Fast XRF imaging and related methods: Using the Maia detector at beamline P06 of DESY for the investigation of cultural heritage

Matthias Alfeld

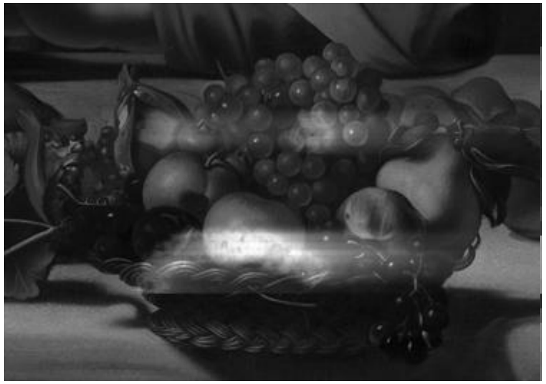
Joint ICTP-IAEA Workshop on Advances in X-ray Instrumentation for Cultural Heritage Applications
Trieste, 15.07.15

Outline

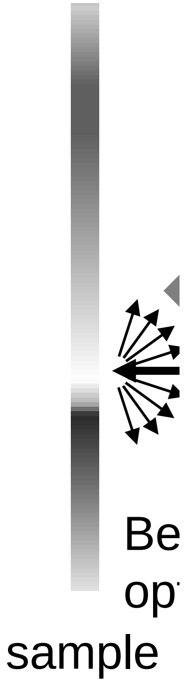
- Motivation: XRF imaging at SR sources
- Beamline P06 of DESY
- The Maia detector
- Application examples
  - U-contaminated *Salmo Salar* gills studied with XRF imaging
  - As in *Ceratophyllum demersum* studied with XRF tomography
  - Degradation of Cr yellow studied with XANES imaging
  - Degradation of minium studied with XRD tomography
- Conclusions

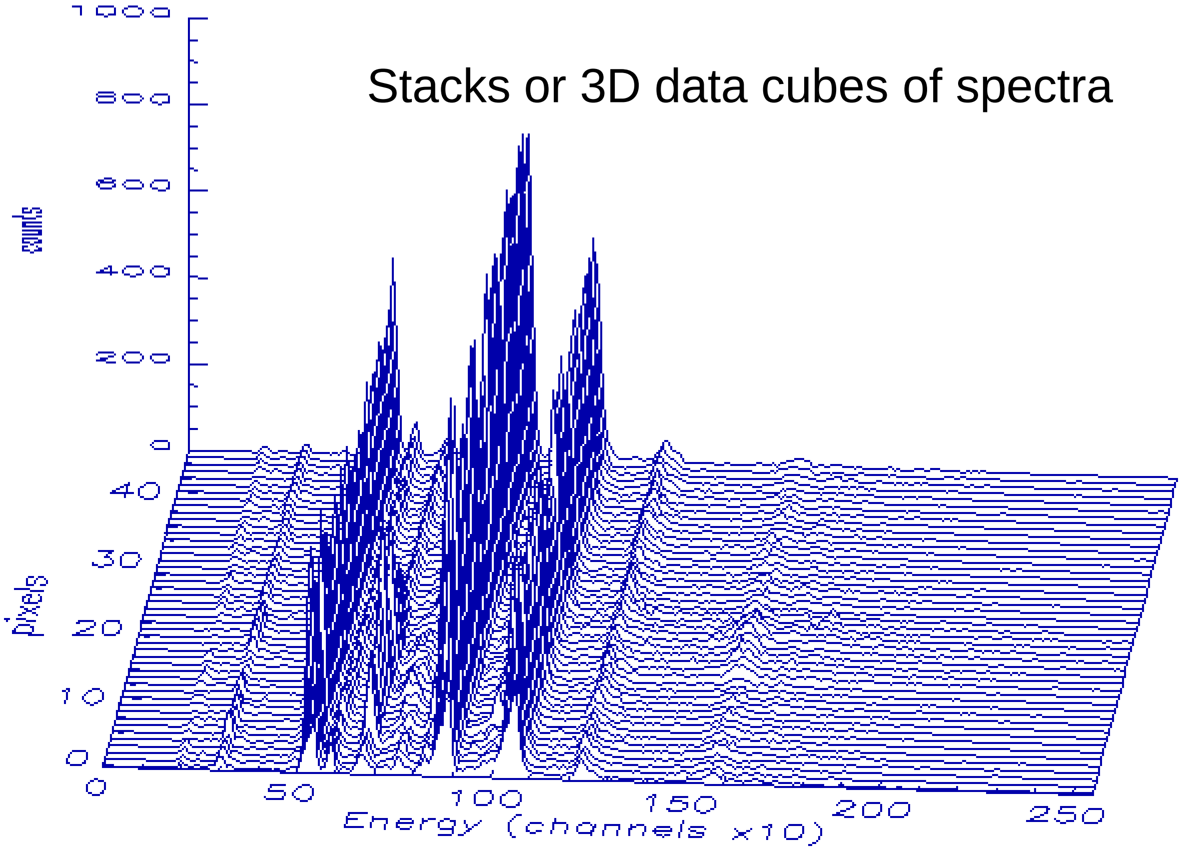
Motivation: XRF imaging at SR sources

- For respresentative results many samples need to be investigated during a beam time and high quality data needs to be obtained.
- High quality XRF images feature:
  - Lateral resolution ->small beams -> X-ray optics (not in this talk)
  - Contrast and high dynamic range -> Number of photons counted
  - Absence of Artefacts -> Number of photons counted and energy resolution



Motivation: XRF imaging at SR sources





Motivation: XRF imaging at SR sources

> Data treatment by least squares (χ^2) fitting

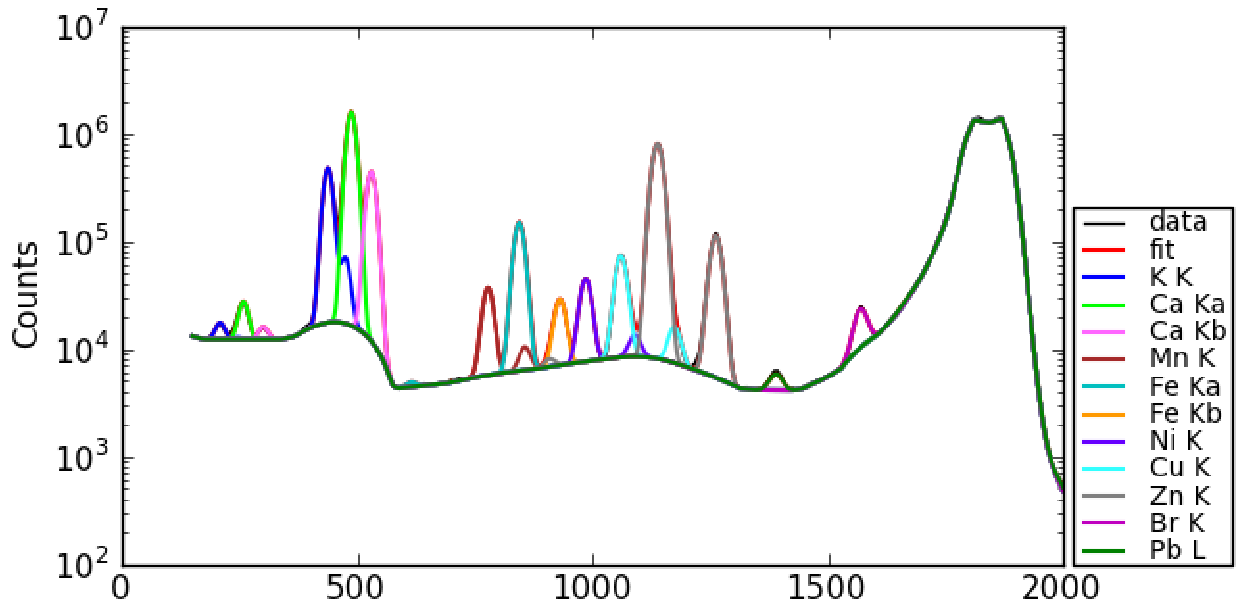
A selected range of cha

$$f_i = a_0 B_i + \sum_{k=1}^{k} a_k ...$$

linear intensit

factors a

background

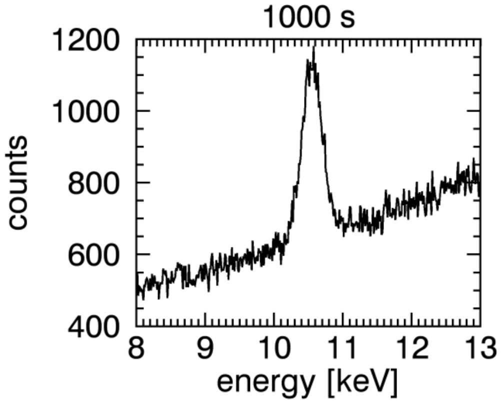


non-linear parameters p. (e.g. energy calibration and detector settings)

$$\chi^2 = \sum_{i=0}^{i} w_i (S_i - f(a_0, a_1, \ldots, p_0, p_1, \ldots))^2$$

Motivation: XRF imaging at SR sources

> Limits of detection (simulation)



Motivation: XRF imaging at SR sources

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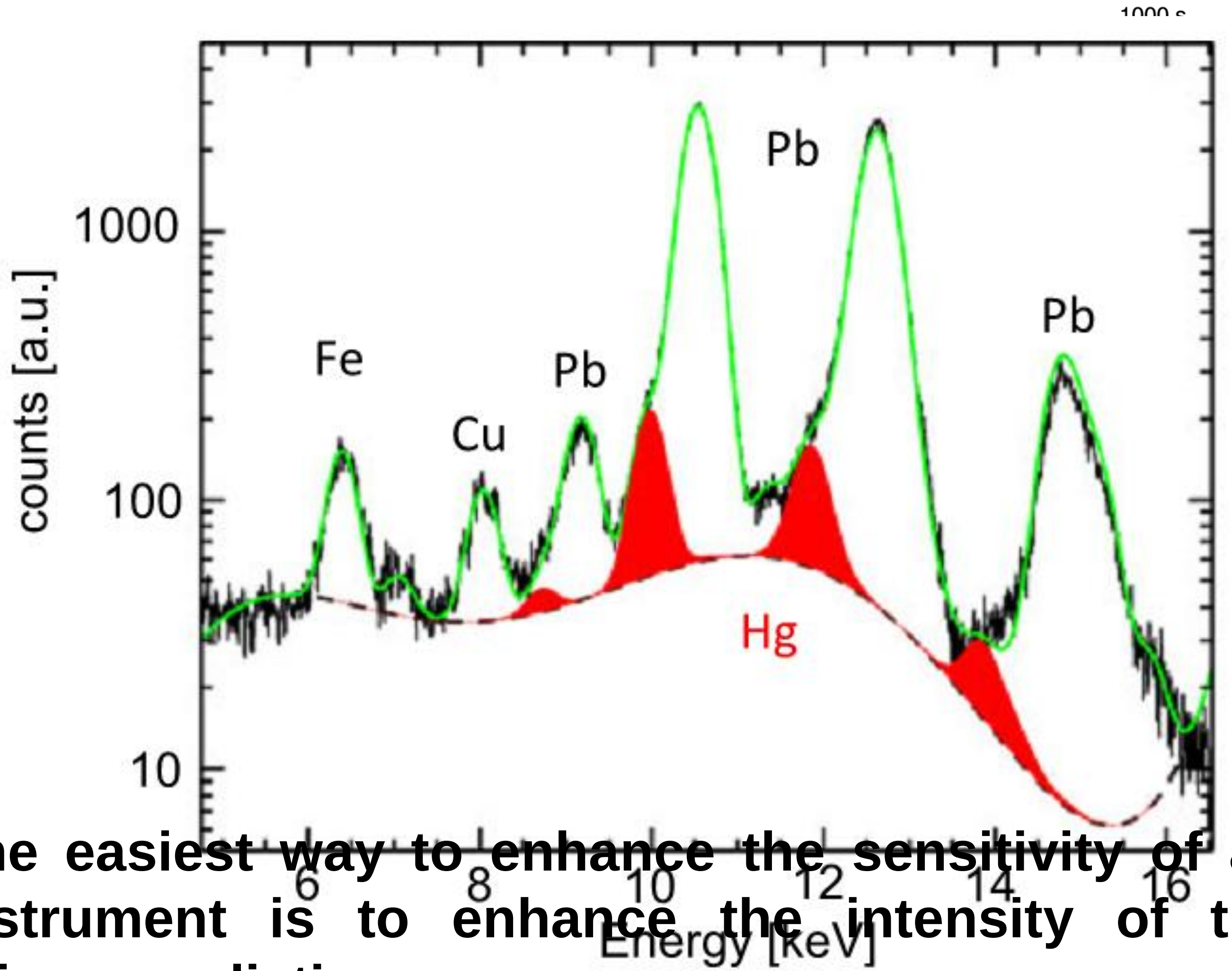
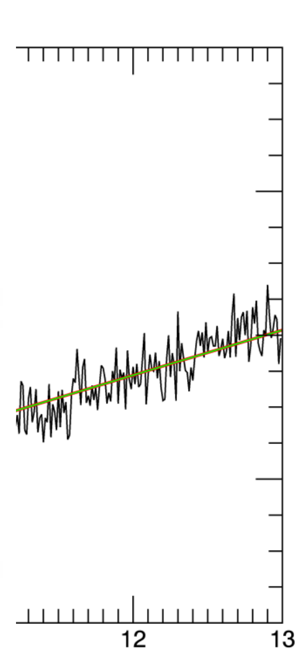




$c_i \cdot (\sqrt{t})$

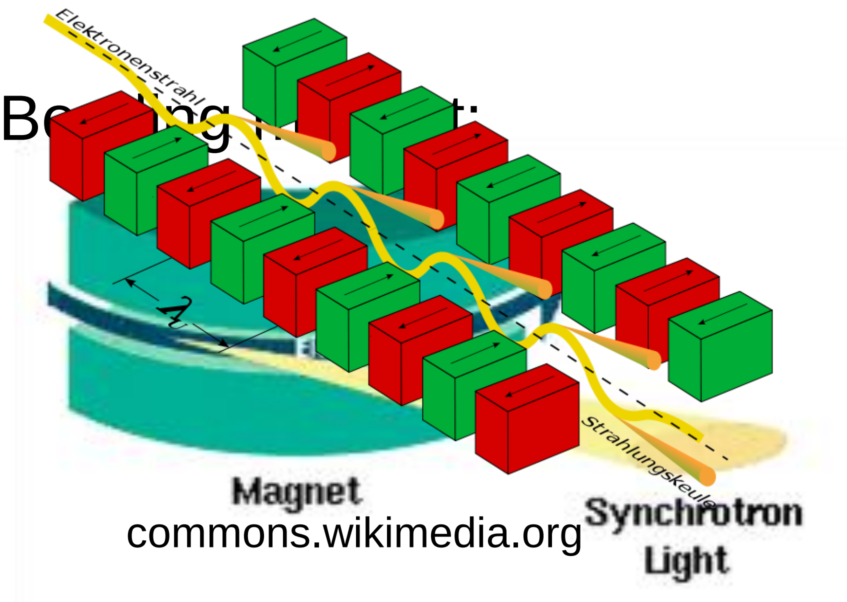
The easiest way to enhance the sensitivity of an instrument is to enhance the intensity of the primary radiation.

M. Alfeld et al., Appl Phys A (2013) 111:157–164

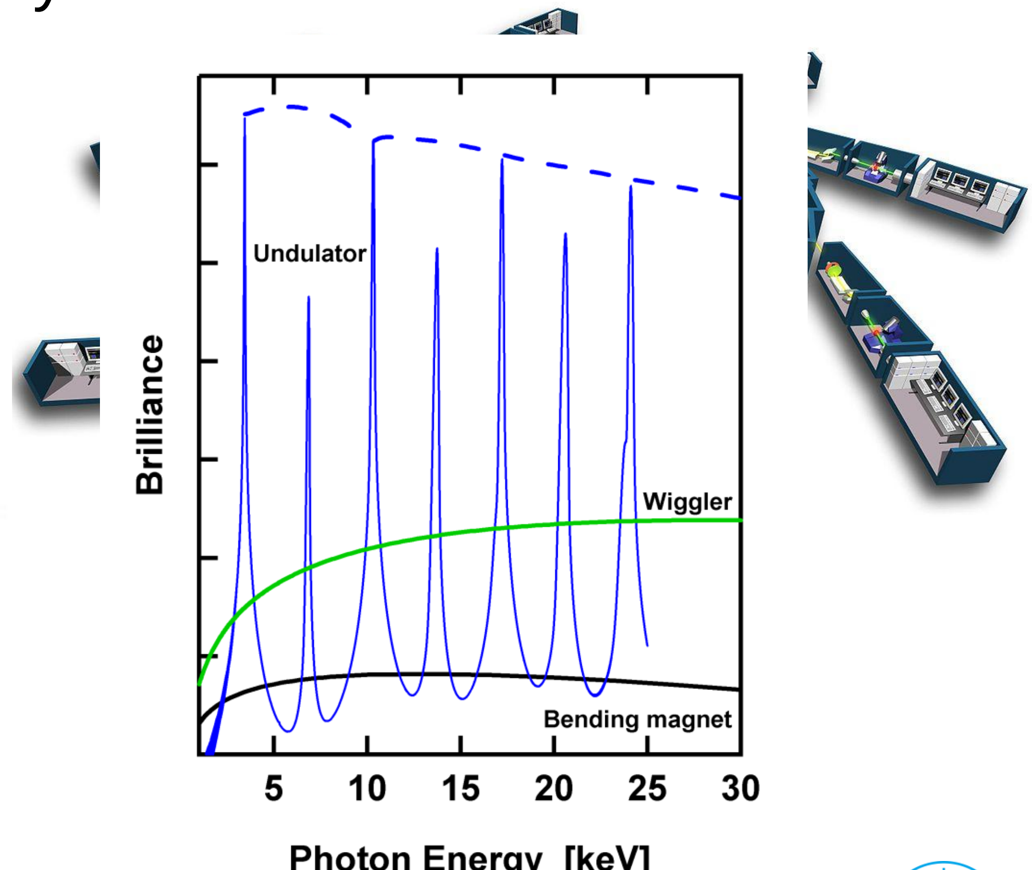
Motivation: XRF imaging at SR sources

Synchrotron:

Be ng t:



commons.wikimedia.org

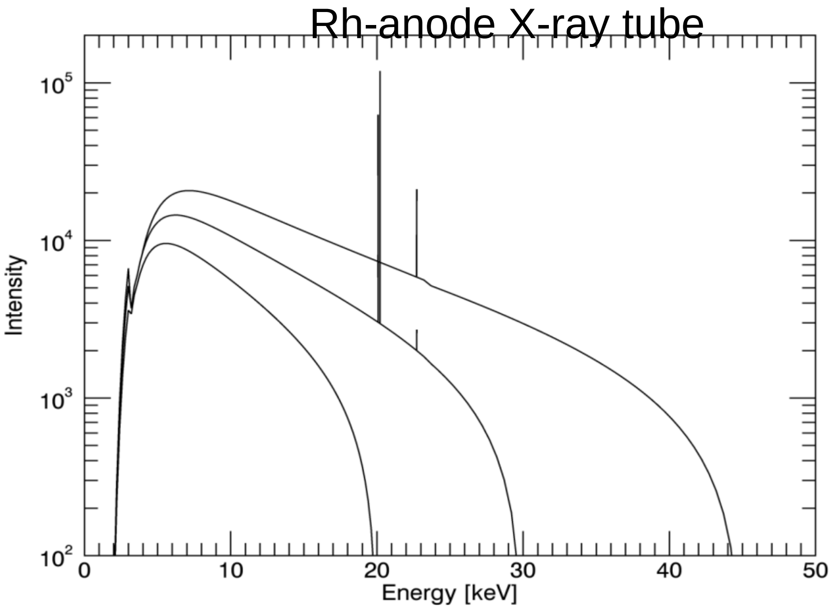


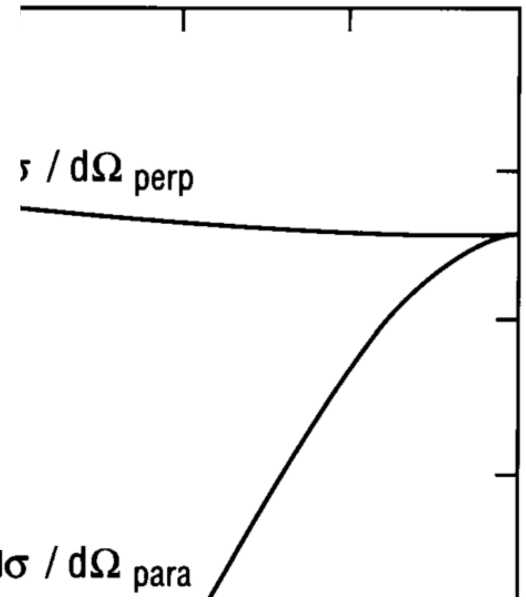
photon-science.desy.de

Images: www.wikipedia.org

SR sources

es





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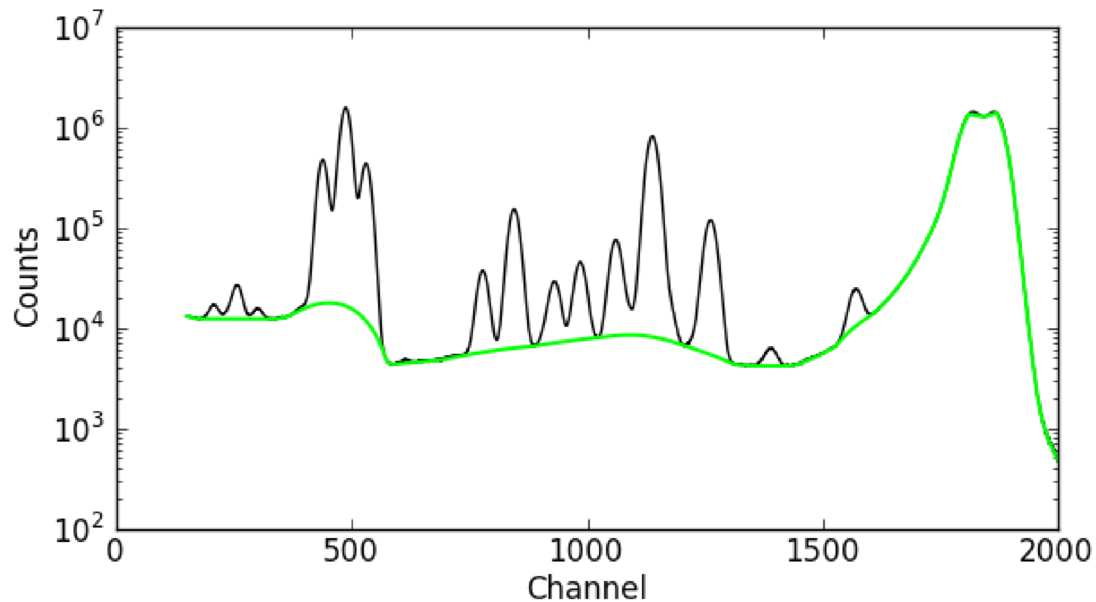

