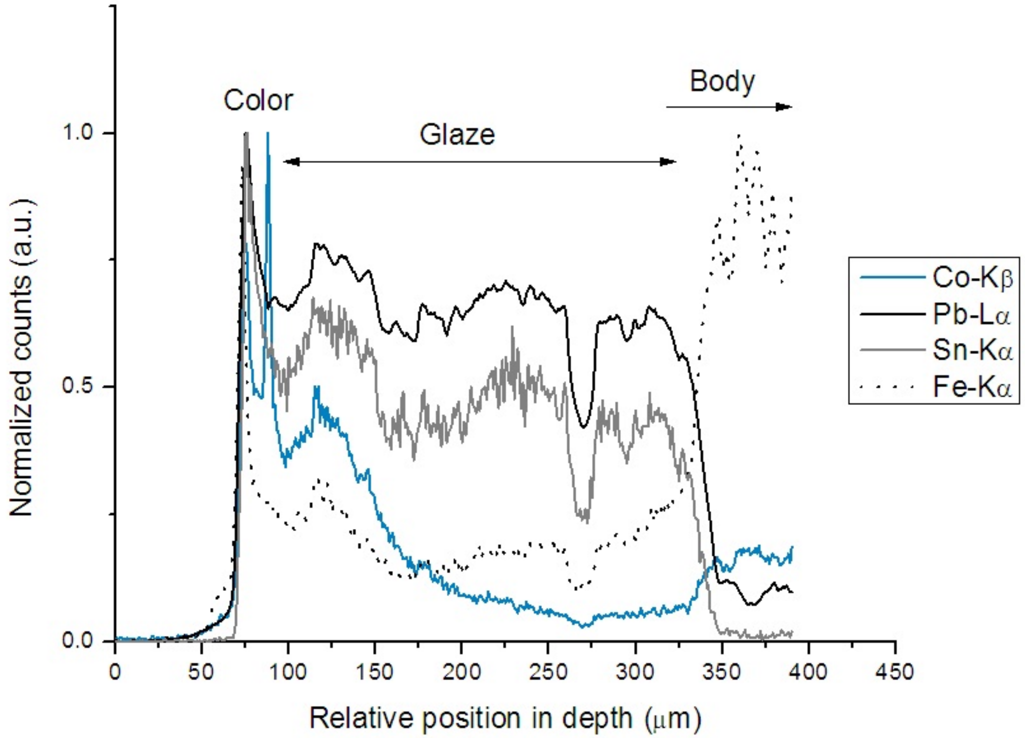
- The chemistry of the pigments and the glaze
- The used firing temperature

And this is what monitored in the work.