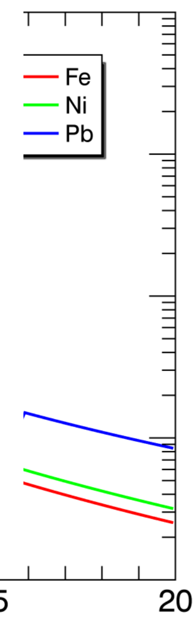

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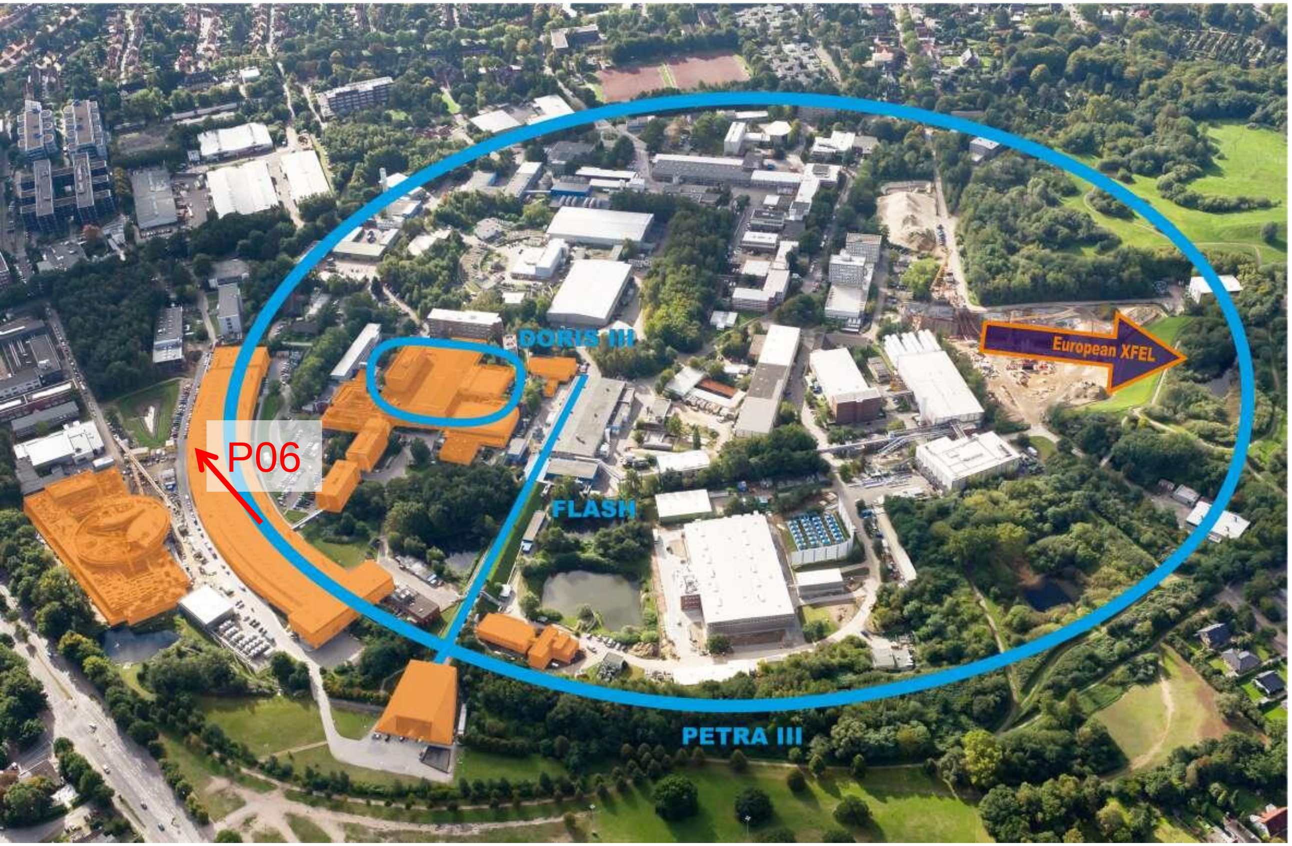
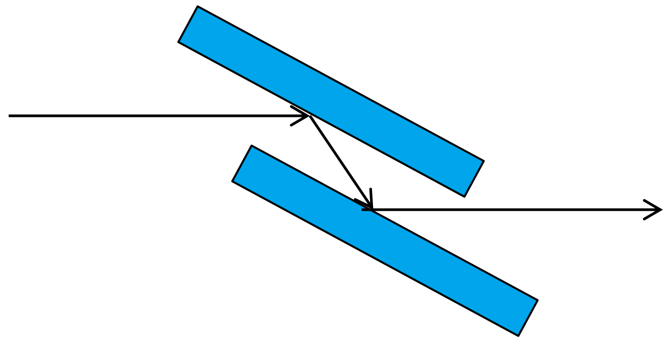
Beamline P06

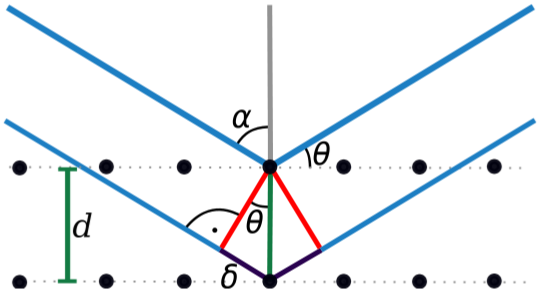


Beamline P06@DESY, Hamburg, Germany:

- Hard X-ray Micro/Nanoprobe
- 3rd generation Synchrotron Radiation source PETRA III
- operational since 2011.

Beamline P06

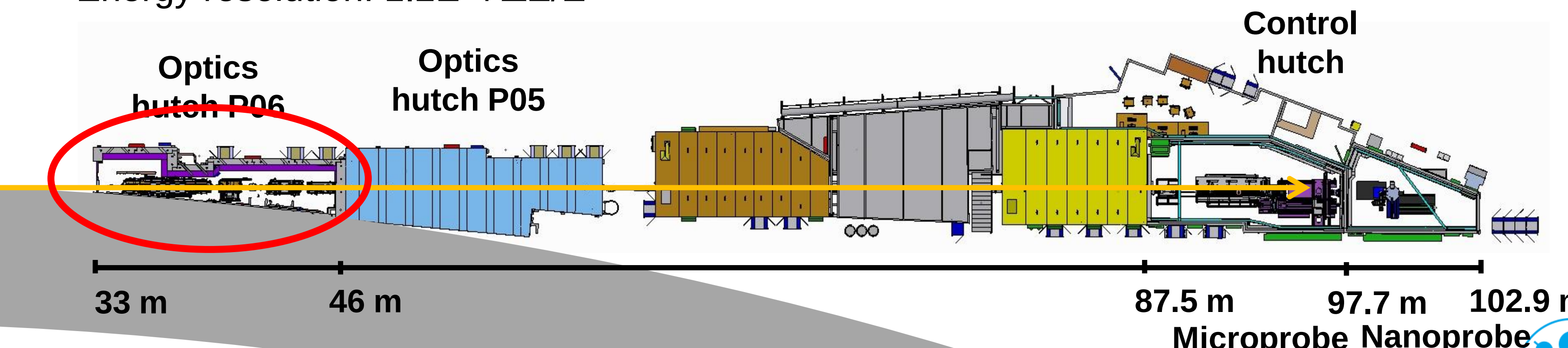




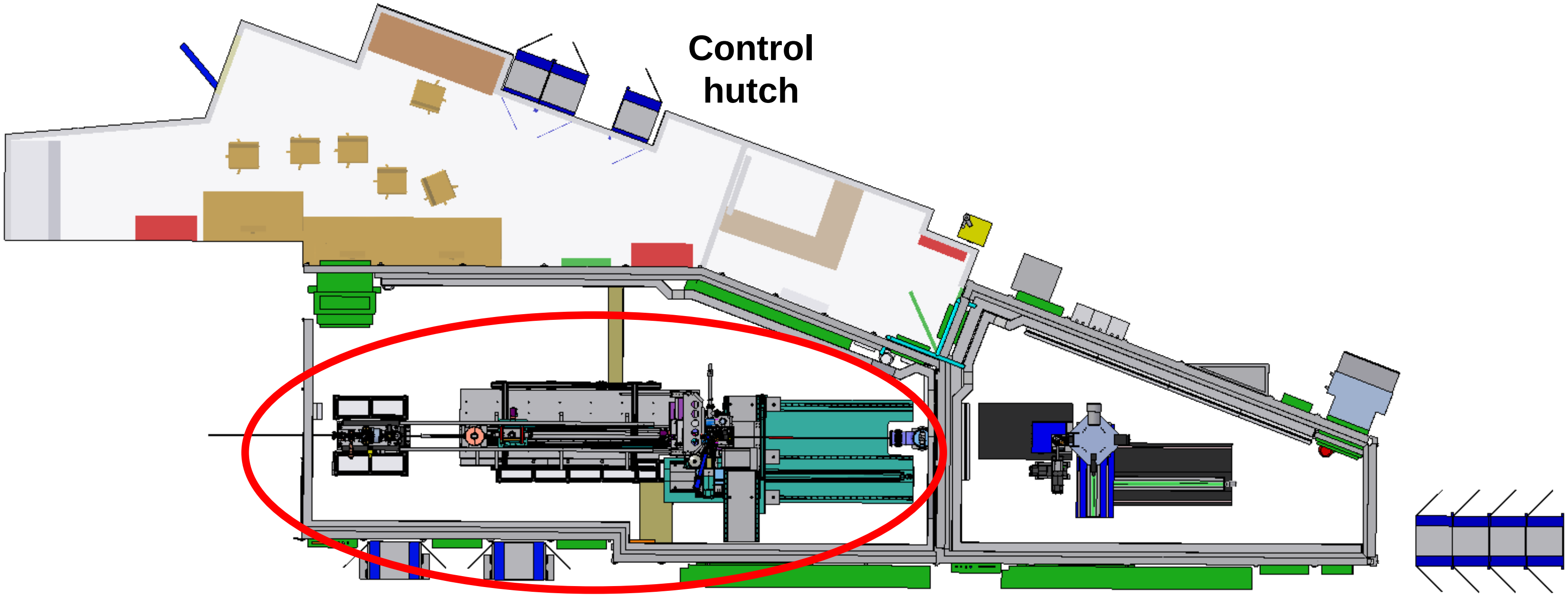
Source: de.wikipedia.org

$$n\,\lambda = 2d\,sin(\theta)$$

Si(111) monochromator based on Bragg reflection
Energy resolution: 1.2E-4 ΔE/E

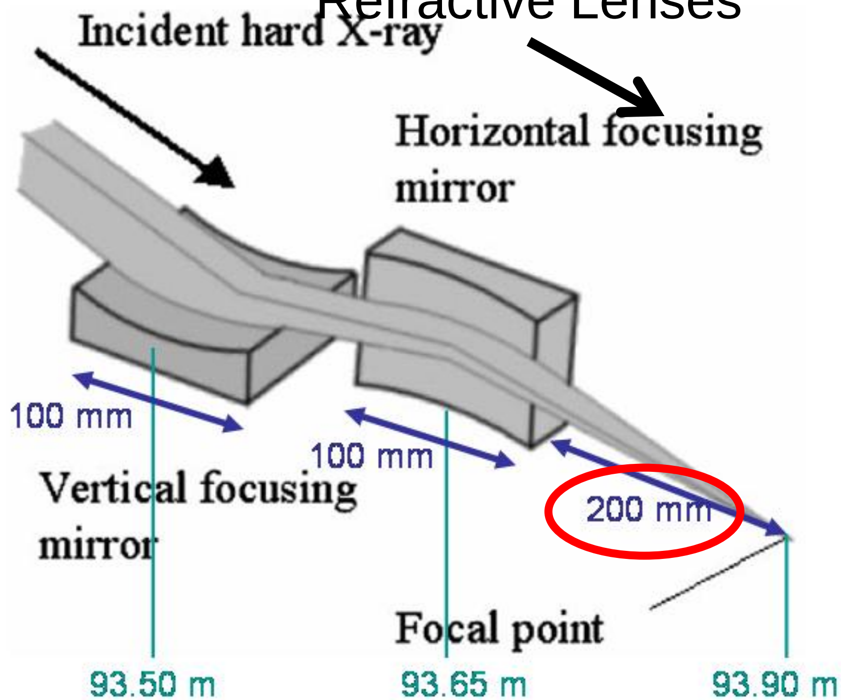


Beamline P06

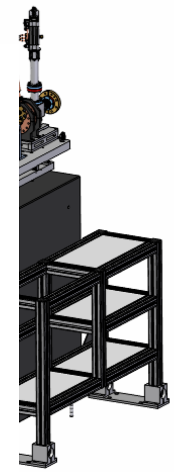


Beamline P06

Compound Refractive Lenses

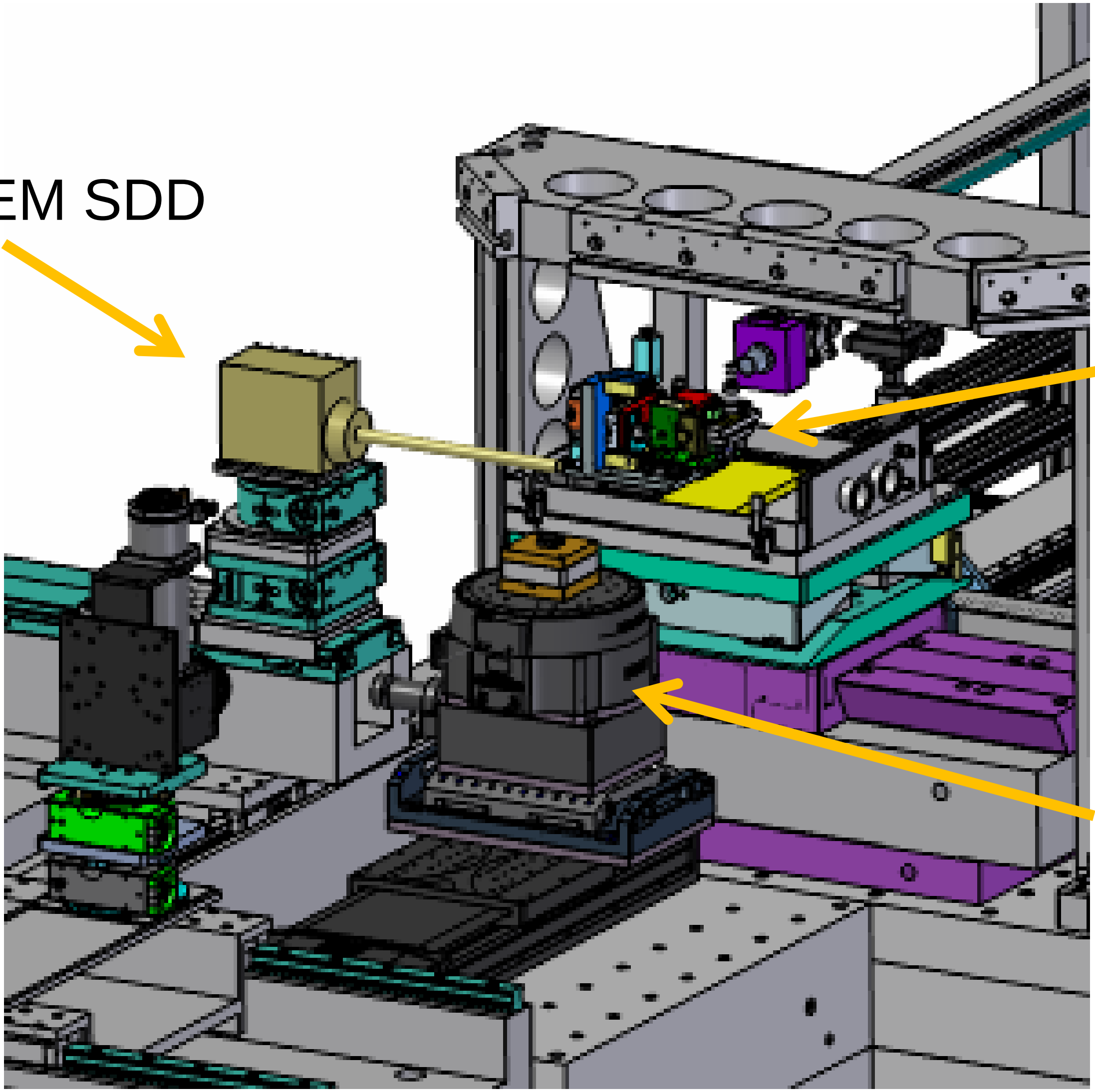


Beam size down to: 300x340 nm^2
Rh-coated. Suitable for 5-23 keV)

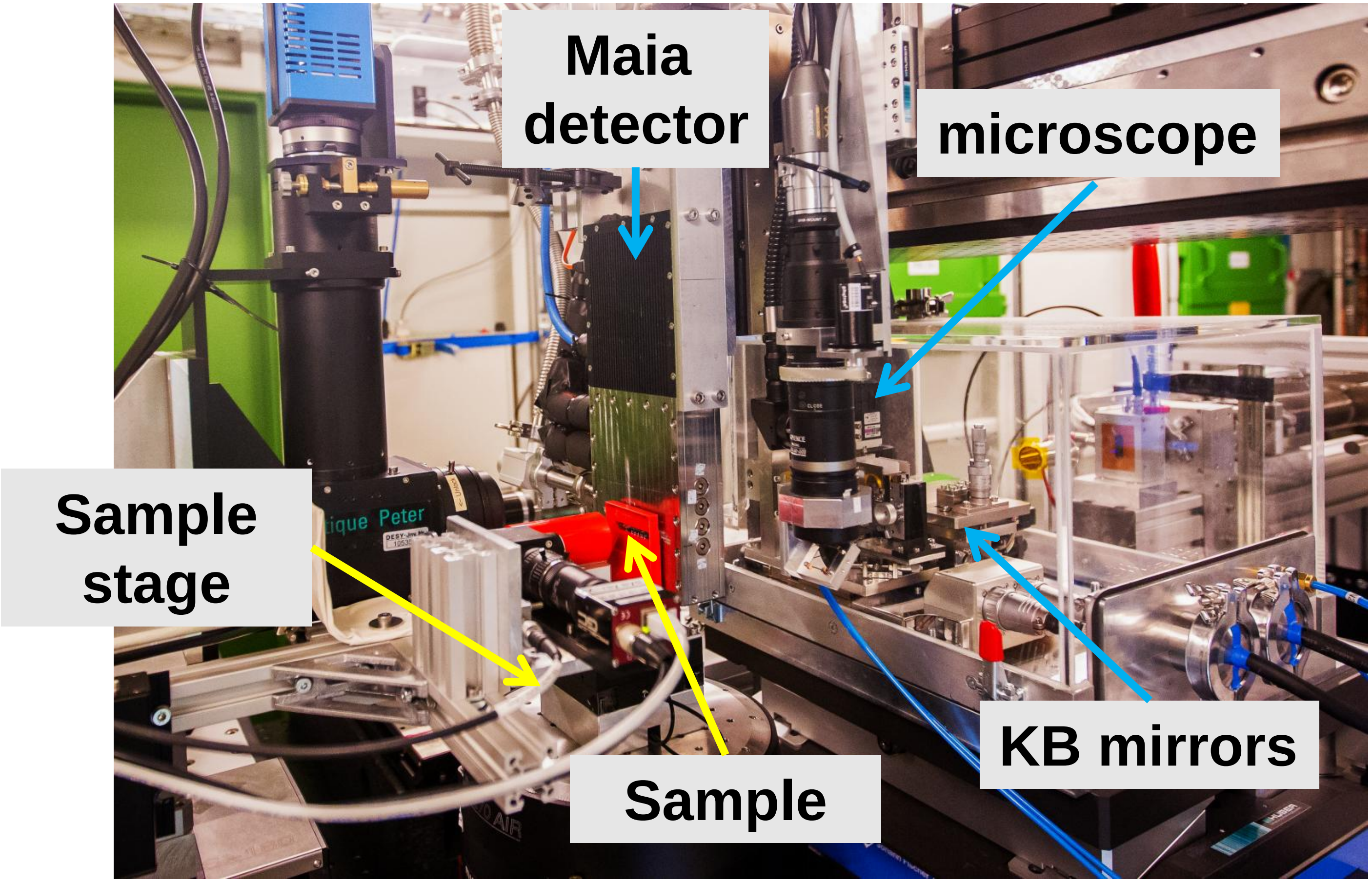


Area detector(s) for tomography and XRD

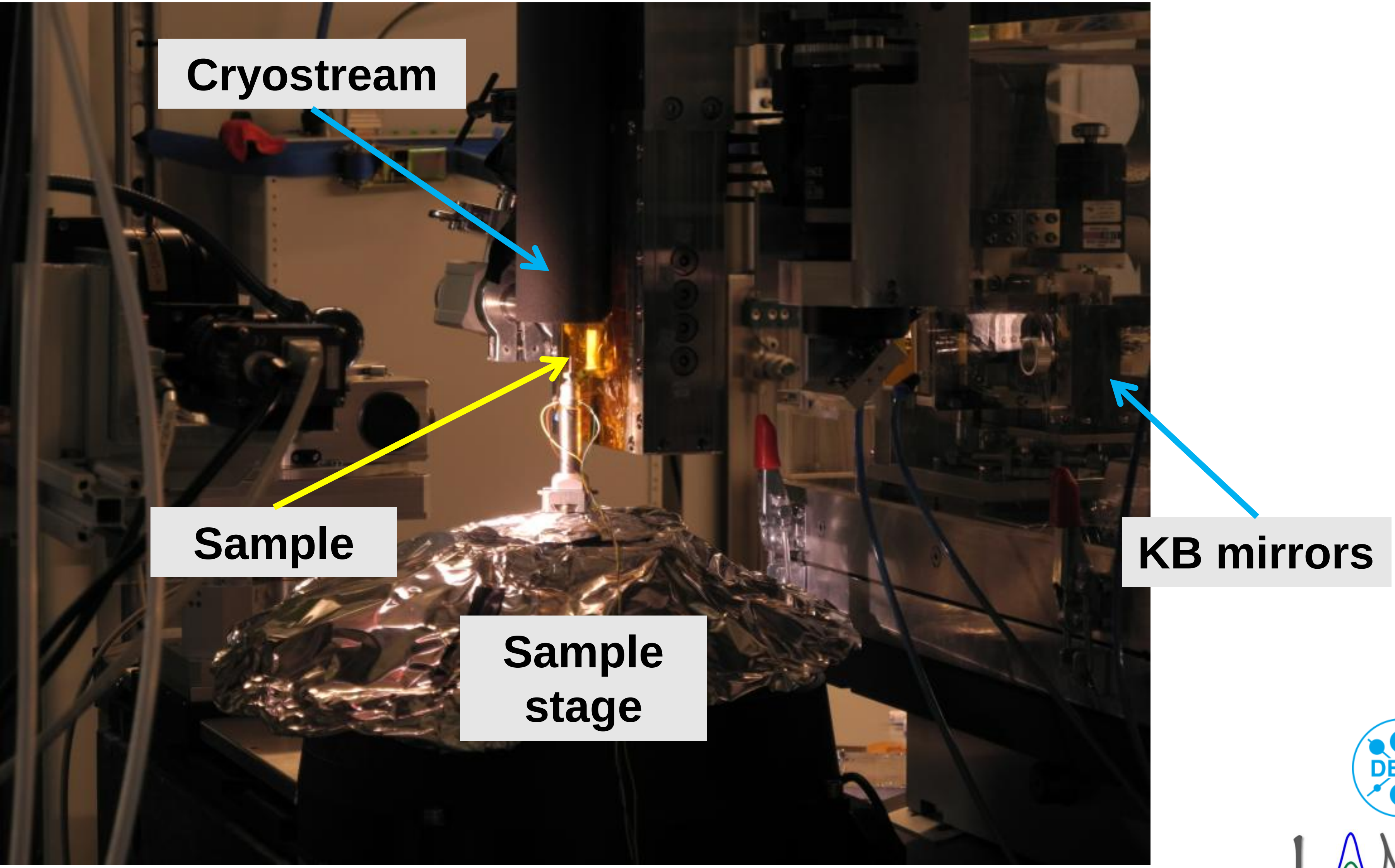
Beamline P06



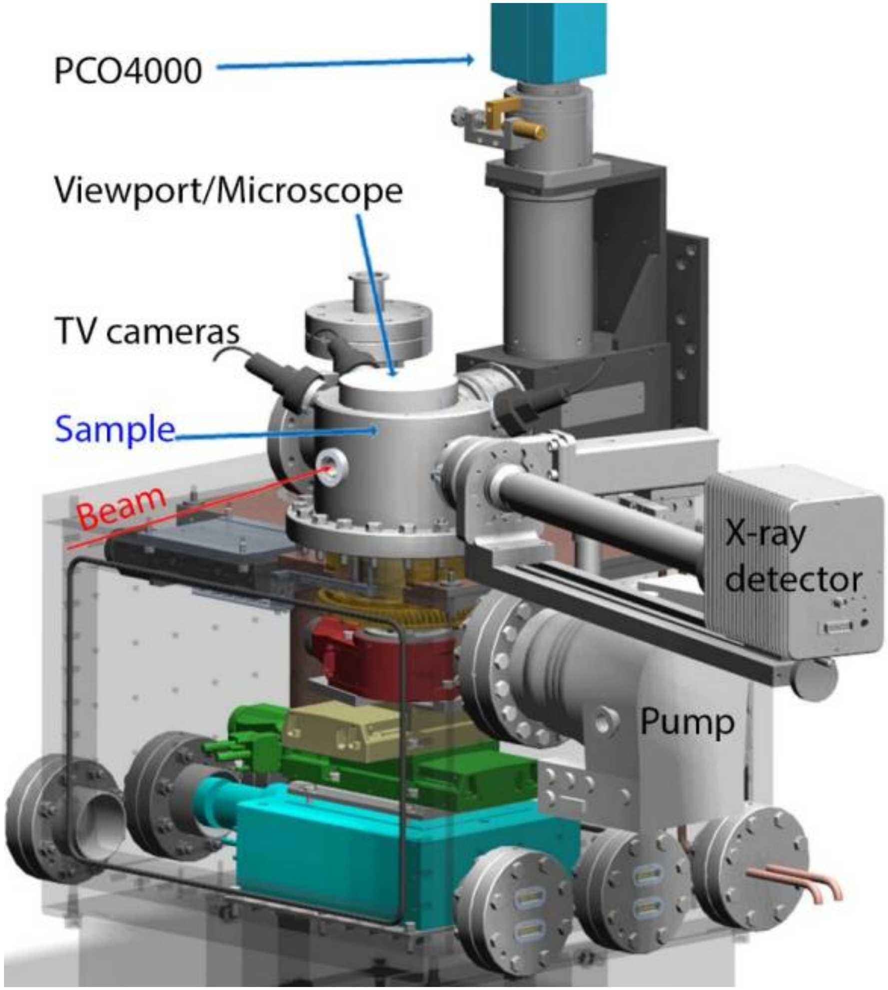
Beamline P06



Beamline P06



Beamline P06

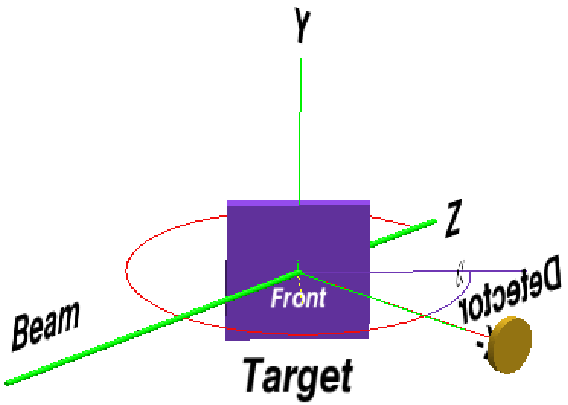


- At beamline P06 a cryo chamber is developed for the investigation of frozen, biological samples by XRF and X-ray (absorption) tomography.