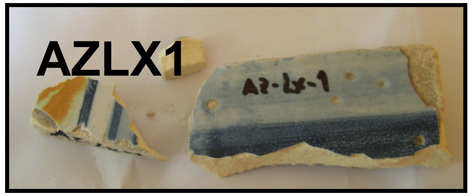
Blue: µ-XRF scans

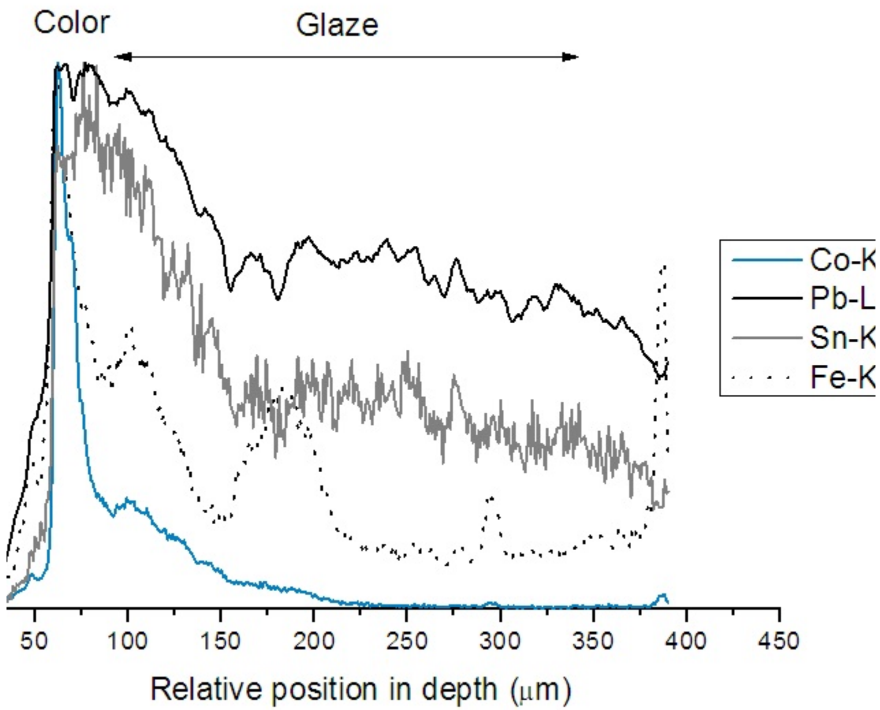
Coimbra tile





Lisbon tile

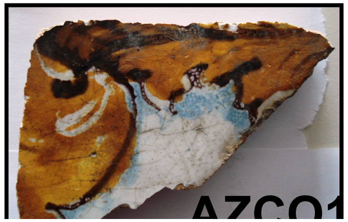




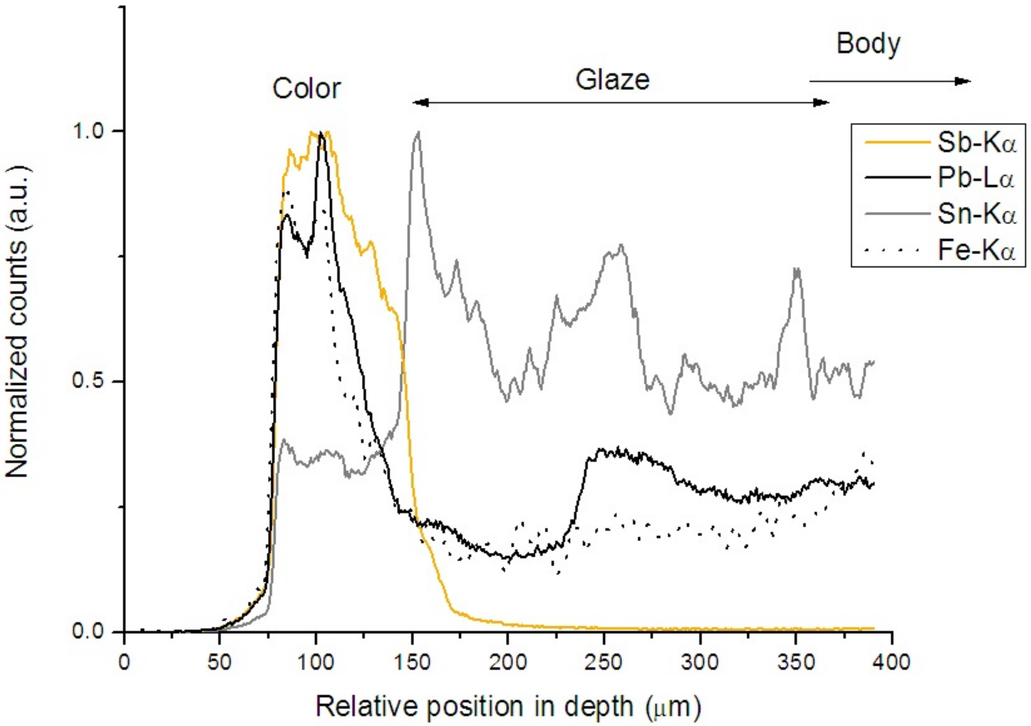
The Co signal from Coimbra tiles show that the pigment is more dispersed into the glaze than in the sample from Lisbon, which means different texture for the glaze.

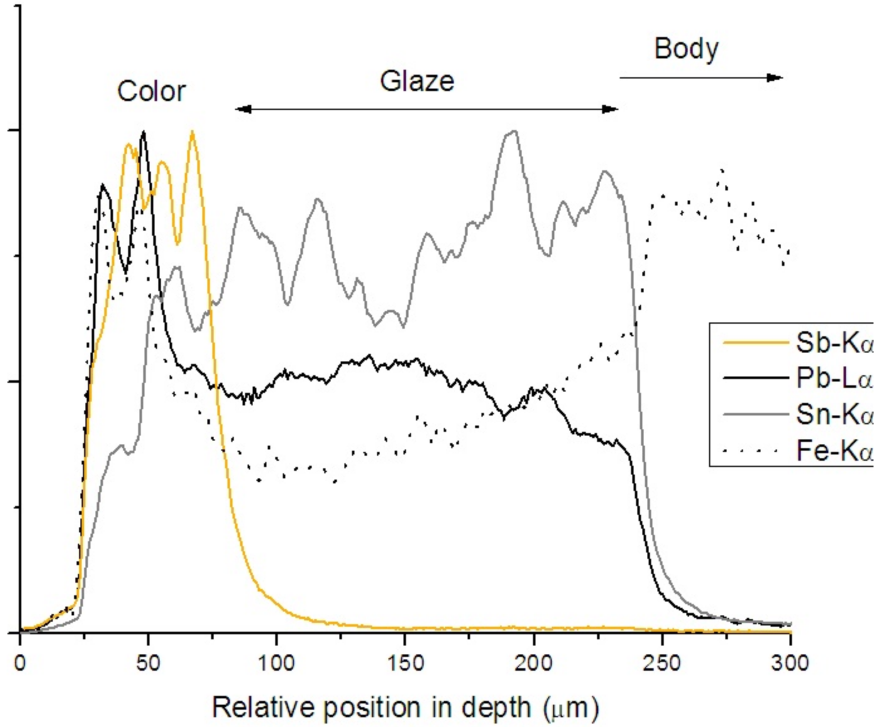
Yellow: µ-XRF scans

Coimbra tile



Lisbon tile





Strong decrease of the Pb signal in tiles from Coimbra in the interface area (color/glaze). This effect is less visible in tile from Lisbon. This may indicate different firing processes. It may have occurred a firing stage just for the color after the base glaze was fired, in sample from Coimbra.

Colour X-Ray Camera (CXC)

New device for high-resolution X-ray imaging

- This is an energy and spatial resolving X-ray camera.
  The basic idea behind this "color X-ray camera" (CXC) is to combine an energy dispersive array detector for X-rays, in this case a pnCCD, with polycapillary optics.

- Imaging is achieved using multiframe recording of the energy and the point of impact of single photons.

- The camera simultaneously records 69 696 spectra
- Energy resolution of 152 eV for Mn Kα with a spatial resolution of 50 µm
- Imaging area of 12.7x12.7 mm^2.
- Is sensitive to photons in the energy region 3 - 40 keV

- An image of an object is formed by the position-sensitive detector which registers individual photons coming to separate pixels.

Colour X-Ray Camera (CXC)

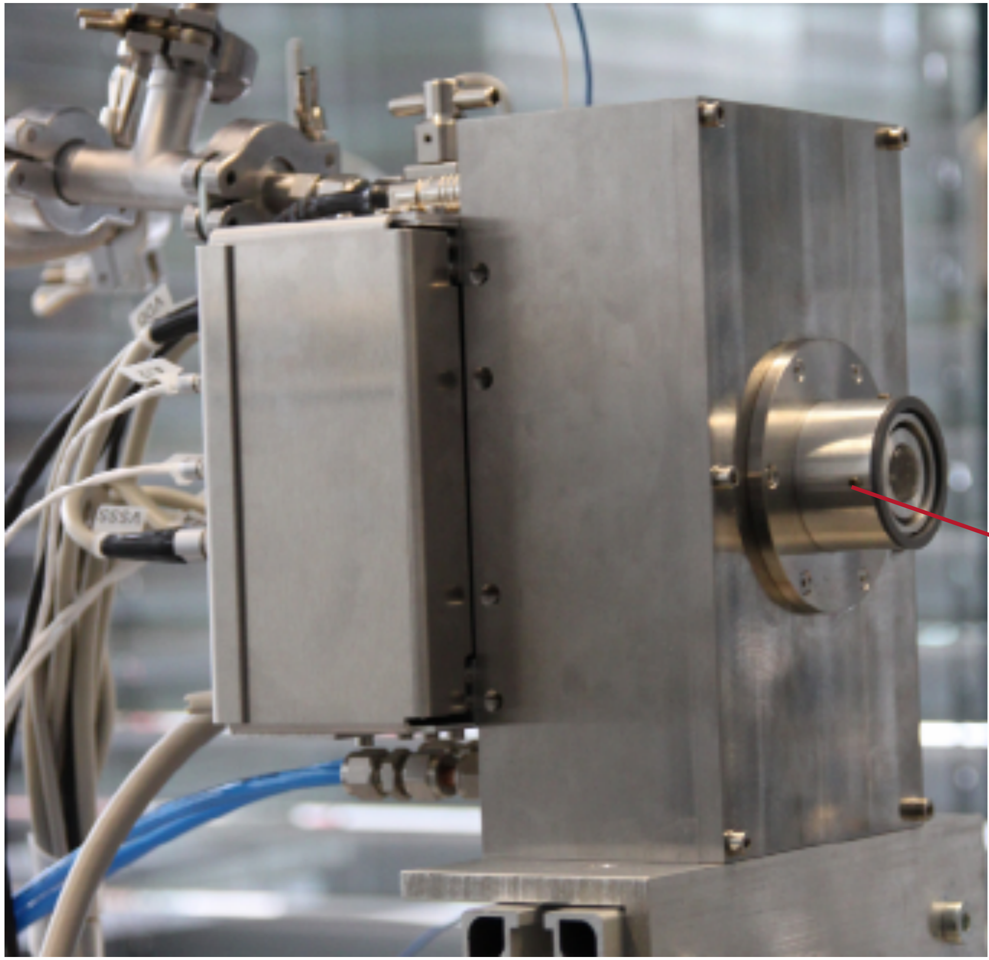
- For X-ray fluorescence mapping (elemental distribution), spatial resolution on a sample can be achieved by complementing the detector with special X-ray optics which “guides” photons from small regions on a sample to corresponding pixels on the detector.