The Maia detector

- Why use the Maia detector?

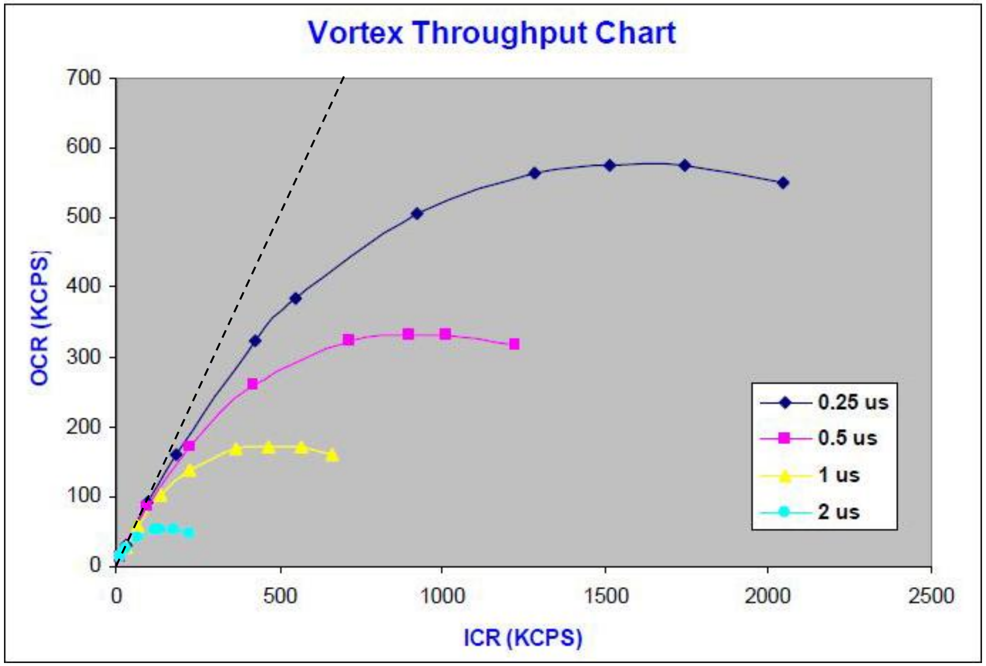
Vortex EM SDD



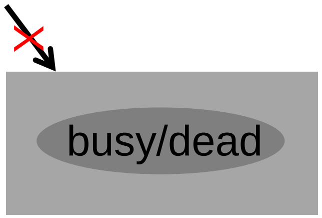
The high intensity primary radiation oversaturates the detector and necessitates the attenuation of the primary beam.

XRF: X-ray fluorescence spectrometry

- More photons are not always better.
  - Dead time



Source: www.hitachi-hitec-science.us, 2013



detector

ICR Incoming Count Rate

OCR Outgoing Count Rate

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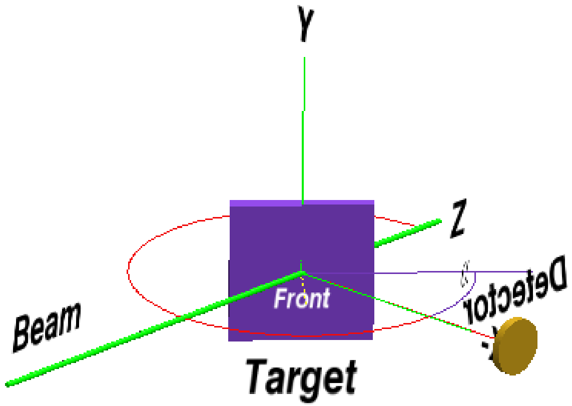
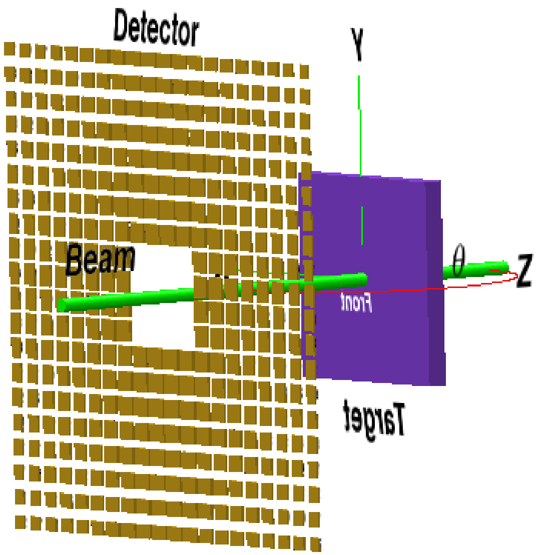
The Maia detector

Vortex EM SDD



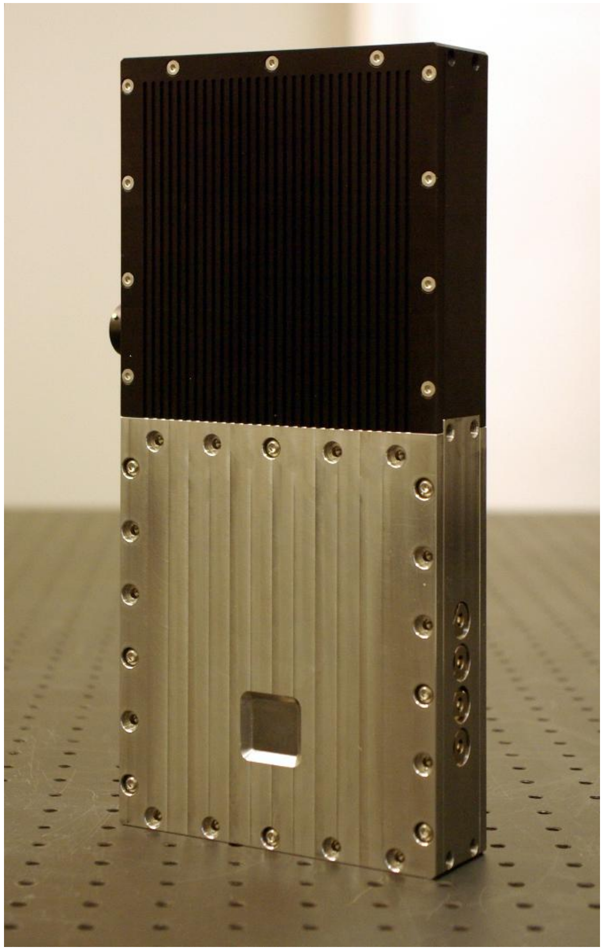
Maia

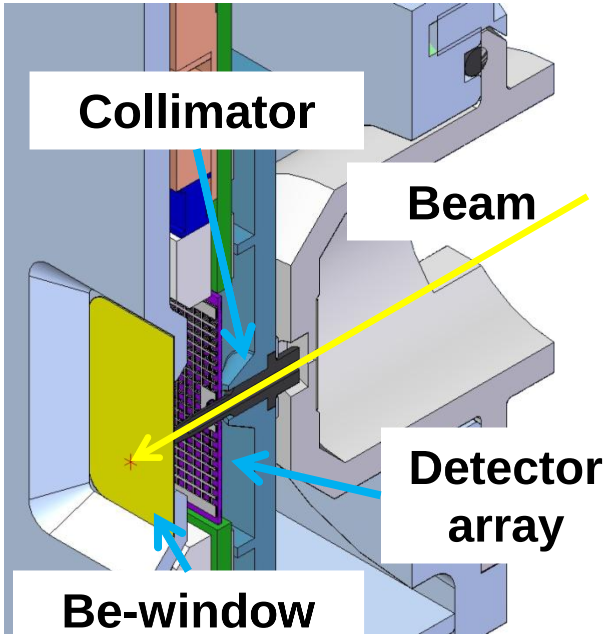


1 detector element
50 mm^2 active area
Solid angle: ~0.12 sr
Count rate: 5x10^5 photons/s
Typical dwell time: 100 ms/pixel

386 detector elements
1 mm^2 active area/element
Solid angle ~1.3 sr
Count rate: 10^7 photons/s
Typical dwell time: 1 ms/pixel

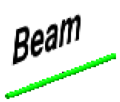
The Maia detector





R. Kirkham, et al., The Maia spectroscopy detector system: engineering for integrated pulse capture, low-latency scanning and real-time processing, AIP Conf. Proc. 1234 (2010) 240-243.
C.G. Ryan, et al., The new Maia detector system: Methods for high definition trace element imaging of natural material, AIP Conf. Proc. 1221 (2010) 9-17.

The Maia detector



1 detector e
50 mm^2 act
Solid angle
Count rate:
Typical dwe

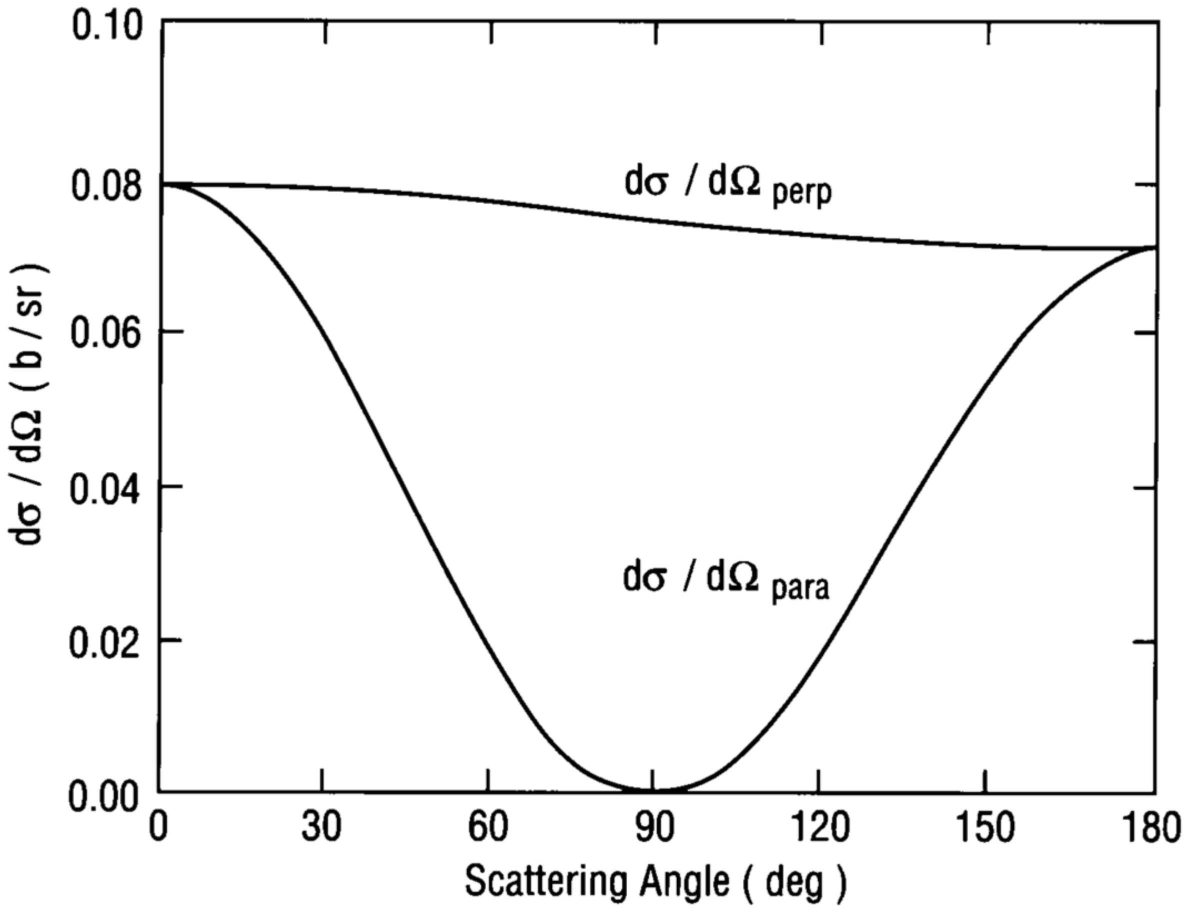
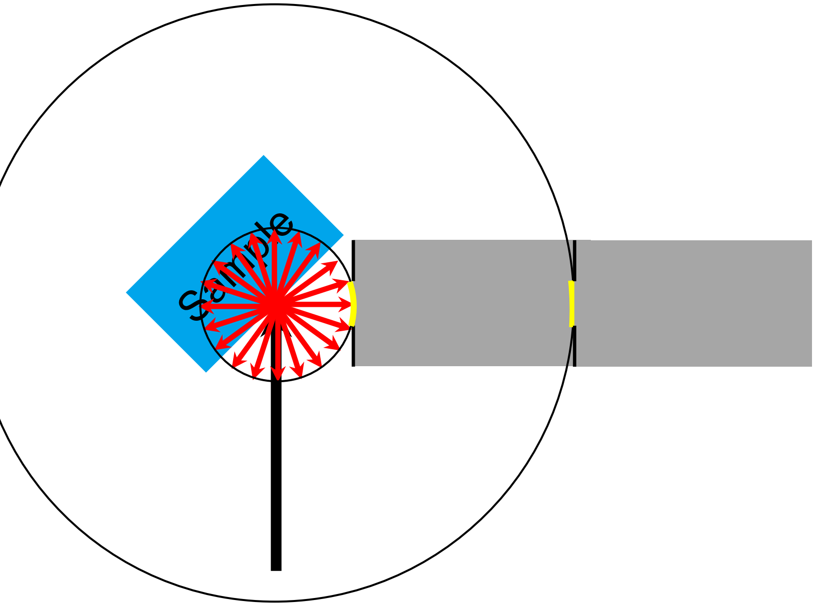


Figure 10 Dependence of incoherent scattering cross sections for x-rays polarized parallel and perpendicular to the plane of the stored electron orbit on the scattering angle. Observation at a scattering angle of 90° gives optimum signal-to-background conditions. (From Jones KW, et al. Ultramicroscopy 24:313, 1988.)

From: K.W. Jones, Synchrotron Radiation-Induced X-ray Emission, in: R.E. Van Grieken, A.A. Markowicz (Eds), Handbook of X-ray Spectrometry, 2nd Edition, Marcel Dekker, Inc., New York, 2002, pp. 513.

XRF: X-ray fluorescence spectrometry

- Solid angle



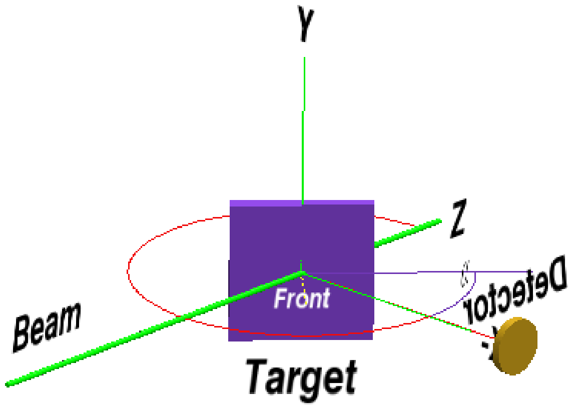
$$\frac{I_{recorded}}{I_{emitted}} = \frac{A_{detector}}{4\pi r^2}$$

$A_{detector}$ active area of detector
r distance of sample to detector

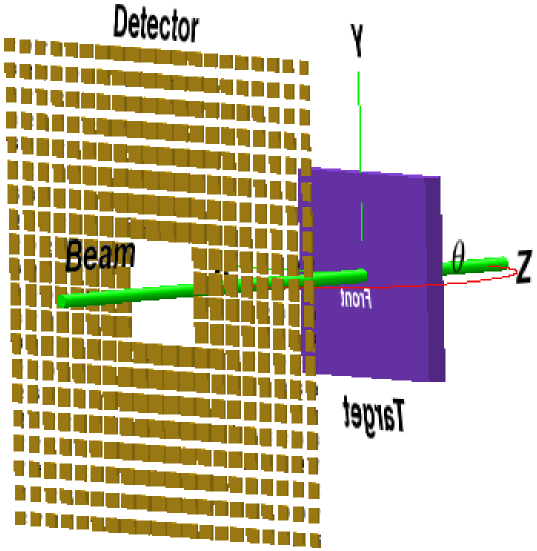
The solid angle Ω is expressed in steradians.
(1 steradians = 1 r²)

The Maia detector

Vortex EM SDD



Maia



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Typical dwell time: 100 ms/pixel

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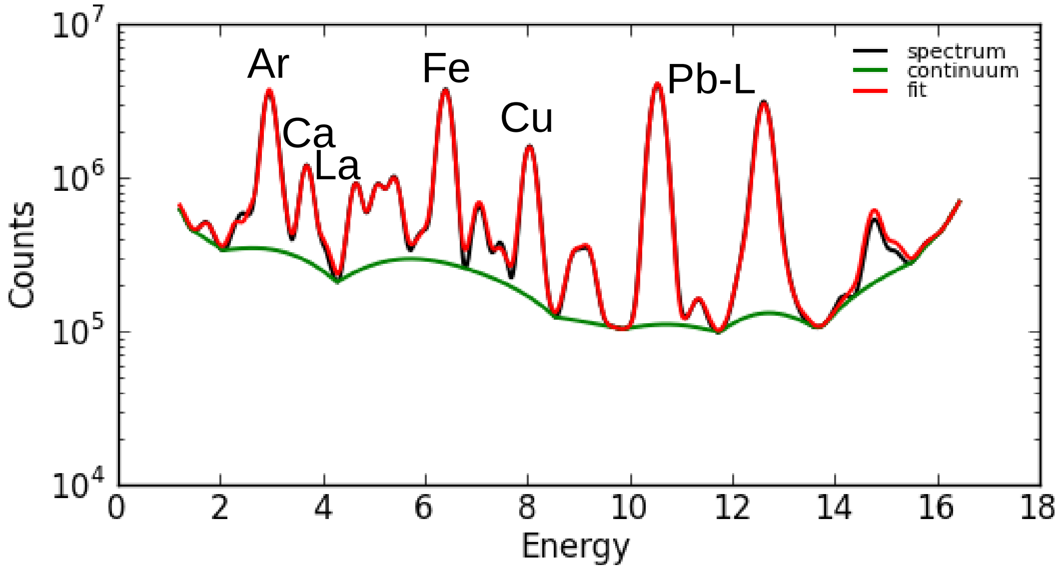
1 mm^2 active area/element
Solid angle ~1.3 sr
Count rate: 10^7 photons/s
Typical dwell time: 1 ms/pixel

The Maia detector

AXO thin film standard @ 19.5 keV
(Sum of 1904 x 1370 scanned pixels, 9130 s live time)



Energy resolution (Mn-K_{α}): ~300 eV

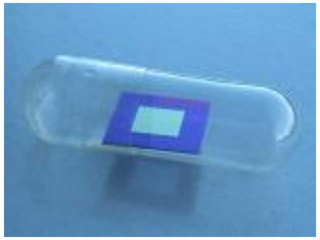


Image: © www.axo-dresden.de

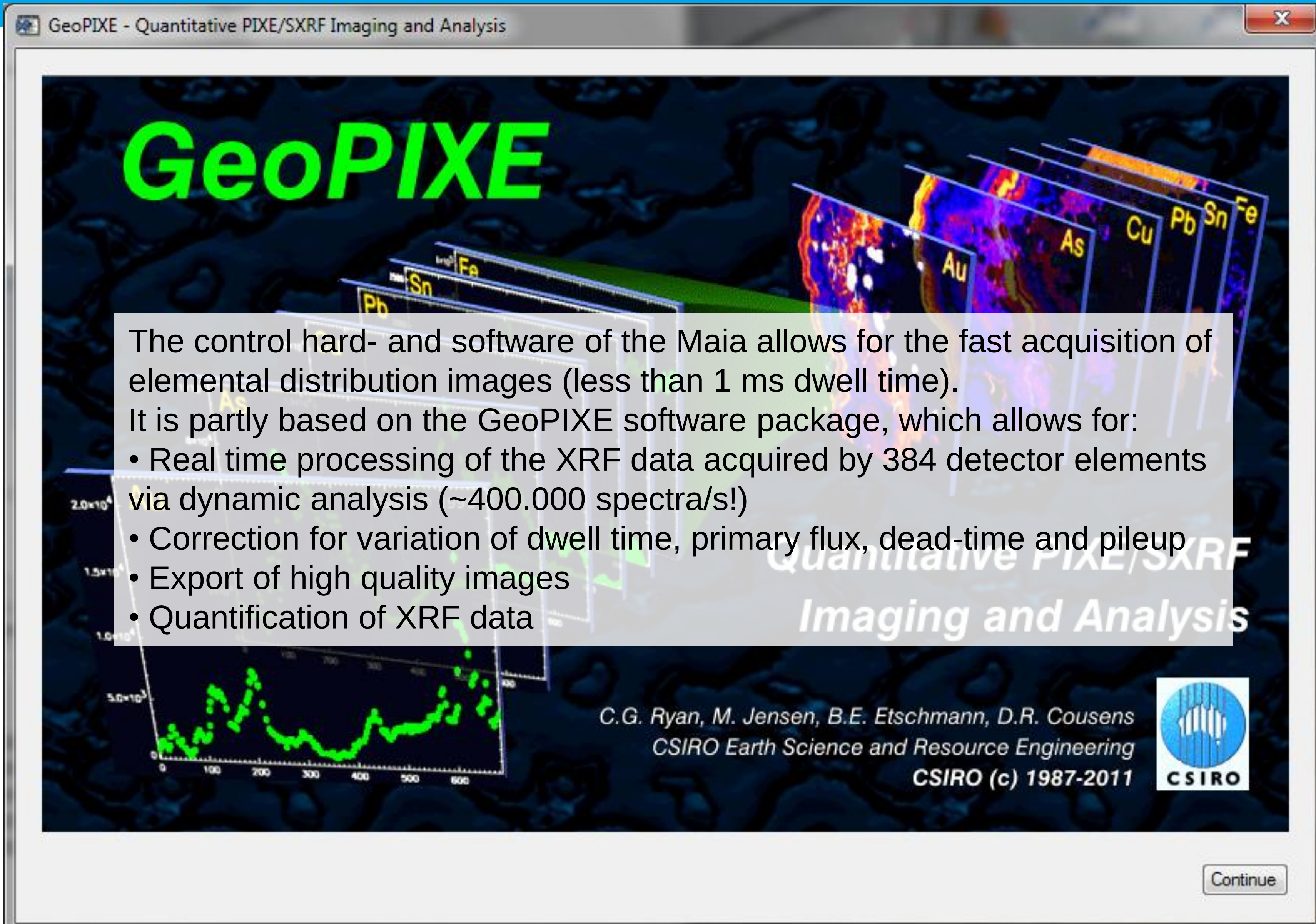
The Maia detector

$$LOD = 3 \cdot c \cdot \frac{\sqrt{I_{back}}}{I_{signal}} \cdot \sqrt{t}$$

Element	Concentration [ng/mm²]	LOD [ng/mm²] for 1 s	LOD [ng/mm²] for 1 ms	Thickness of pure metal layer for 1 ms [nm]
Pb-L_α (10.6 keV)	7.7±1.3	0.045	1.4	12
La-L_a (4.6 keV)	9.0±1.9	0.880	28	460
Cu (8.0 keV)	2.4±0.5	0.047	1.6	18
Fe (6.4 keV)	4.0±0.4	0.110	3.4	43
Ca (3.7 keV)	11.4±5.5	0.760	24	1500

Notes on the limits of detection:
- LODs are energy dependent
- LODs are sample matrix dependent
- The LODs shown present the "best case"

The Maia detector



The control hard- and software of the Maia allows for the fast acquisition of elemental distribution images (less than 1 ms dwell time).

It is partly based on the GeoPIXE software package, which allows for:

• Real time processing of the XRF data acquired by 384 detector elements via dynamic analysis (~400.000 spectra/s!)

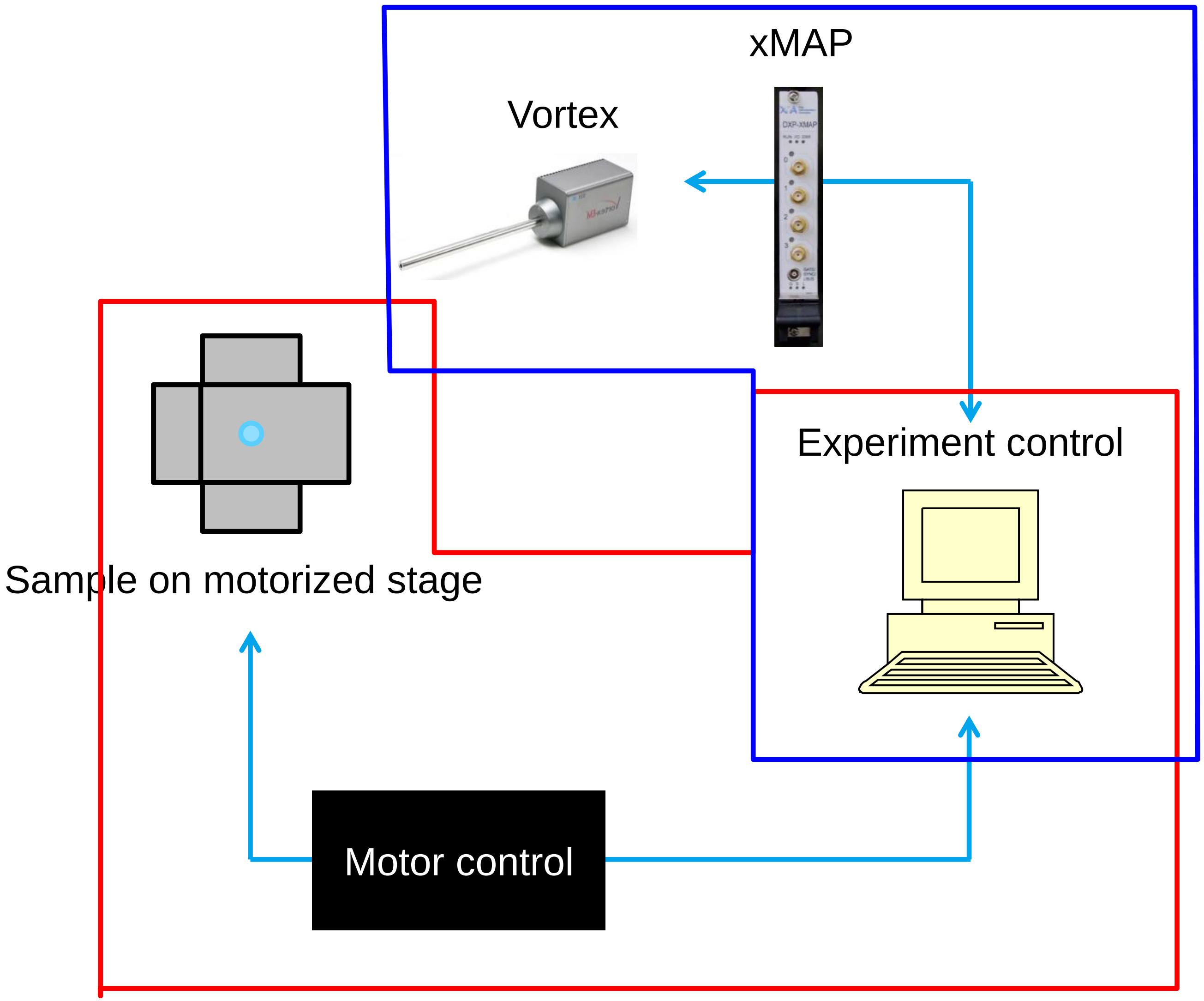
• Correction for variation of dwell time, primary flux, dead-time and pileup

• Export of high quality images

• Quantification of XRF data

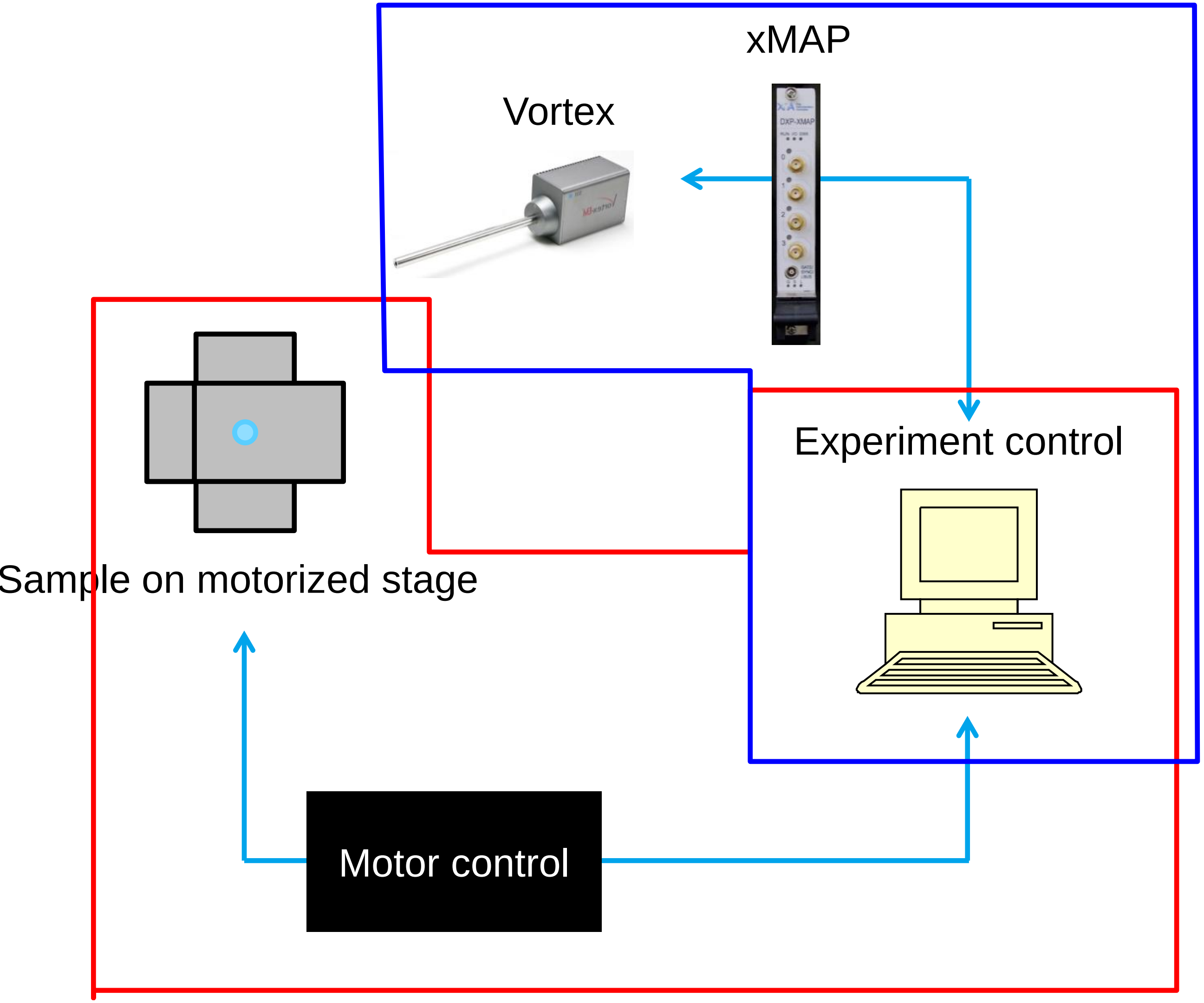
C.G. Ryan, D.R. Cousens, S.H. Sie, W.L. Griffin, G.F. Suter, E. Clayton, Nucl. Instrum. Methods Phys. Res., Sect. B 47 (1990) 55-71.

The Maia detector



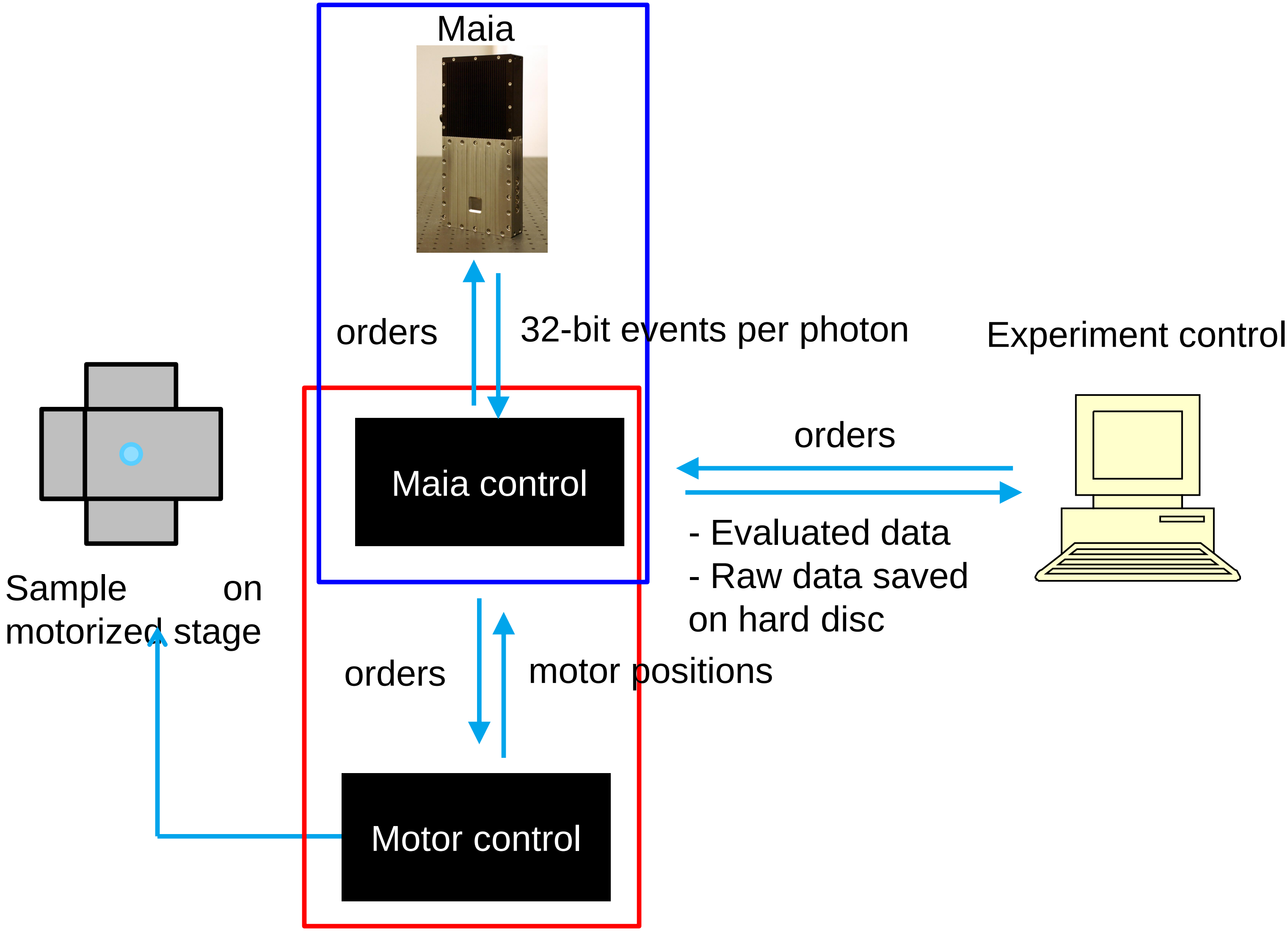
For i pixels do begin
1. Sample is moved
2. Spectrum is acquired
Endfor

The Maia detector



Continuous movement of inner motorized stage
For i pixels do begin
Spectrum is acquired
Endfor

The Maia detector

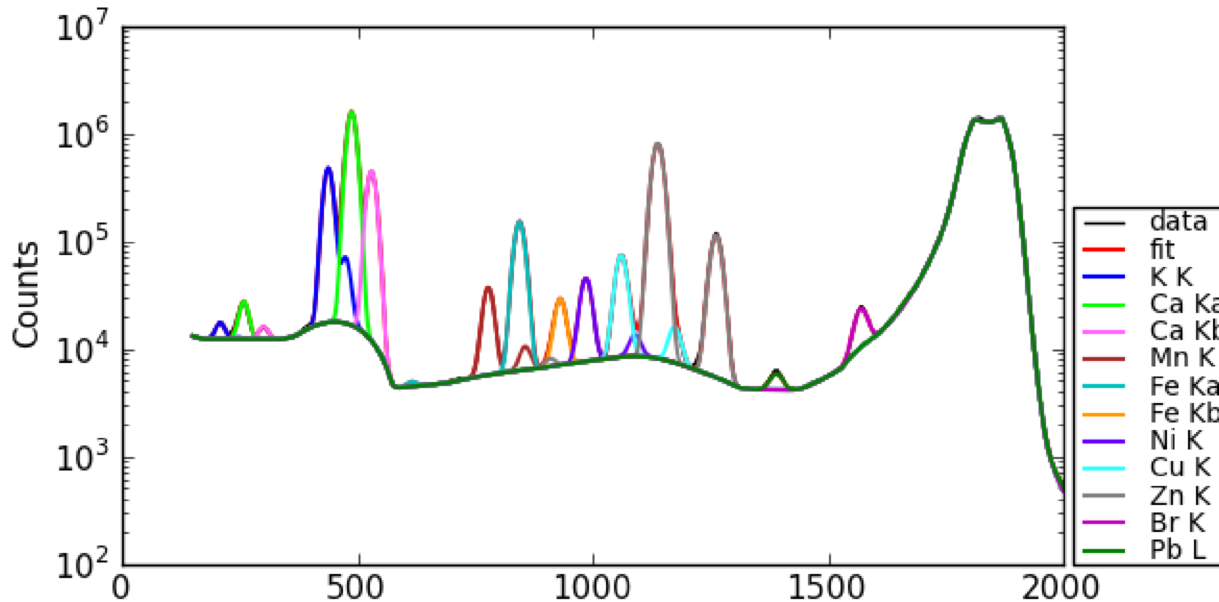


The Maia detector

- Data treatment by least squares (χ^2) fitting

A selected range of cha

$$f_i = a_0 B_i + \sum_{k=1}^{k} a_k \ldots$$



linear intensit

factors a

non-linear parameters p. (e.g. energy calibration and detector settings)

background

$$\chi^2 = \sum_{i=0}^{i} w_i (S_i - f(a_0, a_1, \ldots, p_0, p_1, \ldots))^2$$

The Maia detector

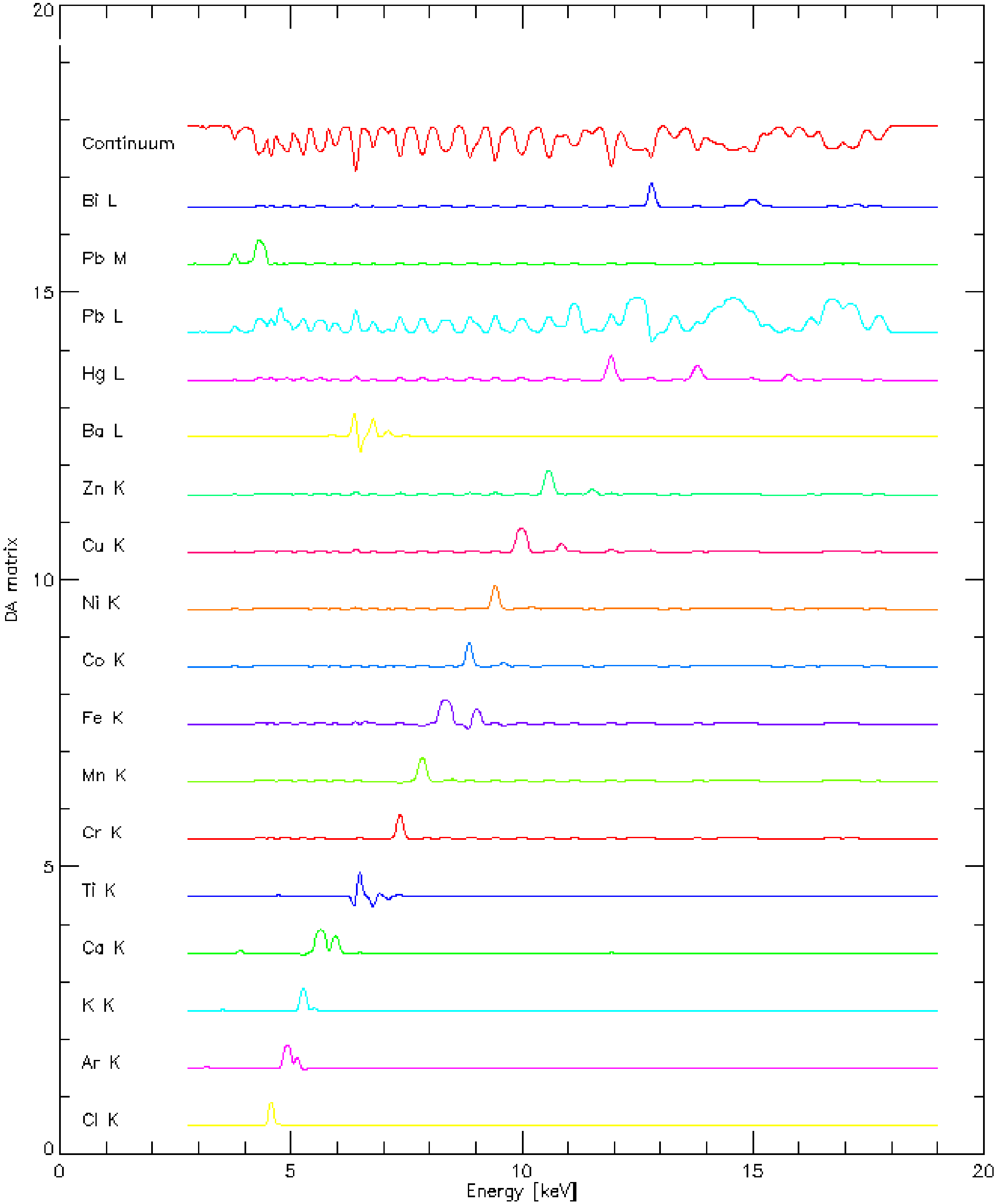
- Data treatment by linear least squares (χ) fitting

$$f_i = a_0 B_i + \sum_{k=1}^{k} a_k y_{i,k}$$

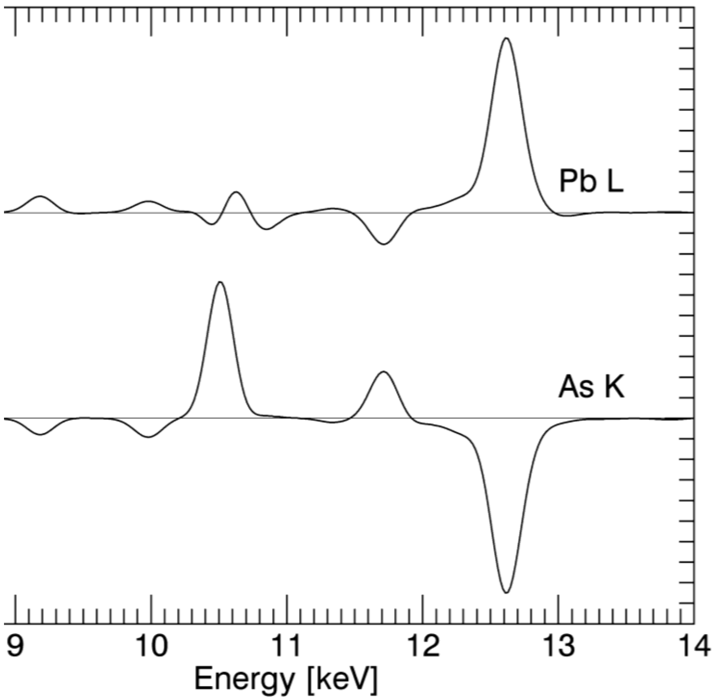
background

linear intensity factors a

Peak profile, dependent on non-linear parameters p. (e.g. energy calibration and detector settings)



Dynamic Analysis matrix



Res., Sect. B 104 (1995) 157-165.

The Maia detector

- The Maia detector produces a steady stream of 32-bit „events“.
- These events are processed on a custom FPGA, which also allows for online data evaluation via DA.
- On special occaision, e.g. when the beam enters a new pixel, a special 32-bit event is created that documents this.