- For the X-ray colour camera, polycapillary optics are used containing a large number of straight channels with diameters in the range for **obtaining a 1:1 image** on the detector.

- The transparency of the polycapillary is typically in the order of 75- 80% which ensures acceptable intensity losses at the entrance of the CXC.

  Such high-performance microstructured glass is a product of intensive technological research and development of many years at the Institute for Scientific Instruments.

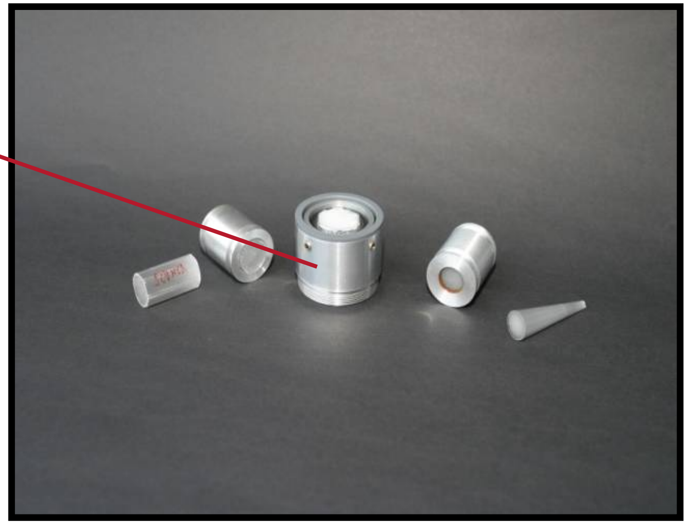
Colour X-Ray Camera (CXC)



IFG Institute for Scientific Instruments

IAP

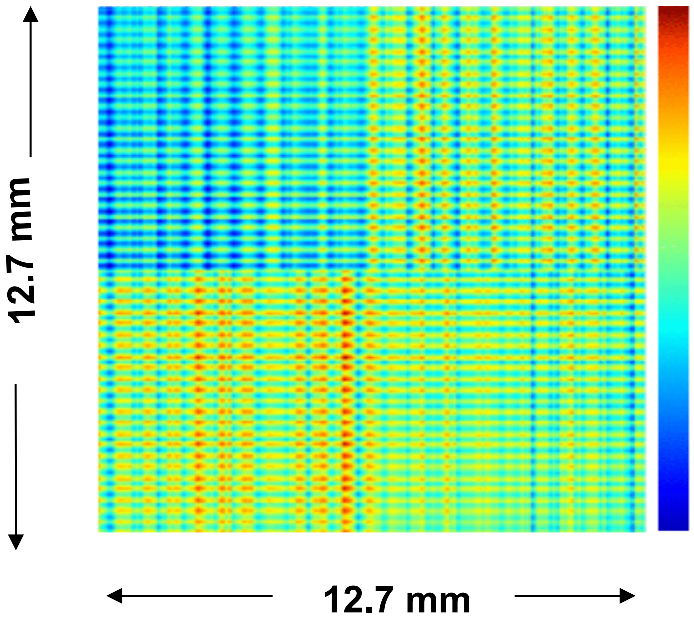
For the CXC, optics are available with different magnification factors. E.g., 1:1, 1:3, …



O. Scharf et al., Compact pnCCD-Based X-ray Camera with High Spatial and Energy Resolution: A Color X-ray Camera. Anal. Chem., 2011, 83 (7), pp 2532–2538.

Colour X Ray Camera (CXC)

Each pixel is an energy dispersive detector with 4096 channels
30 min acquisition time



Imaging area	12,7 x 12,7 mm²
Pixel size	(48 x 48) μm²
Number of Pixels	264 x 264
Pixel redout speed	28 MPixels/s
Framerate	400 Hz
Sensitive thickness	450 μm
Quantum efficiency	>95%@3-10 keV, >30%@20 keV
Noise	<3e⁻/Pixel
Energy resolution	152 eV @ Mn Kα