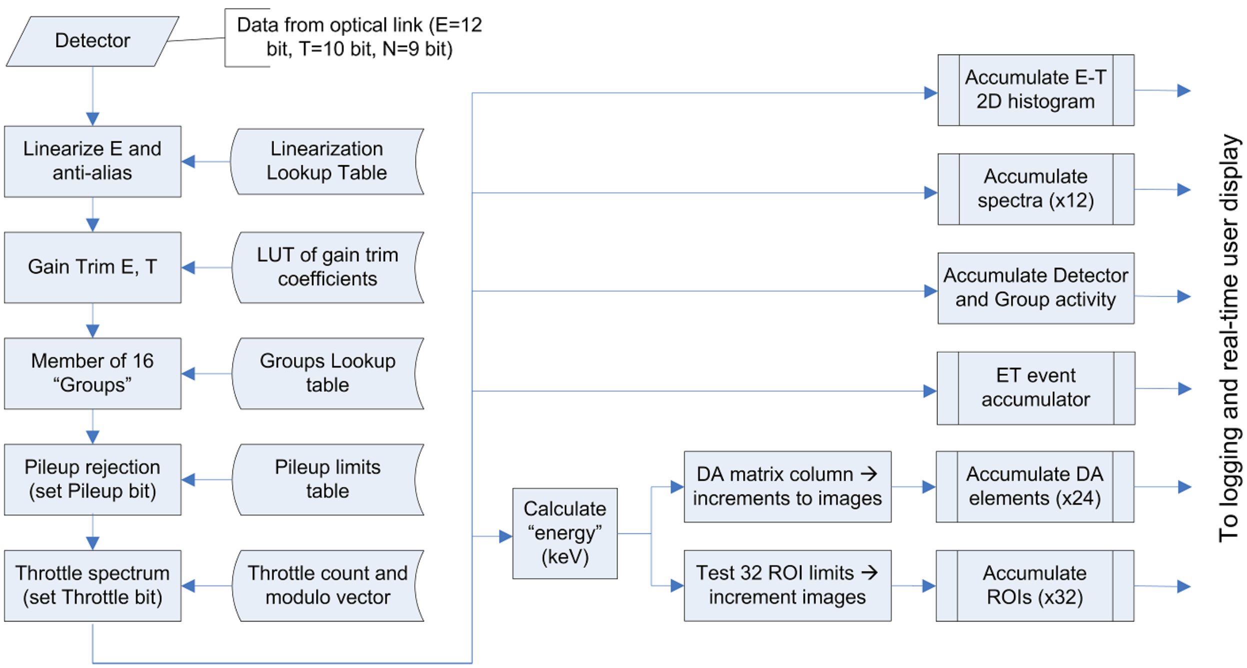


FIGURE 3. Photon event processing pipeline in the FPGA in the Processing subsystem.

From: R. Kirkham, et al., The Maia spectroscopy detector system: engineering for integrated pulse capture, low-latency scanning and real-time processing, AIP Conf. Proc. 1234 (2010) 240-243.

The Maia detector

- Advantages of the Maia detector system:
  - High sensitivity: Large solid angle
  - High sensitivity: Low dead time per detector element
  - Fast scanning due to efficient control hard-and software
- Disadvantage:
  - Moderate energy resolution (280-300 eV @ Mn-K_{α})
  - Enhanced scatter contribution (compensated by enhanced sensitivity)

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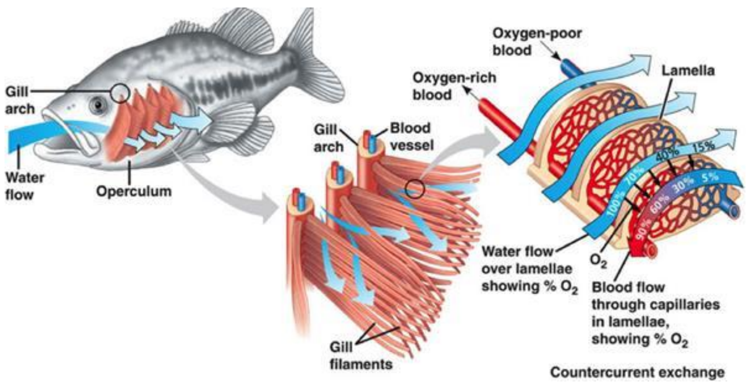
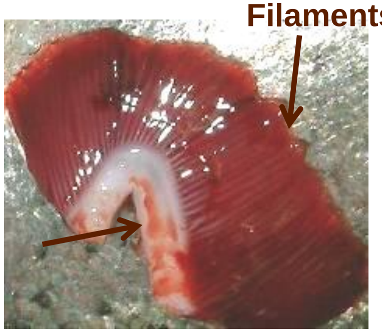
Application Examples

Gills = interface fish/water

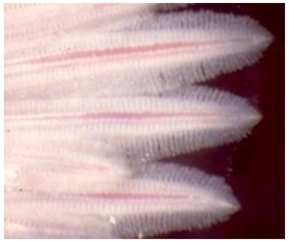


Filaments

Gill arch



Gill filament

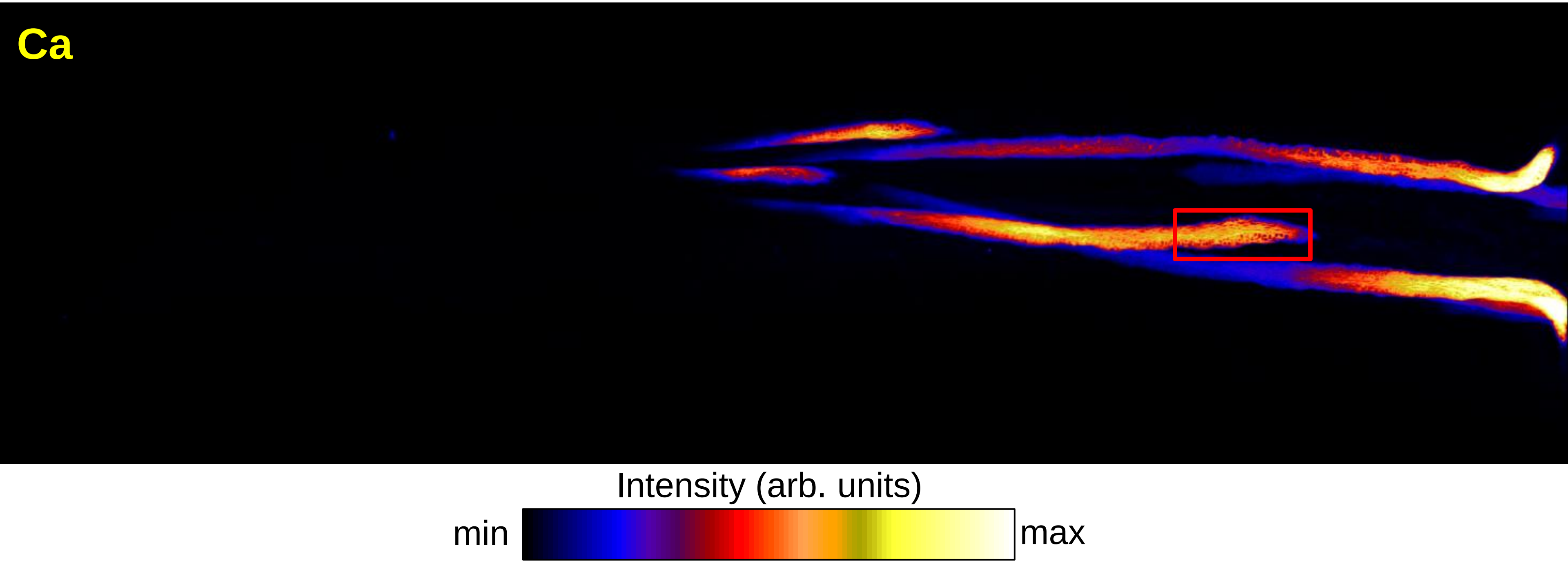


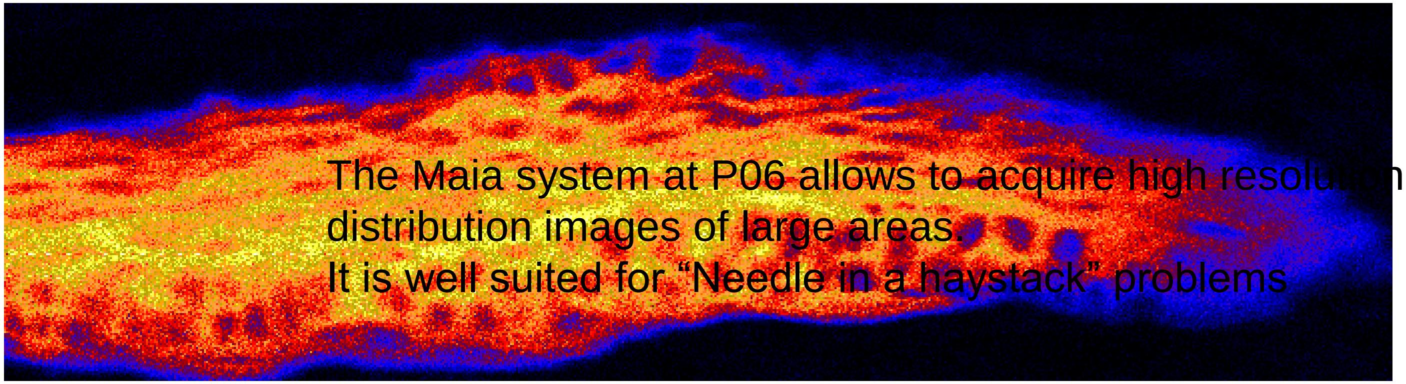
Question: Is U actively taken up in the gills of Atlantic Salmon (*Salmo Salar*)?

- Atlantic Salmon was exposed for 96 hours to U (6 mg/L)
- Gills were removed from the fish and freeze dried
- Scanned with Maia at P06:
  - 0.5x0.5 µm step size
  - 4x1.165 mm^2 Area
  - 1.2 ms dwell time
  - 18 keV
  - ~8 hours measurement time

In collaboration with:
S. Cagno, O. Lind, B. Salbu: Norwegian University of Life Sciences (NO)
G. Nuyts, F. Vanmeert, K. Janssens: University of Antwerp (BE)

Application Examples





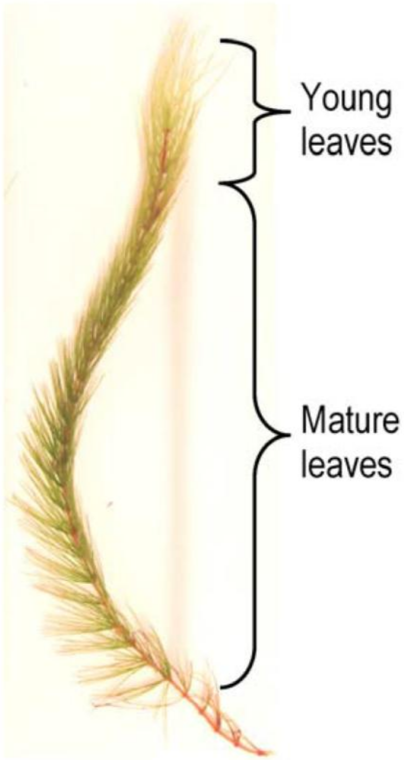
700x190 µm

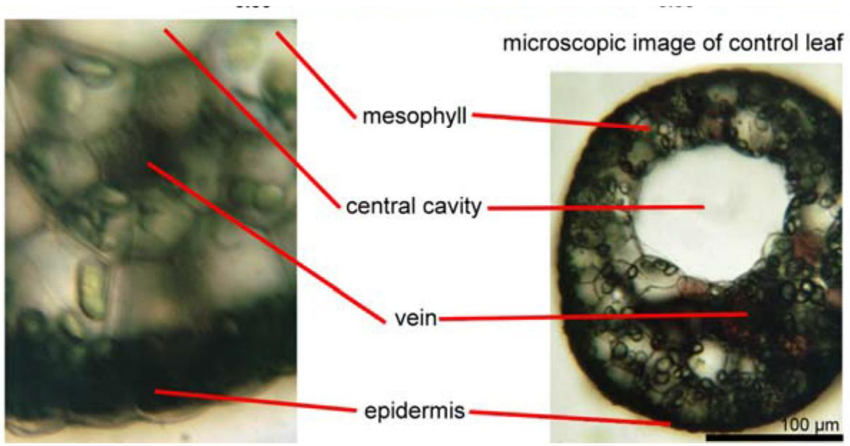
The Maia system at P06 allows to acquire high resolution elemental distribution images of large areas.
It is well suited for “Needle in a haystack” problems

- Explain tomography???XXX

XRF tomography

Distribution of As in *Ceratophyllum demersum*



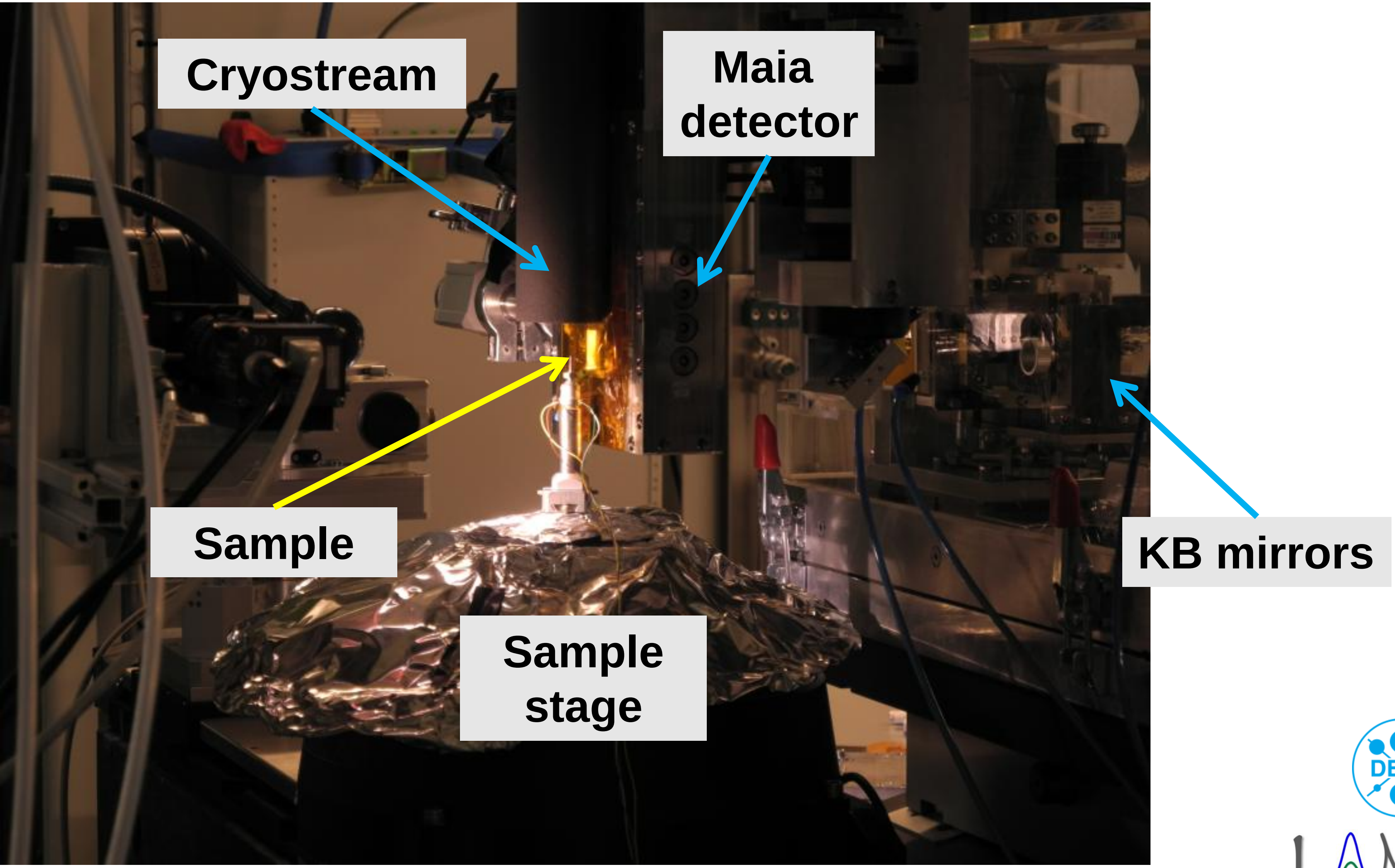


- *Ceratophyllum demersum* was grown in 0 to 5 µM As solution.
- After harvesting leafs and cleaning: Transfer to glass capillaries
- Shock-freezing in supercooled isopentane
- First XRF tomography experiment with Maia at P06

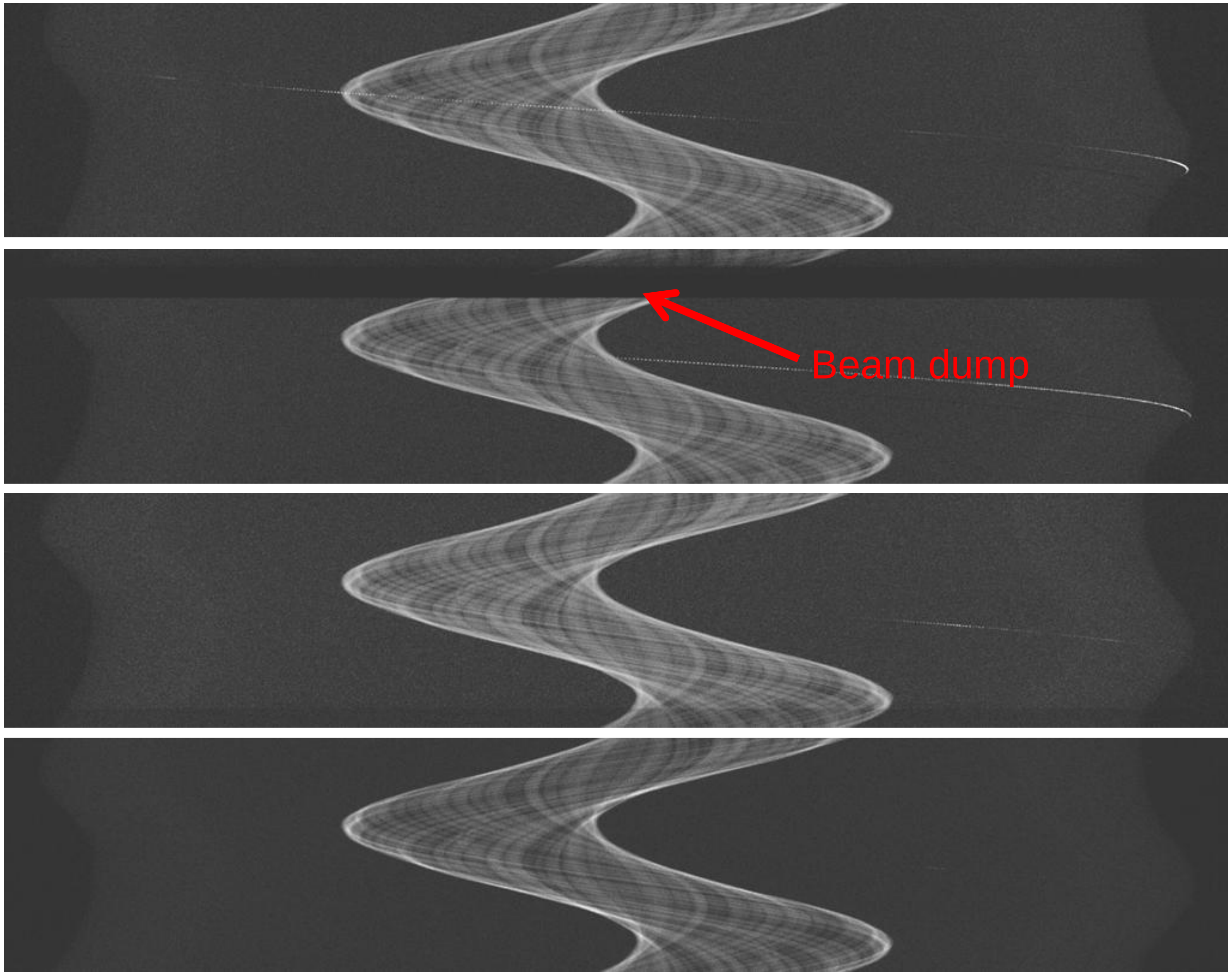
Data acquired in collaboration with:
Seema Mishra (University of Konstanz, DE)
Hendrik Kuepper (Academy of Sciences of the Czech Republic, CZ)

Images reproduced from:
Mishra S et al. Plant Physiol. 2013;163:1396-1408

XRF tomography

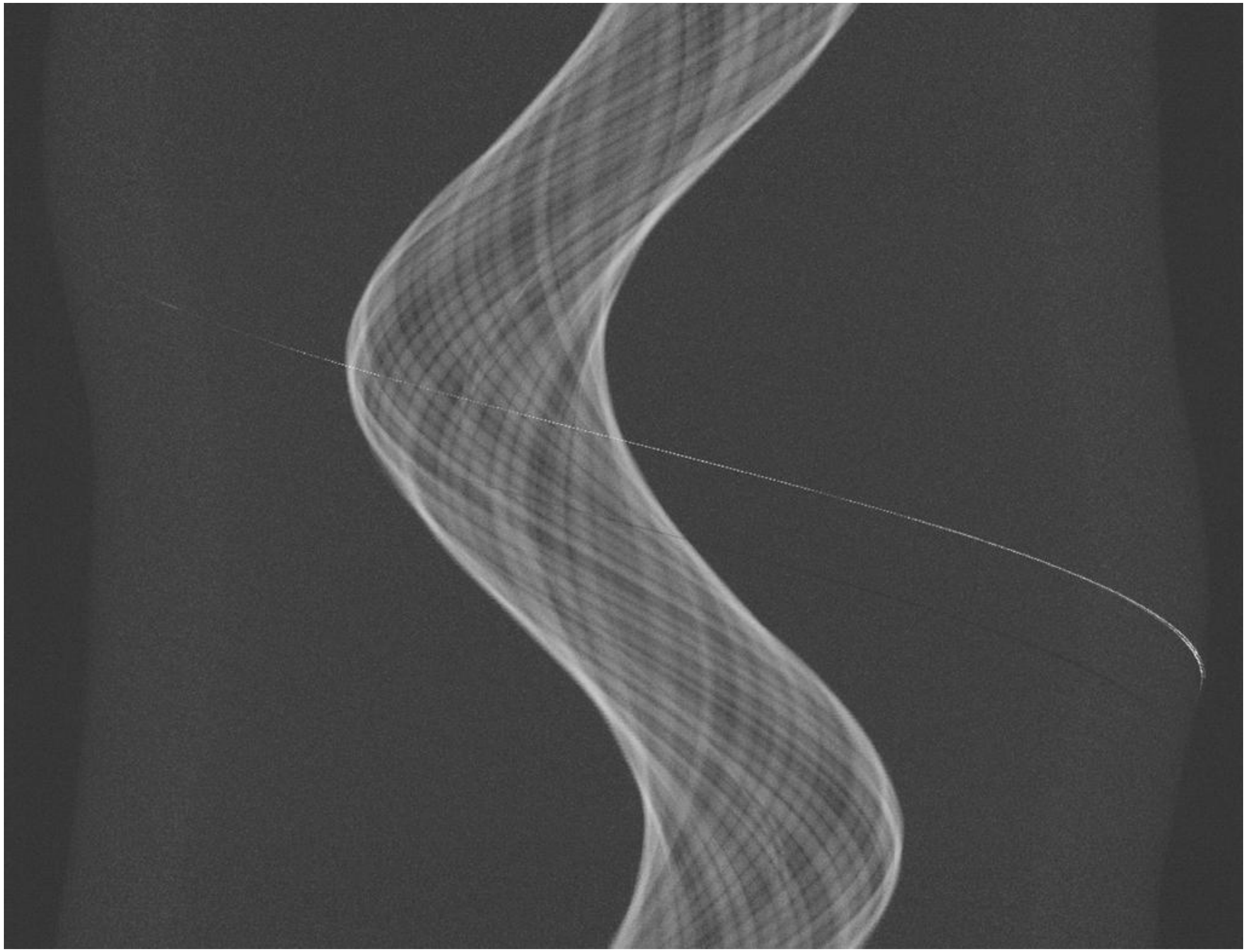


XRF tomography



4 sinograms were acquired:
- 4709 x 240 nm steps
- 900 x 0.4 degree steps
- 0.1 degree offset
- 1.2 ms dwell time
- 2 hours each

XRF tomography

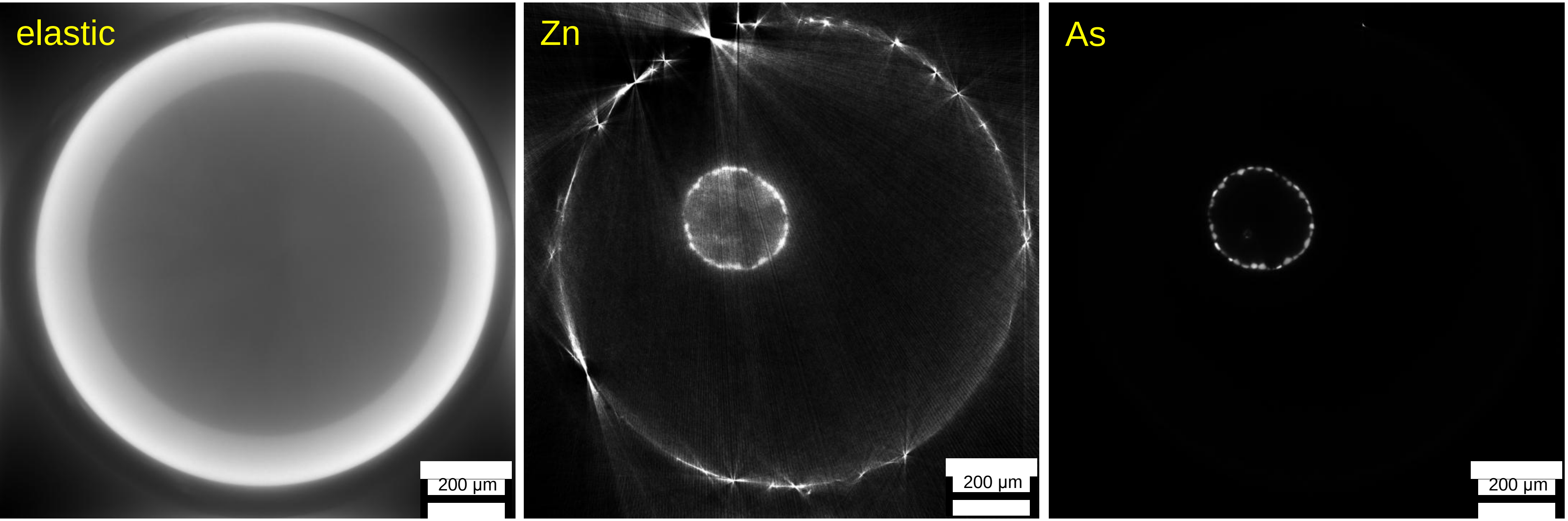


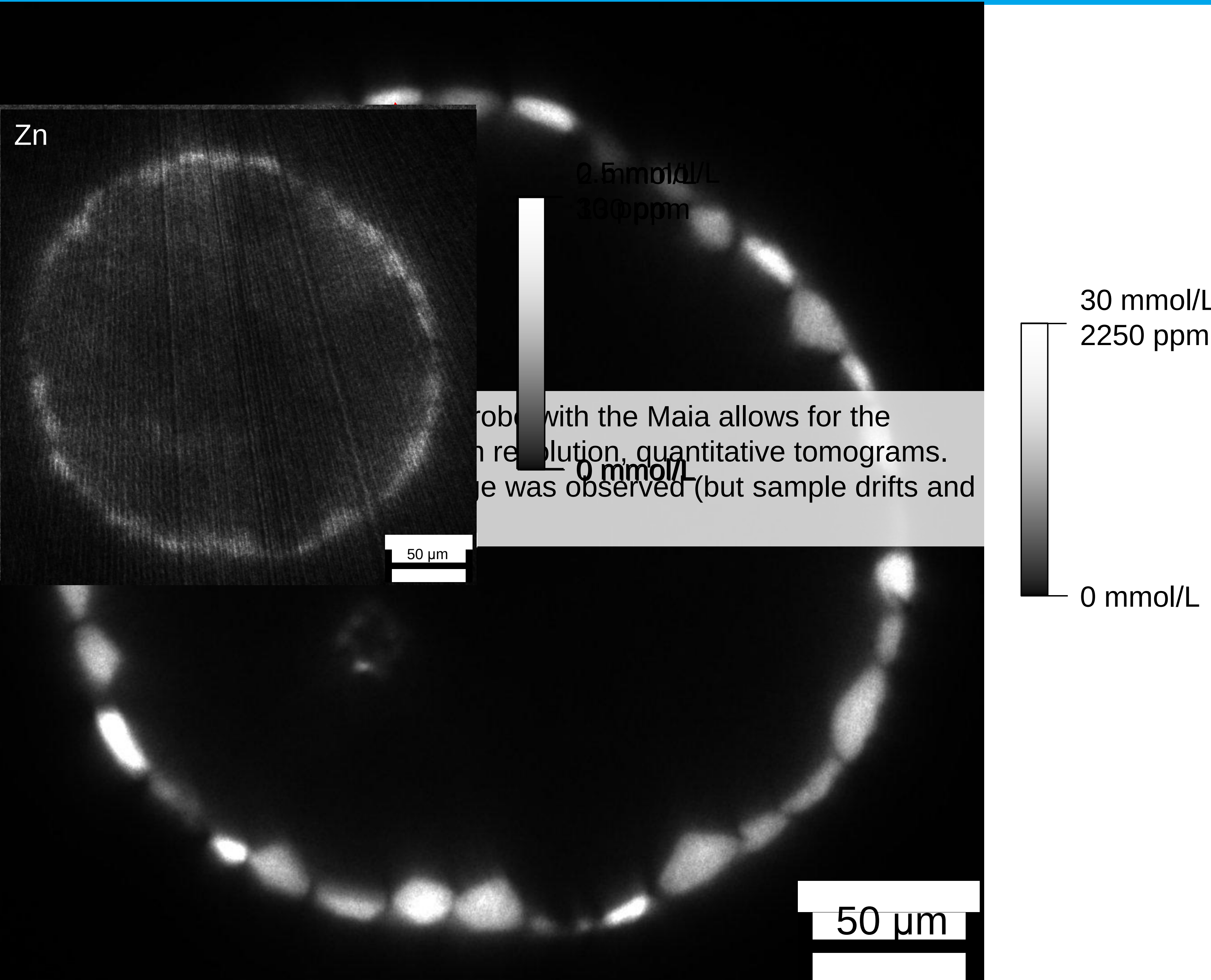
The sinograms were drift corrected and joined:

- 4709 x 240 nm steps
- 3600 x 0.1 degree steps

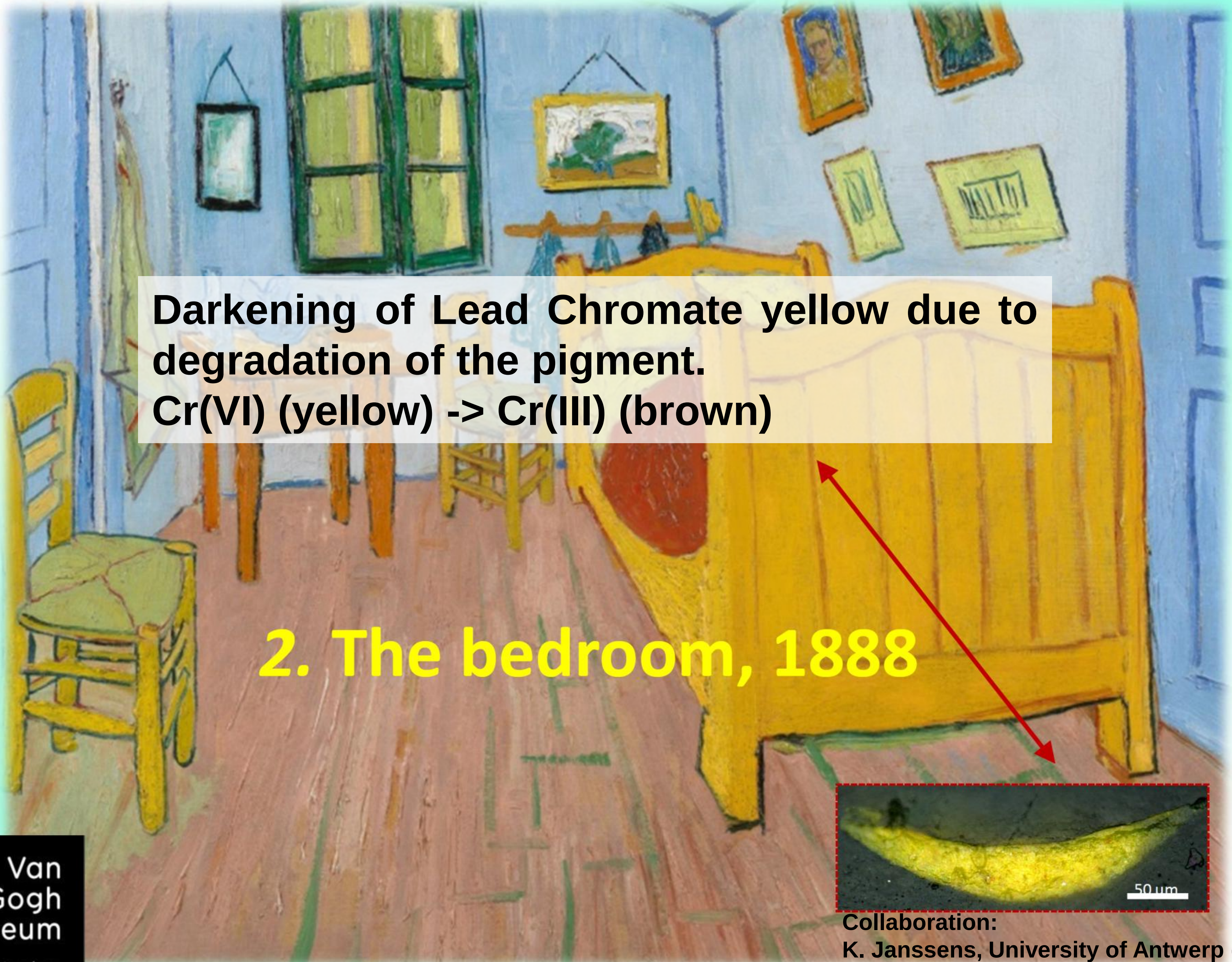
Image reconstruction: MLEM routine from XRDUA (W. De Nolf, F. Vanmeert and K. Janssens, J. Appl. Crystallogr. 2014, 47, 1107-1117)

XRF tomography





robe with the Maia allows for the
n resolution, quantitative tomograms.
ge was observed (but sample drifts and



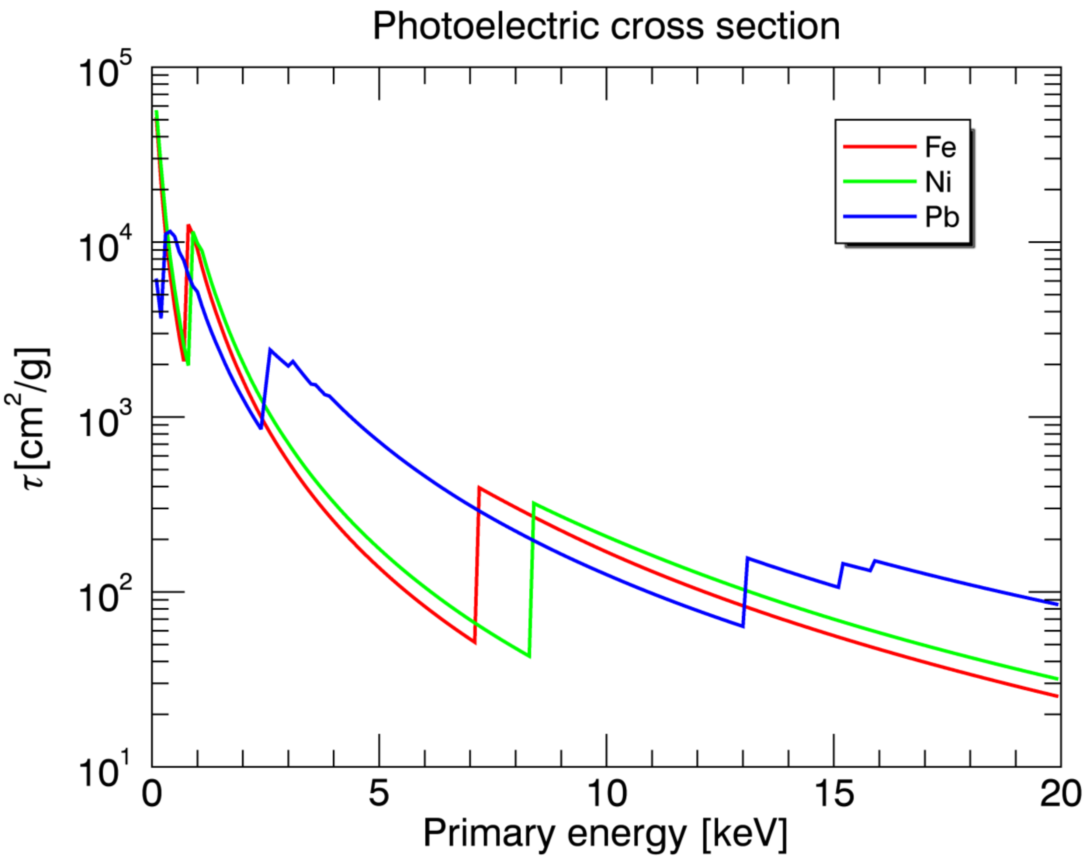
Darkening of Lead Chromate yellow due to degradation of the pigment.
Cr(VI) (yellow) -> Cr(III) (brown)

2. The bedroom, 1888

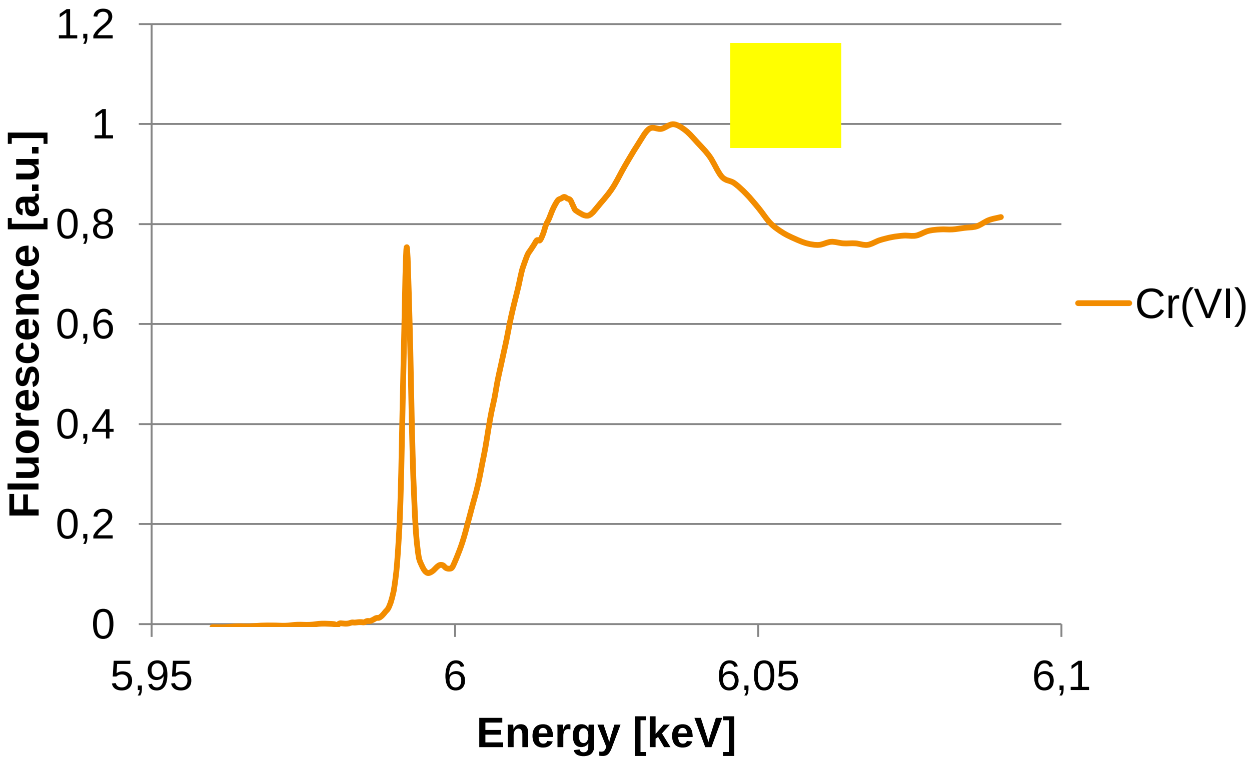
Collaboration:
K. Janssens, University of Antwerp (BE)
L. Monico, University of Perugia (IT)

Van Gogh Museum
Amsterdam

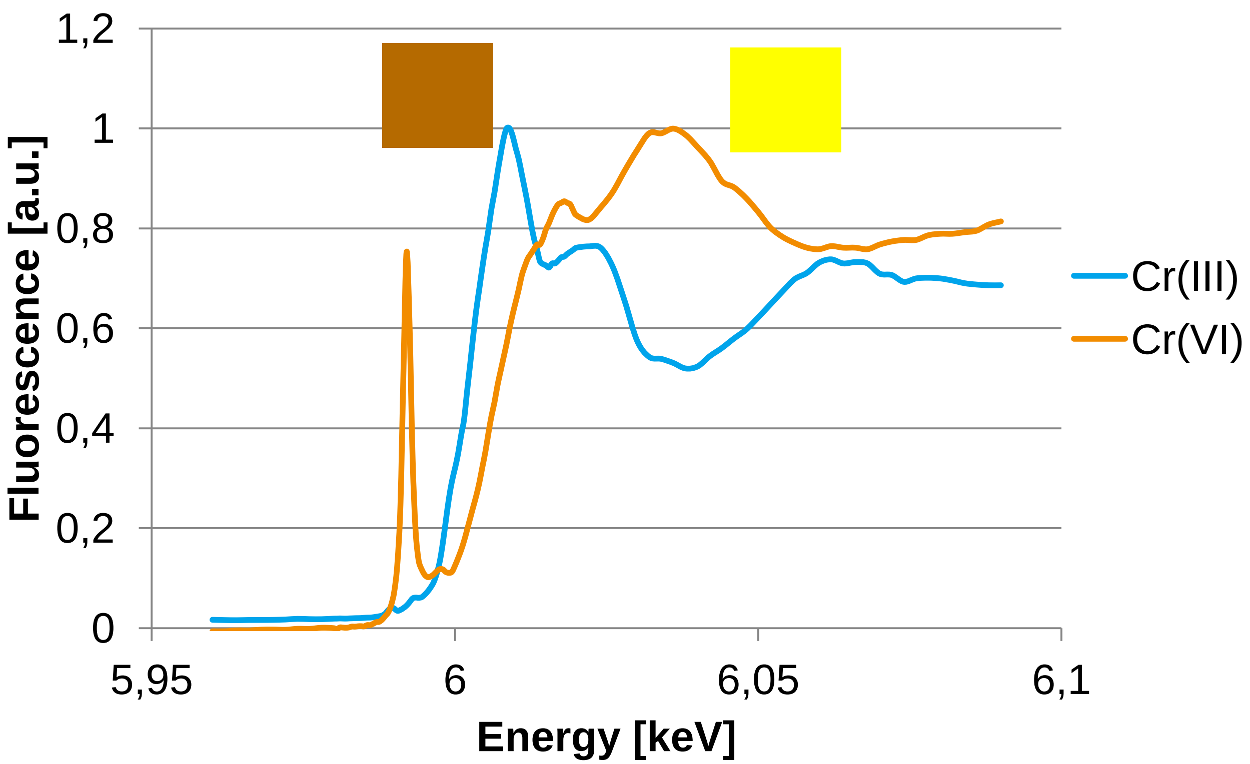
XANES: X-ray Absorption Near Edge Structure



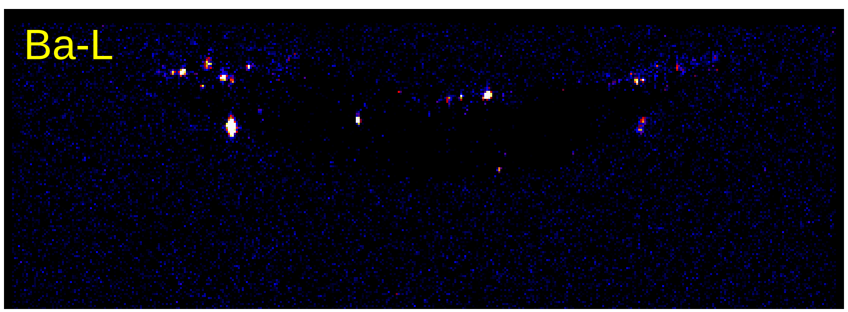
XANES: X-ray Absorption Near Edge Structure

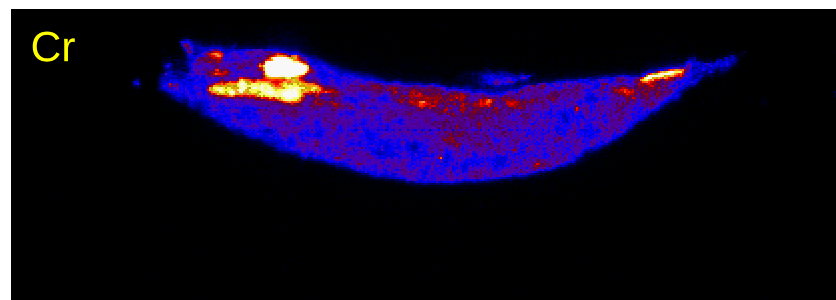


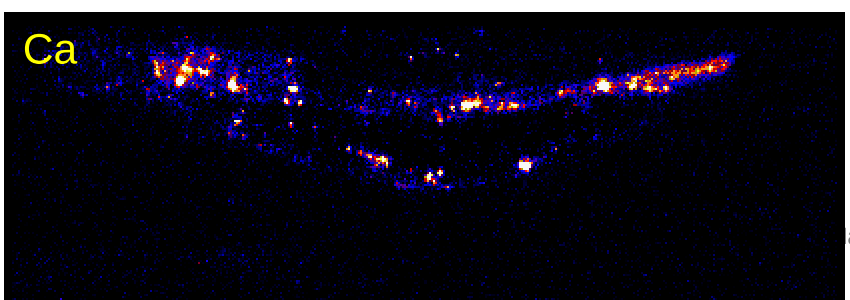
XANES: X-ray Absorption Near Edge Structure