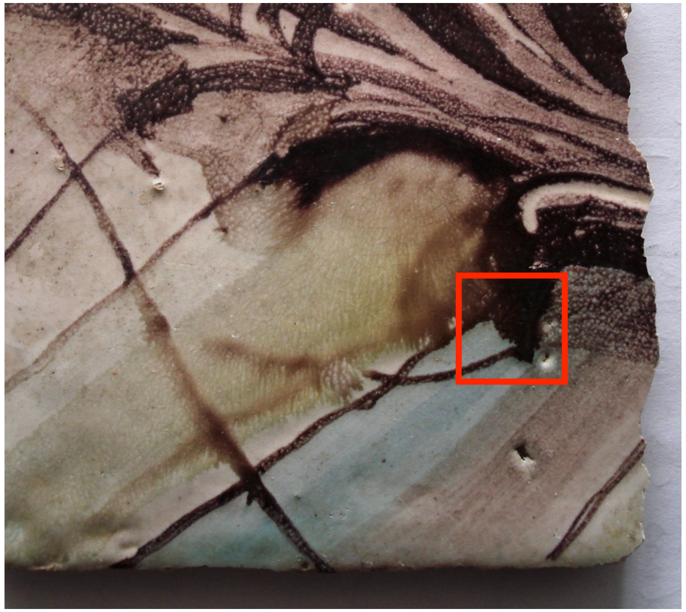
Picture taken without beam showing the noise of each pixel

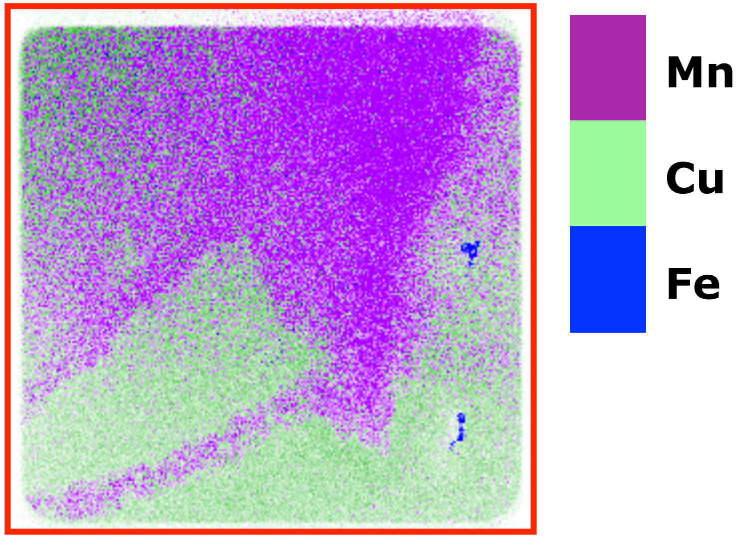
CXC: Results

Elemental surface mapping in one shot (optics removed)