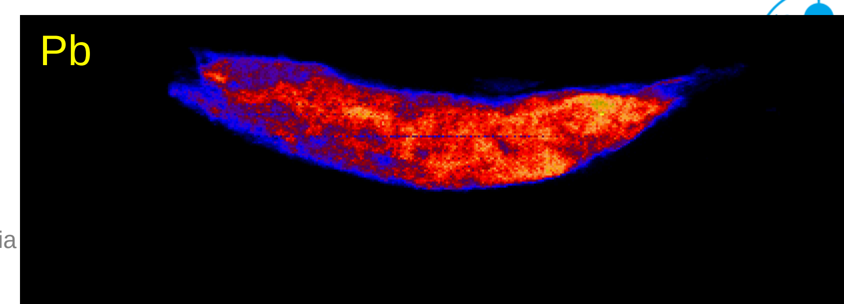


Scan area: 420x150 µm
Step size: 1 µm
Dwell time: 3 ms/pixel
Measurement time of one image: 3.5 minutes
Energy range: 5.96 to 6.088 keV in **125 scans**
Measurement time: ~8 hours

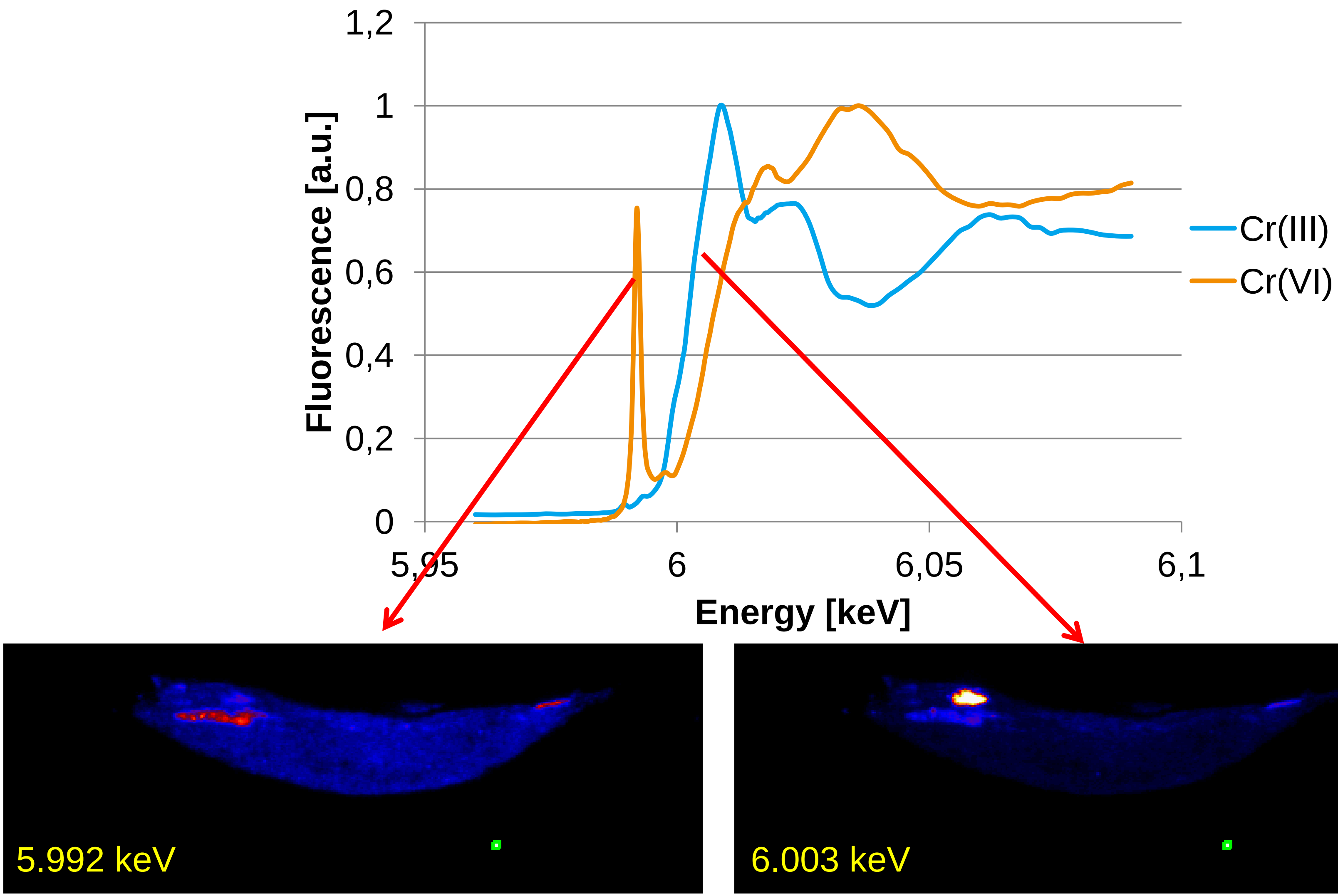




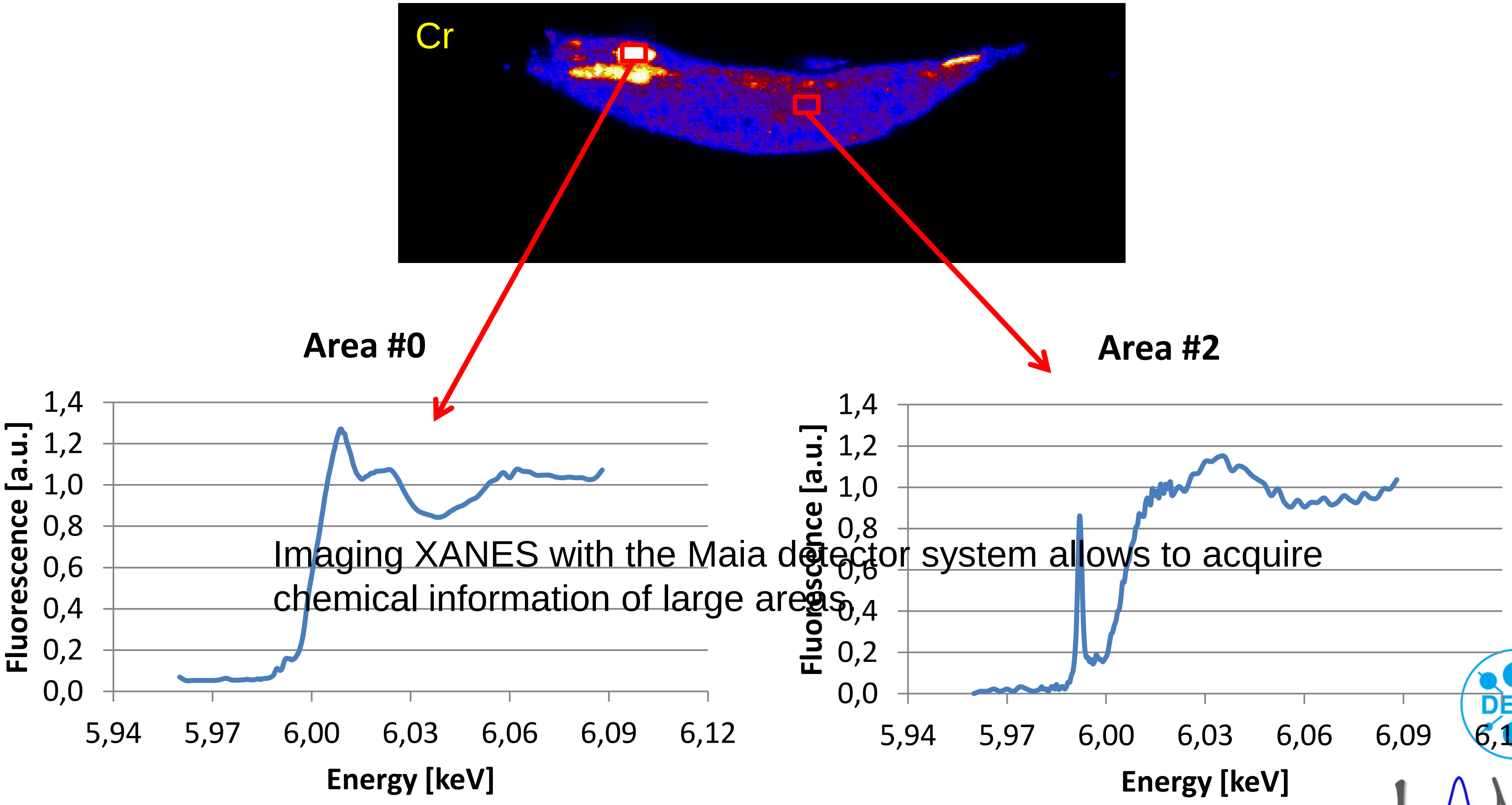




XANES: X-ray Absorption Near Edge Structure



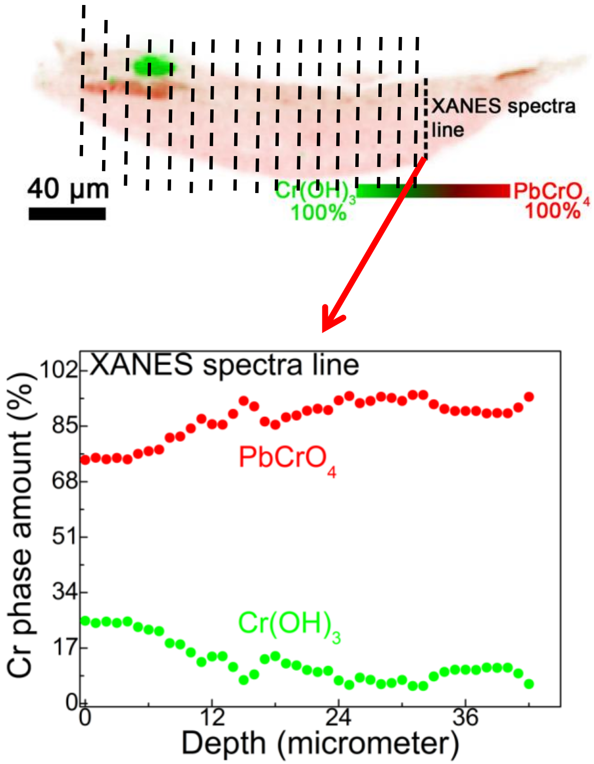
XANES: X-ray Absorption Near Edge Structure



Imaging XANES with the Maia detector system allows to acquire chemical information of large areas.

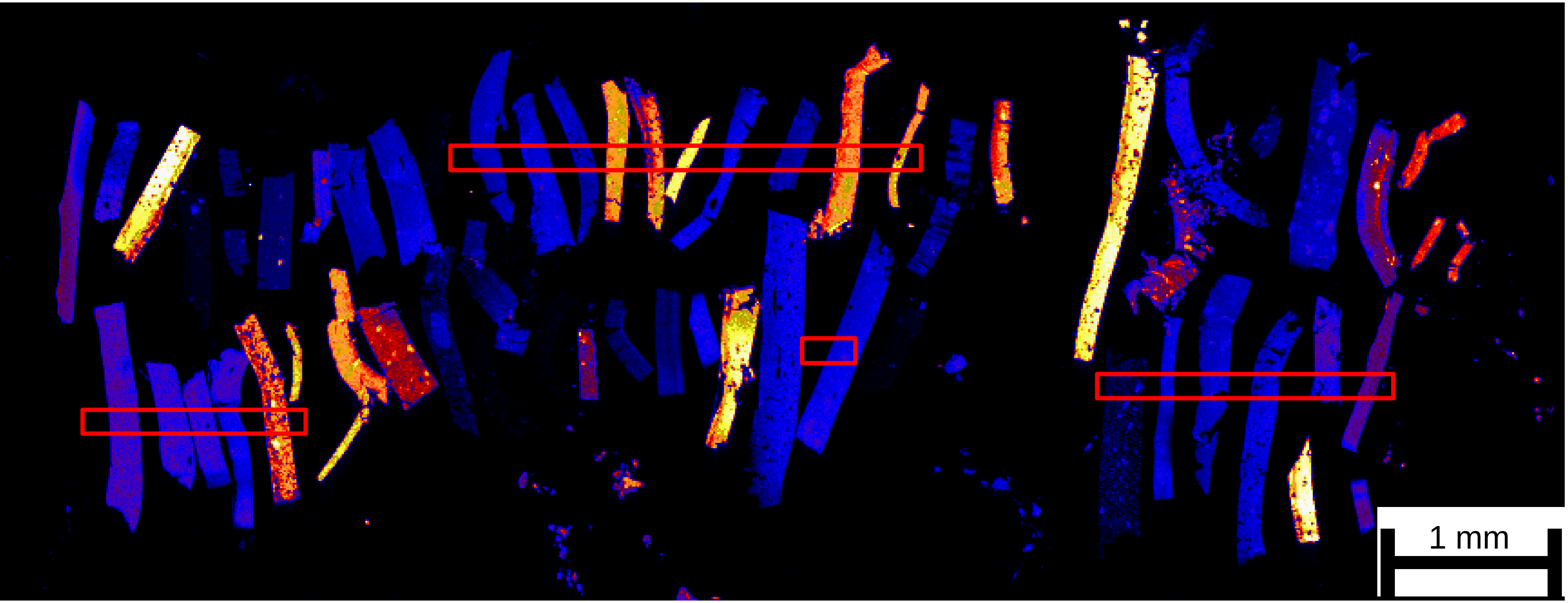
XANES: X-ray Absorption Near Edge Structure

- The full spectral data allows to identify the species present throughout the sample.
- From this data „degradation depth profiles“ can be obtained.
- As this can be done on any location the results are more representative than a simple line scan.



L. Monico, et al., *J. Anal. At. Spectrom.*, 2015, **30**, 613-626

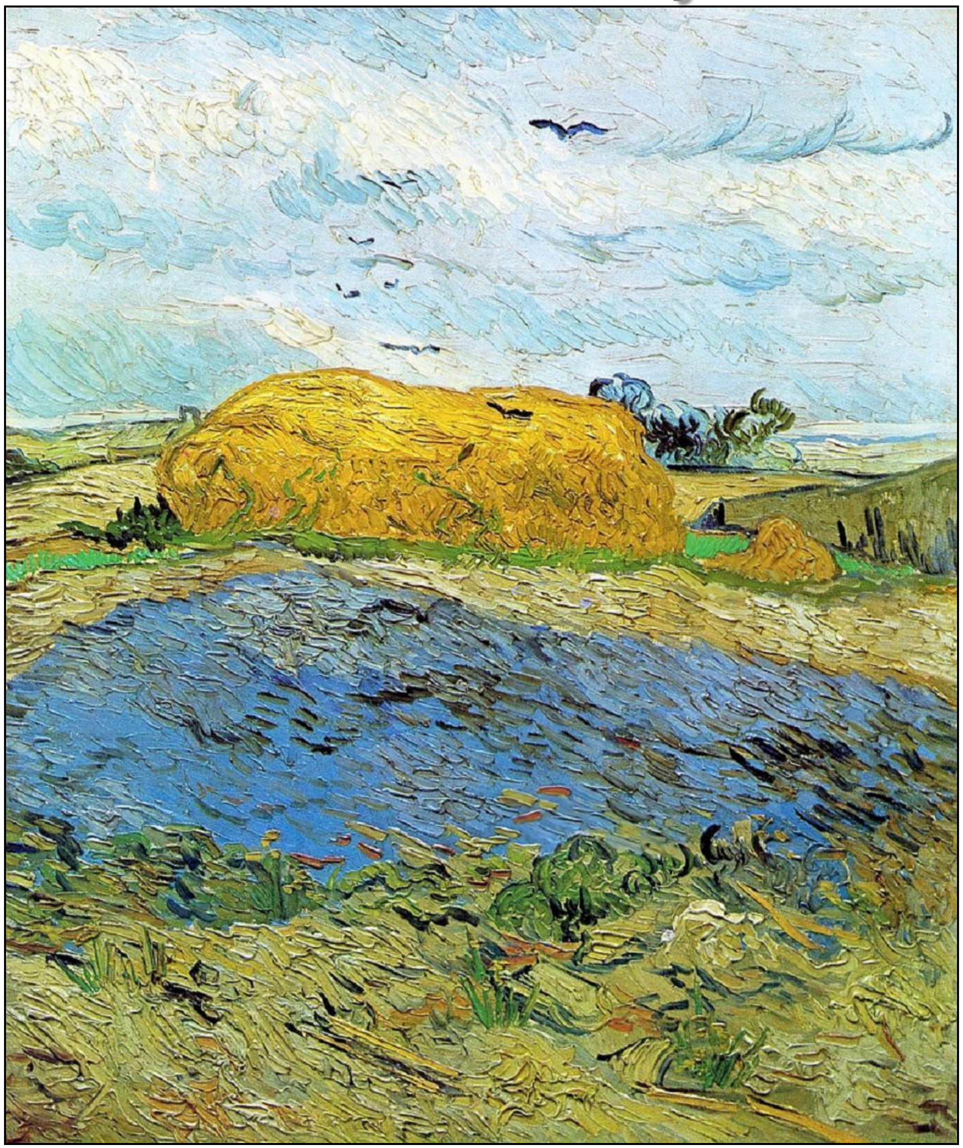
XANES: X-ray Absorption Near Edge Structure

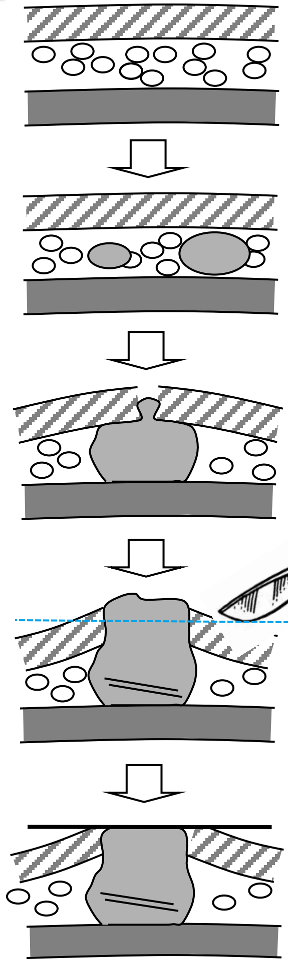


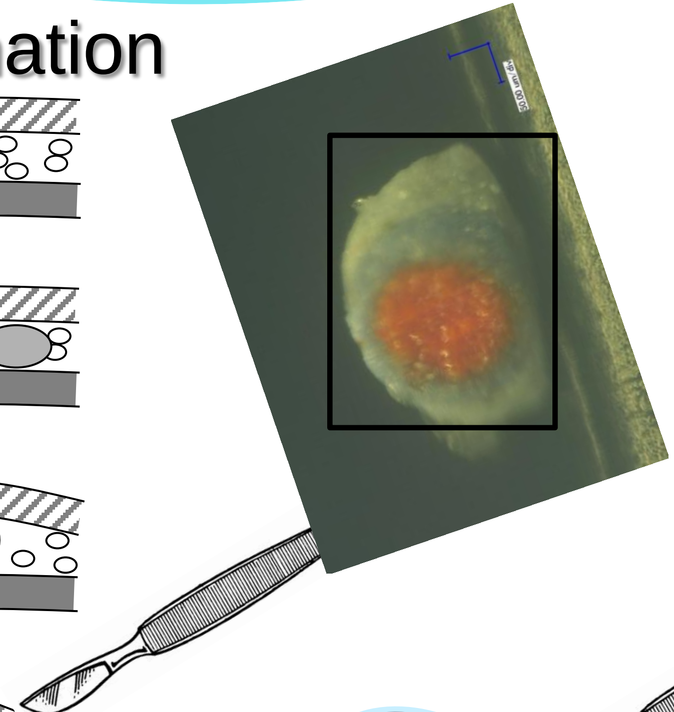
52 artifically aged samples of Cr yellow mounted on one plate. (10 µm step size, 1 ms dwell time, 900x330 pixels, 6 minutes)

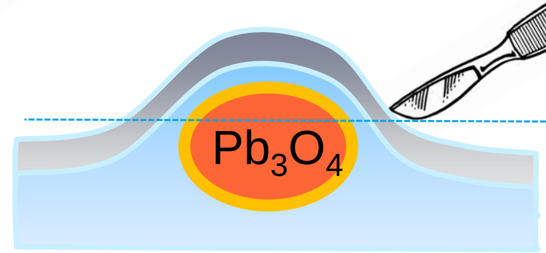
- Full spectral XANES imaging with the Maia detector allows for the investigation of multiple, closely mounted samples in randomly chosen areas.

Metal-carboxylate soap formation







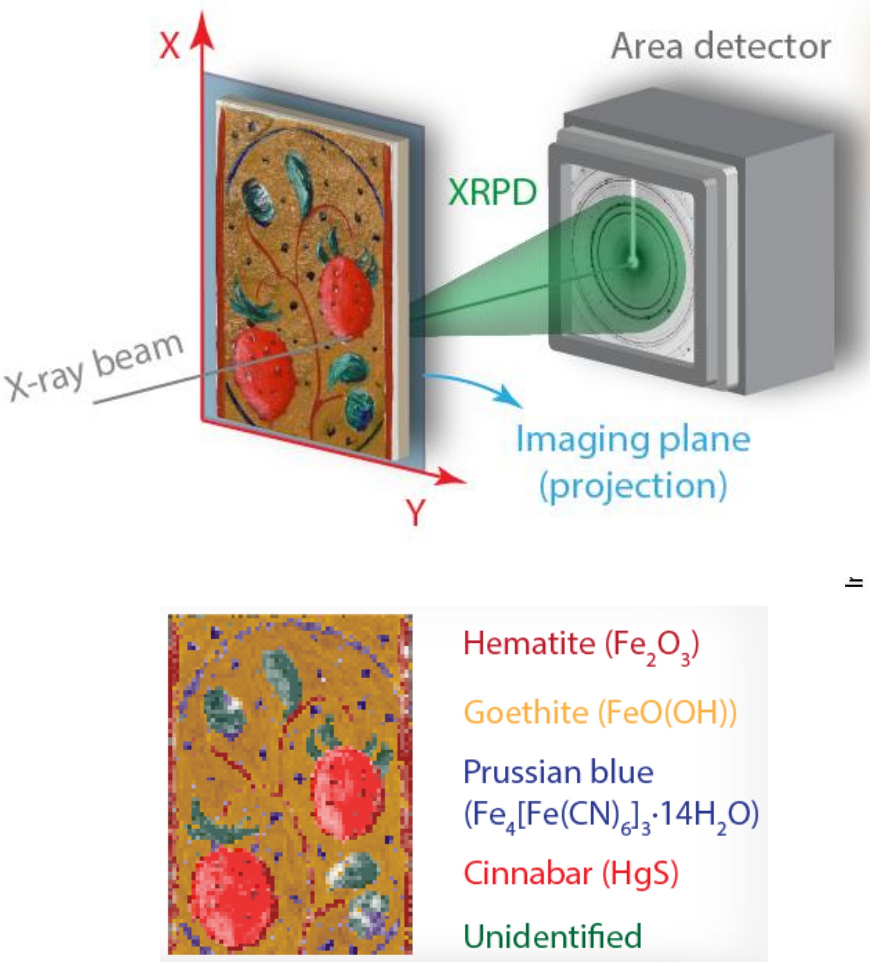


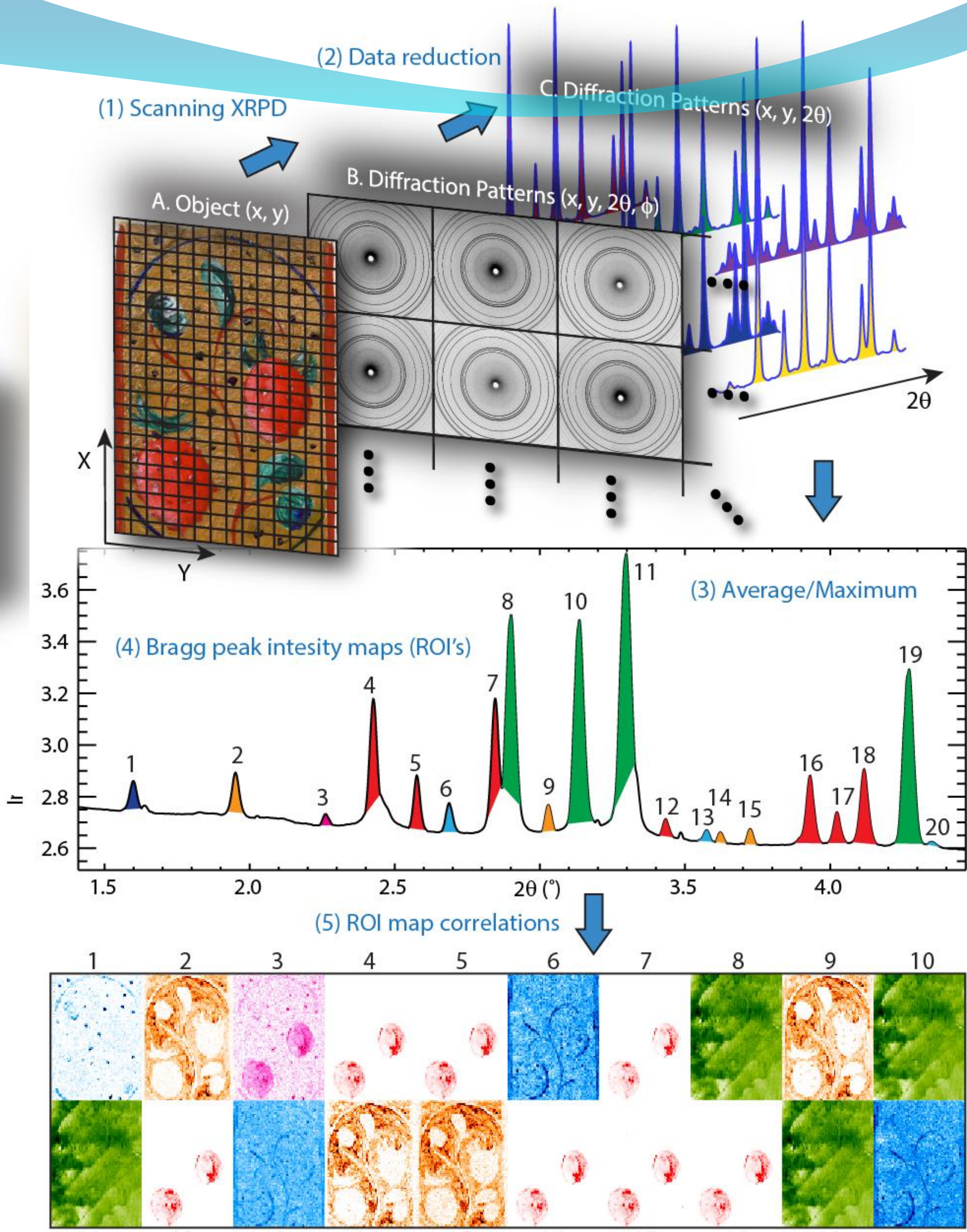
Minium degradation

Landscape with Haystack
1890 (F 563 / JH 2121), 64 x 52 cm,
Kröller-Müller Museum, NL