Coimbra tile

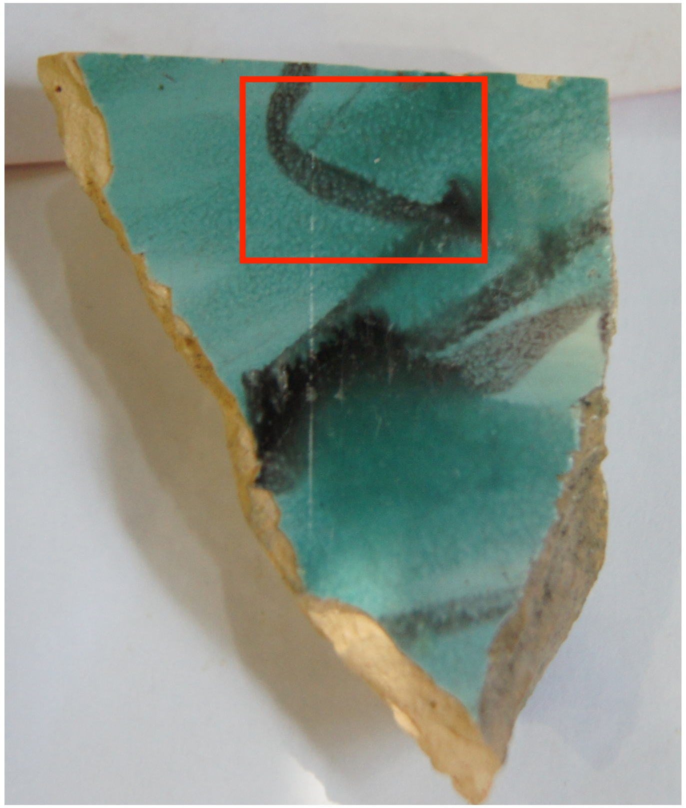
AZCO2

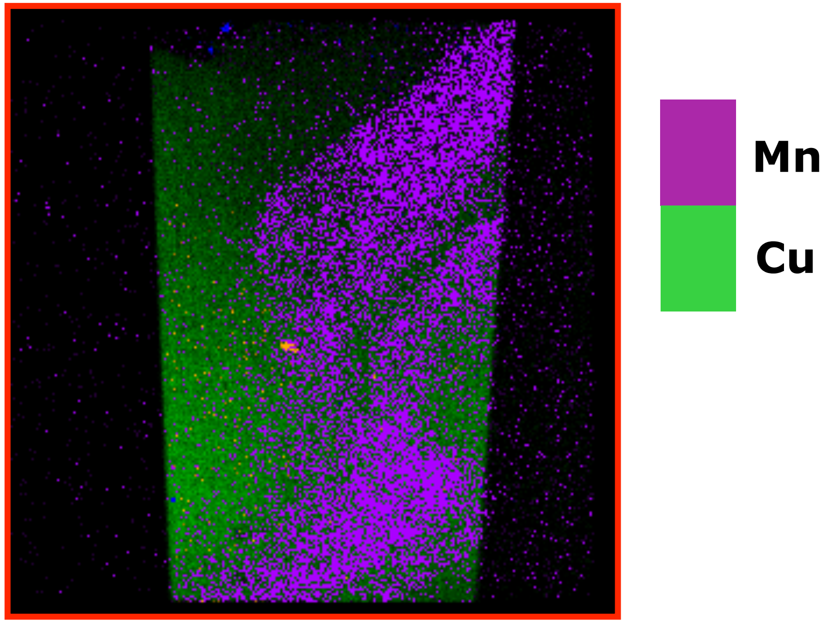




CXC: Results

Coimbra tile
AZCO3

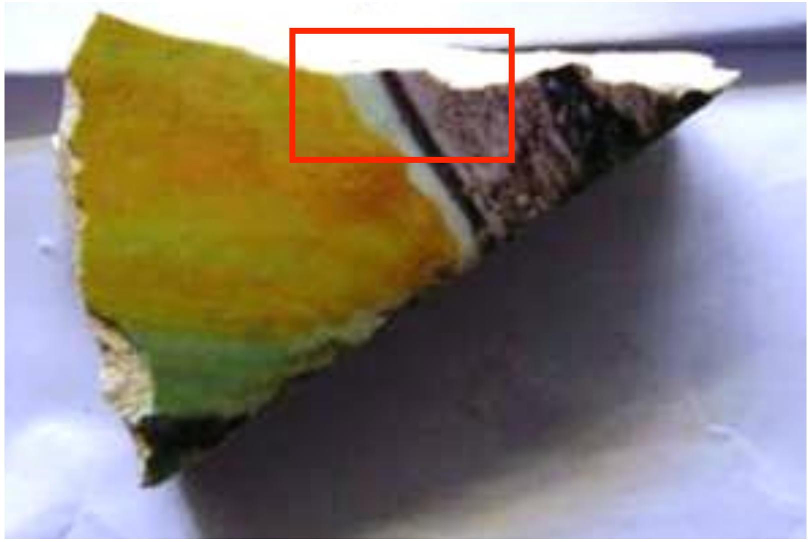


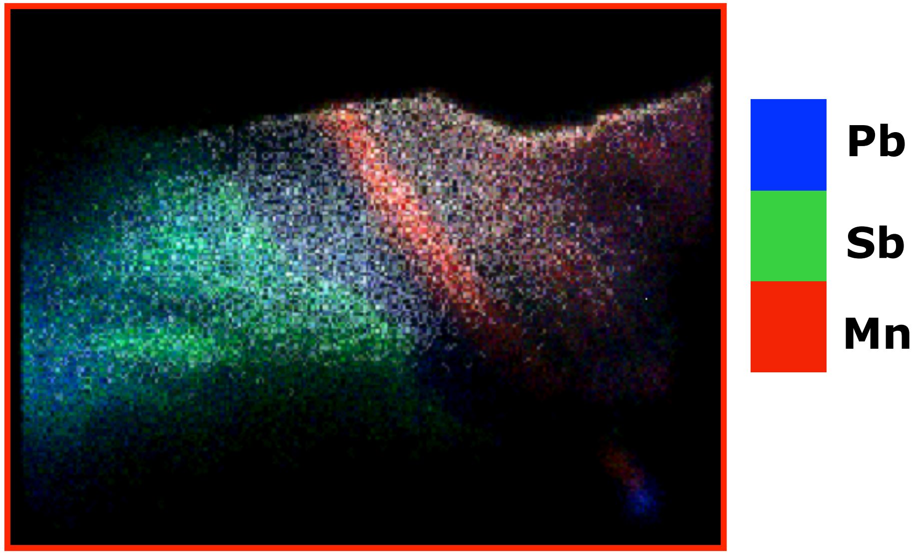


CXC: Results

Lisbon tile

AZLX2

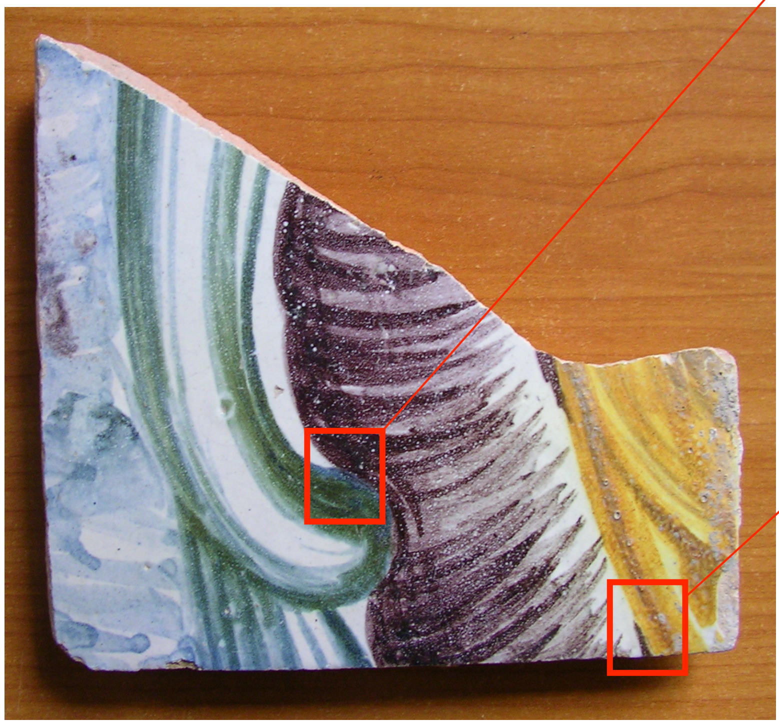


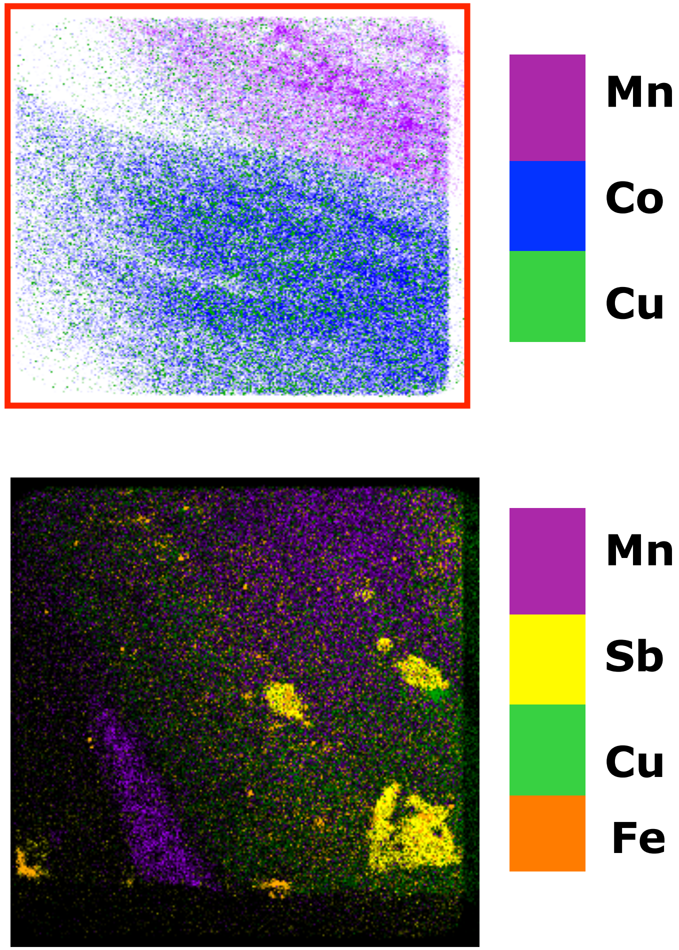


CXC: Results

Lisbon tile

AZLX9





Comparison of the several systems μ-XRF

System	Moving Sample	Spacial resolution	Imaging area	Detecting system	Acquisition time
CXRC	No	48 μm	12.7 x 12.7 mm^2	264 x 264 pixels. Each pixel is a detector of 4096 channels	30 min
CRL	XYZ	0.1 μm	5 mm	Si(Li)	1 min/step
Confocal systems	XYZ	30-100 μm	5 mm	Si(Li)	A few h
Curved crystals	XYZ	10-100 μm	5 mm		A few h
pinholes	XYZ	200 μm	5 mm		A few h
Large area detectors	No	10 cm			30 min

Overview

A. Guilherme, M.L. Carvalho, S. Pessanha, J. dos Santos and J. Coroado, "Study on polychrome lead-glazed Portuguese faiences using a **portable μ-EDXRF** beam" Spectrochmica Acta B, 65, 328-333 (2010)

A. Guilherme, **M. L. Carvalho**, C. Seim, B. Hesse, B. Kanngießer, J.M.F. dos Santos and J. Coroado "**μ-XRF (conventional and 3D) and SEM-EDS** in Portuguese glazed ceramics: advances on the manufacture techniques", **Spectrochmica Acta Atomic Spectroscopy Part B 66 297-307 (2011)**

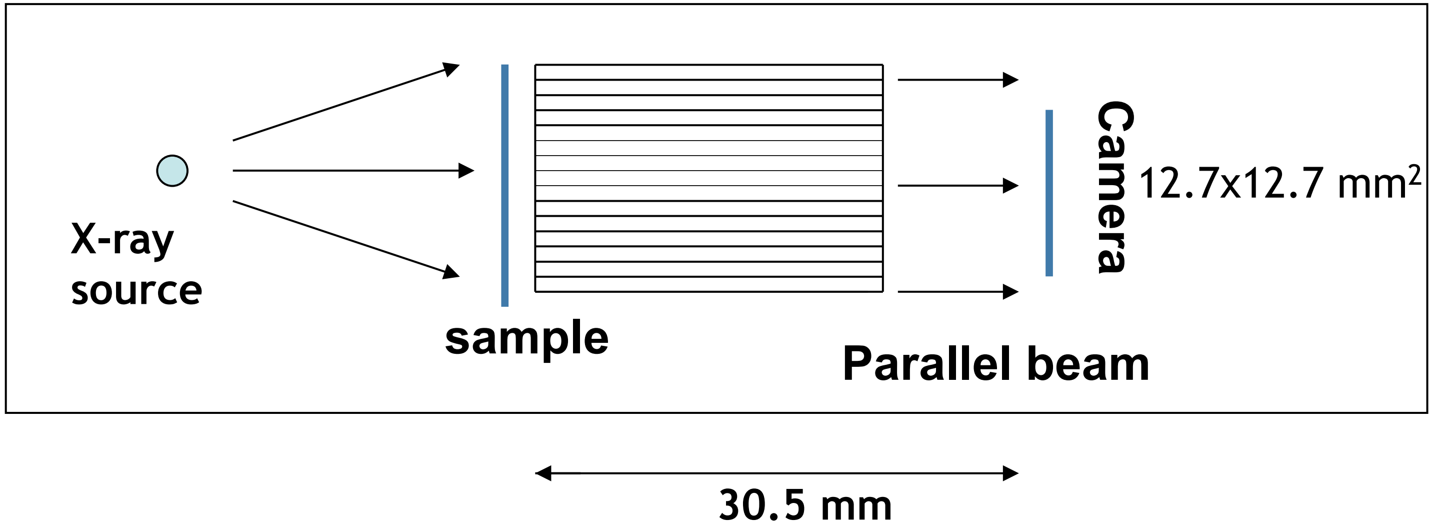
A. Guilherme, G. Buzanichb, M. Radtke, U. Reinholz, J. Coroado, J.F. Dos Santos, M. L. Carvalho, "**Synchrotron Micro-XRF with Compound Refractive Lenses (CRLs)** for tracing key elements on Portuguese glazed ceramics", **Journal of Analytical and Atomic Spectroscopy, J. Anal. At. Spectrom., 27, 966-974 (2012)**

A. Guilherme, G. Buzanich and M. L. Carvalho, "**Focusing systems for X-ray micro beam: an overview**", **Spectrochmica Acta Part B Atomic Spectroscopy doi.org/10.1016/j.sab. 2012.07.021 (2012)**


AR
THANK YOU FOR YOUR ATTENTIO

Comparison of Optics for Colour X-Ray camera and CRL

Polycapillary lens



Acq time 30 min

48 µm diameter each polycapillary

(CRL 0.1 µm resolution) – sample has to be moved
Acquisition time 1 min/step

Conclusions

• The pictures obtained by the Colour X Ray Camera show surface elemental mappings.

• In a single shot (30 min) onto a chosen area, one can easily obtain elemental information about a certain sample.

• The sample is not moved

Summarizing

- CRL (1 µm beam) has proved to be suitable for tracing key elements in the colour and glaze;

- Differences in the diffusion abilities of each **pigment** throughout the glaze were observed:

- The yellow pigment, being much more dense than the blue pigment, is less diffused into the glassy matrix;
- Conversely the layer of the yellow colour is thicker (ca. 100 µm) than the blue colour (30 µm);

• Comparing the Co signal of the two blues, the one from Coimbra has diffused deeper into the glaze than the one from Lisbon.

Chemical composition of the glazes;

• Comparing the two yellows, there is a higher drop of the Pb signal in the tile from Coimbra in the interface area (color/glaze). This effect is less visible in tile from Lisbon. This may indicate different firing processes. It may have occurred a firing stage just for the color after the base glaze was fired, in the sample from Coimbra.