(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

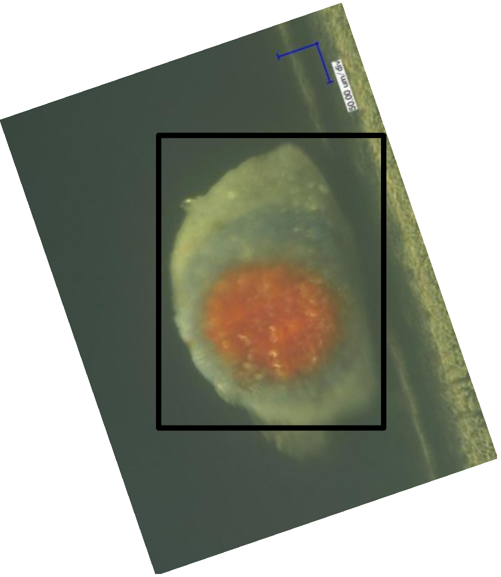
A. 2D projective imaging:

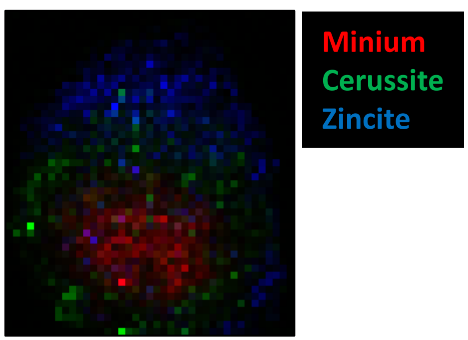




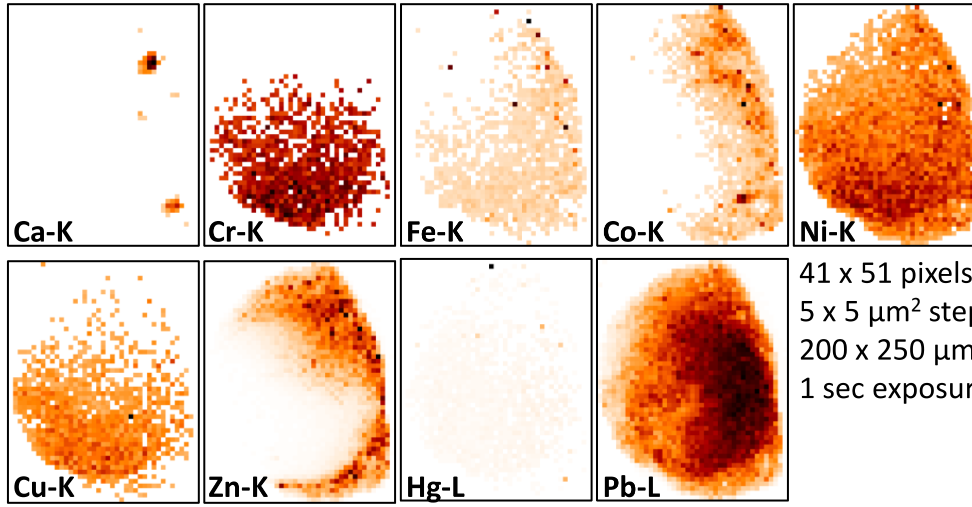
(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

Sample Van Gogh F563
μ-XRF/μ-XRD

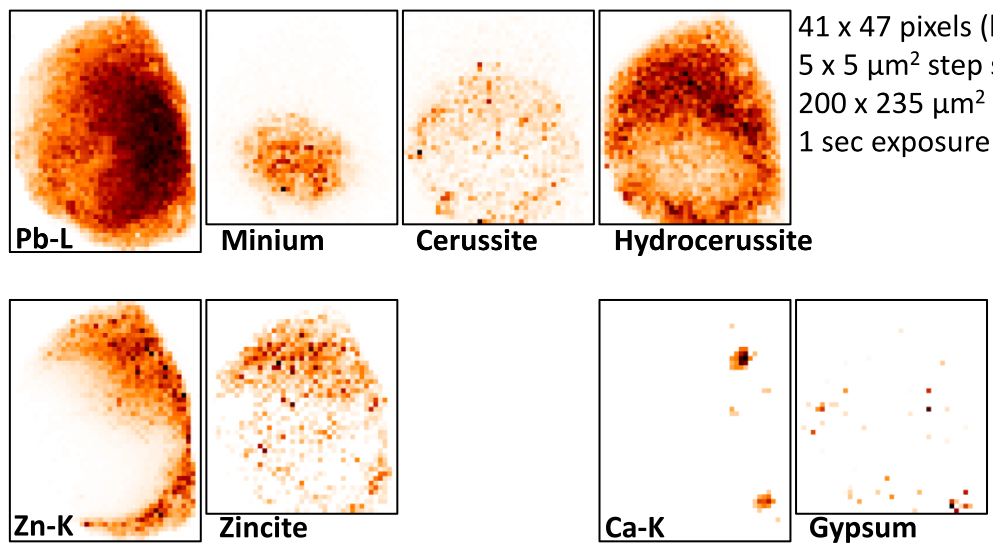




μ-XRF



41 x 51 pixels (h x v)
5 x 5 μm^2 step size
200 x 250 μm^2 scan size
1 sec exposure



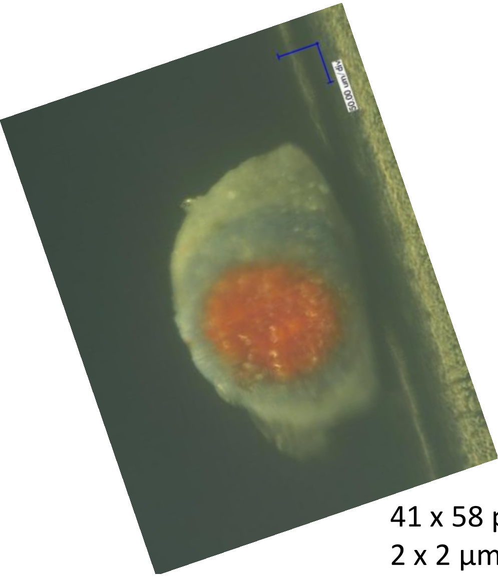
41 x 47 pixels (h x v)
5 x 5 μm^2 step size
200 x 235 μm^2 scan size
1 sec exposure

μ-XRF /μ-XRD

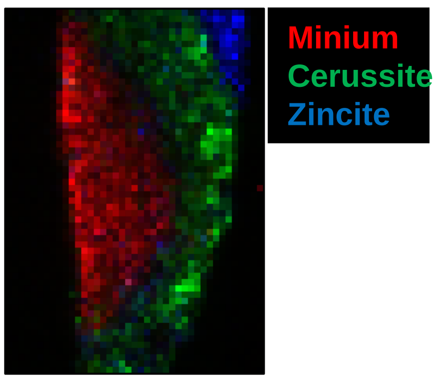
(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

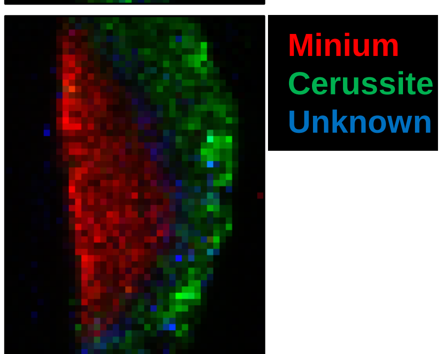
SIDEVIEW

Sample Van Gogh F563
μ-XRF/μ-XRD

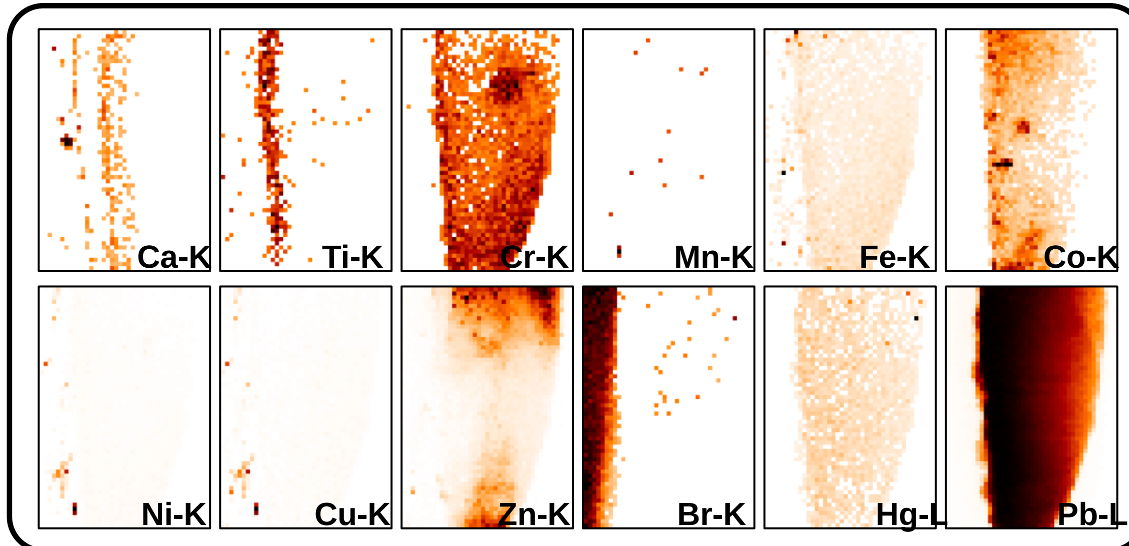


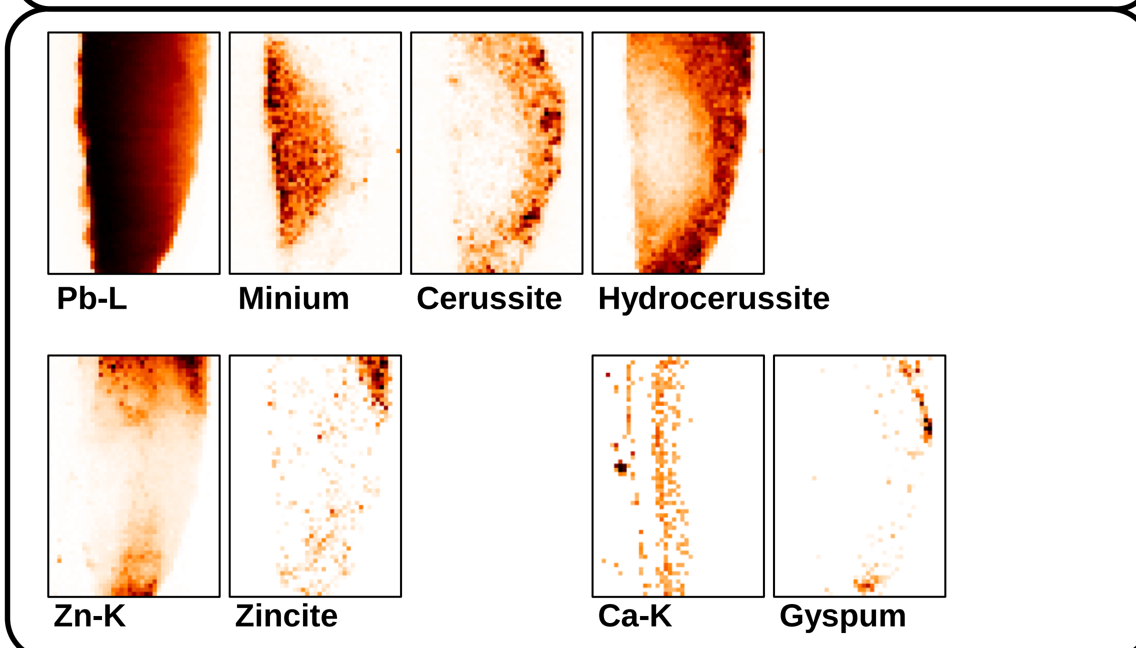
41 x 58 pixels (h x v)
2 x 2 μm^2 step size
80 x 114 μm^2 scan size
1 sec exposure





μ-XRF



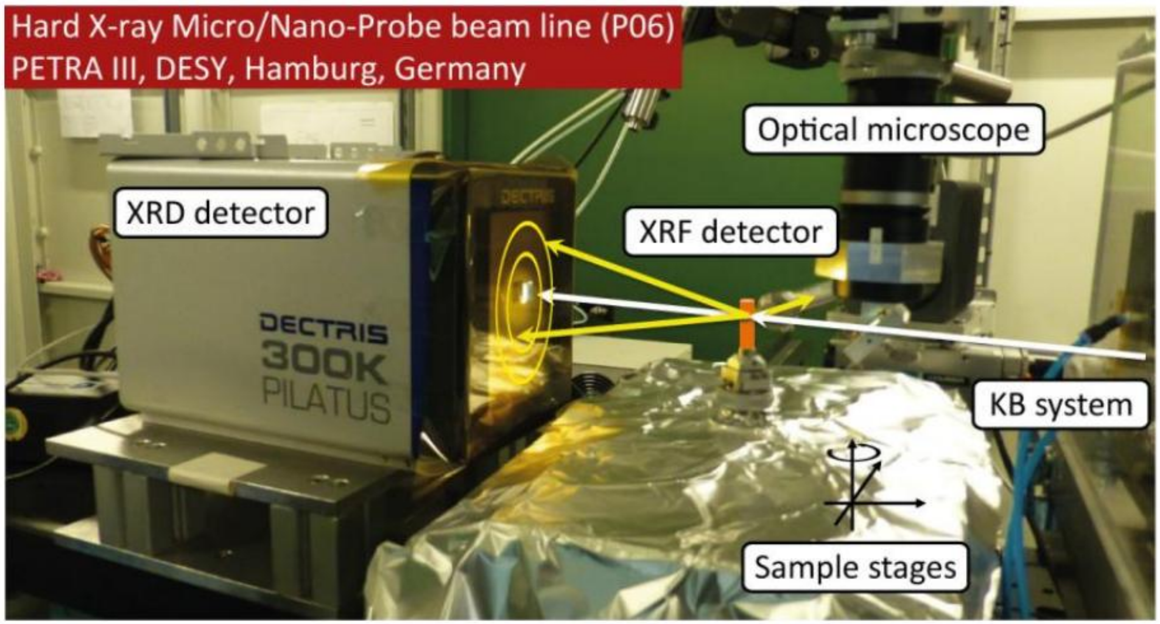


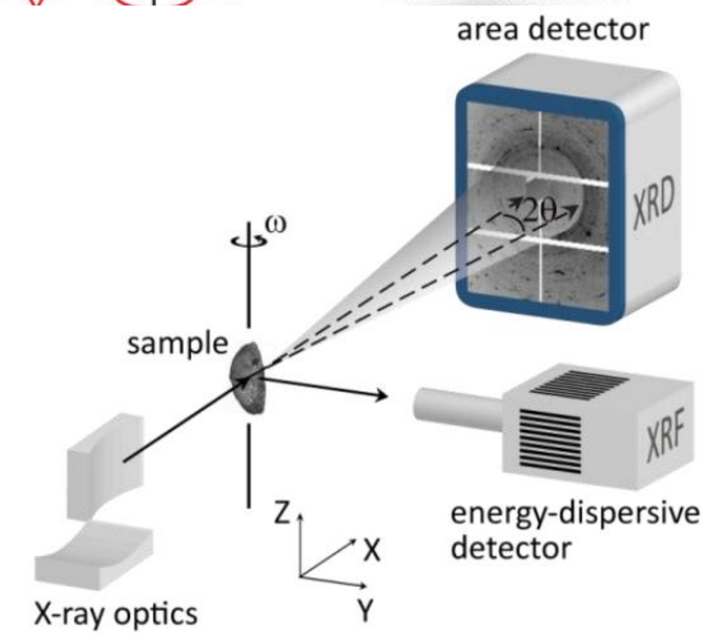
μ-XRF /μ-XRD

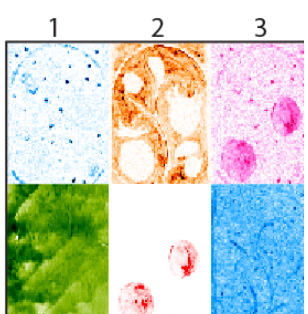
(c) K. Janssens, F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

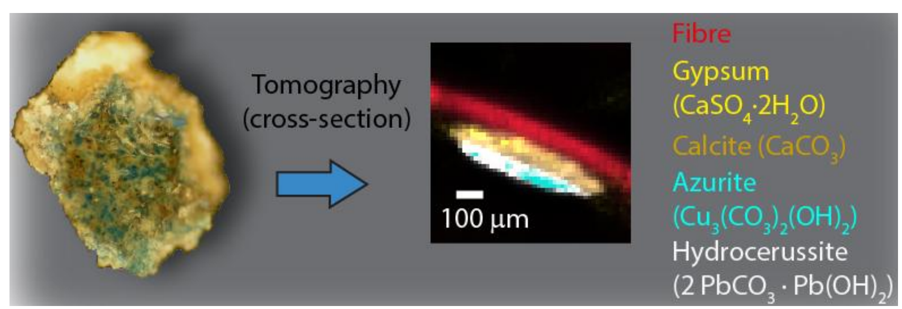
A. 2D projective imaging:

B. Tomographic imaging:



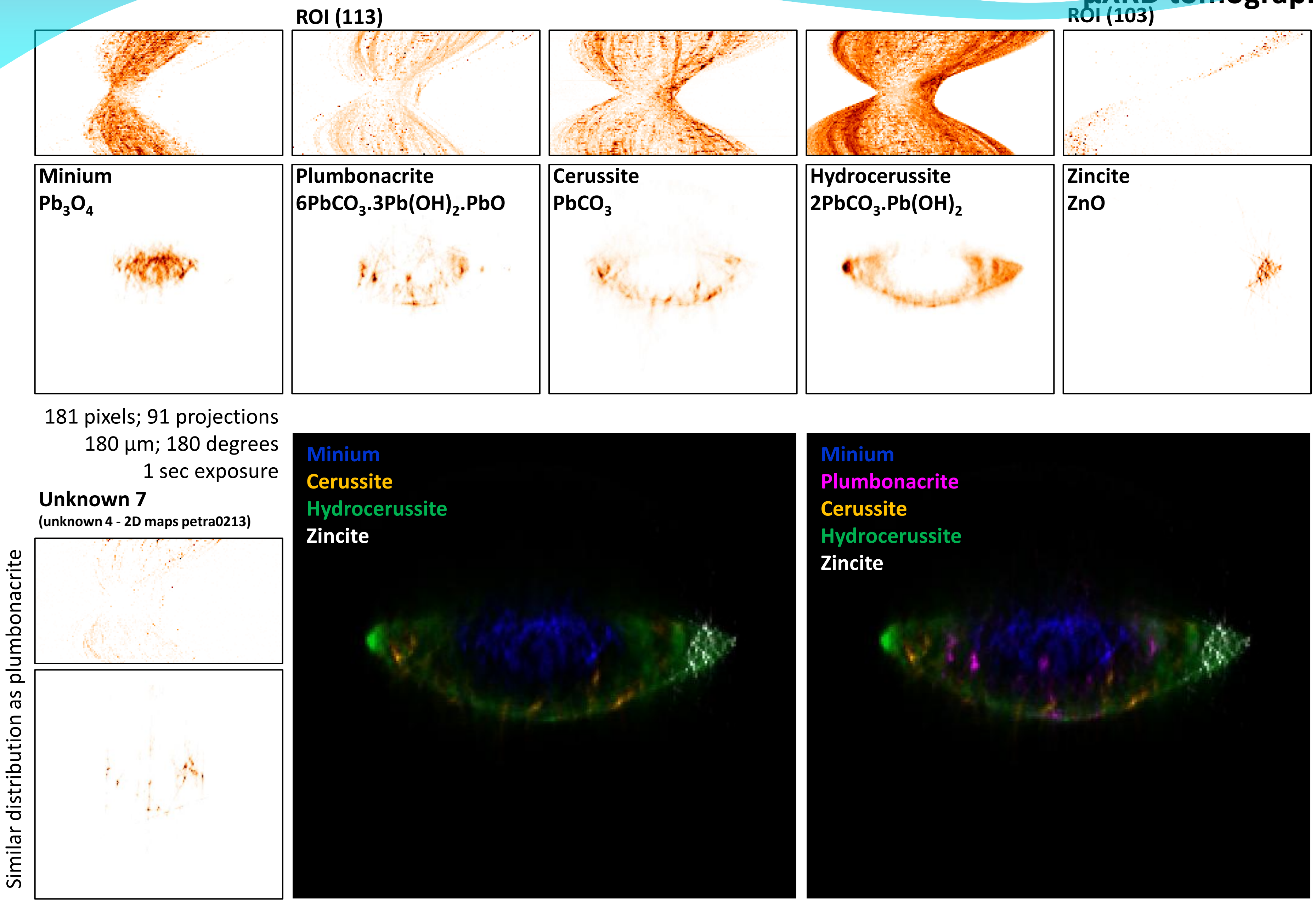






(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

Van Gogh F563
µXRD tomography



Minium degradation pathway

Previously unknown intermediate product

$PbO_2.2PbO$ → unknown phase

↓

$3PbCO_3.Pb(OH)_2.PbO$

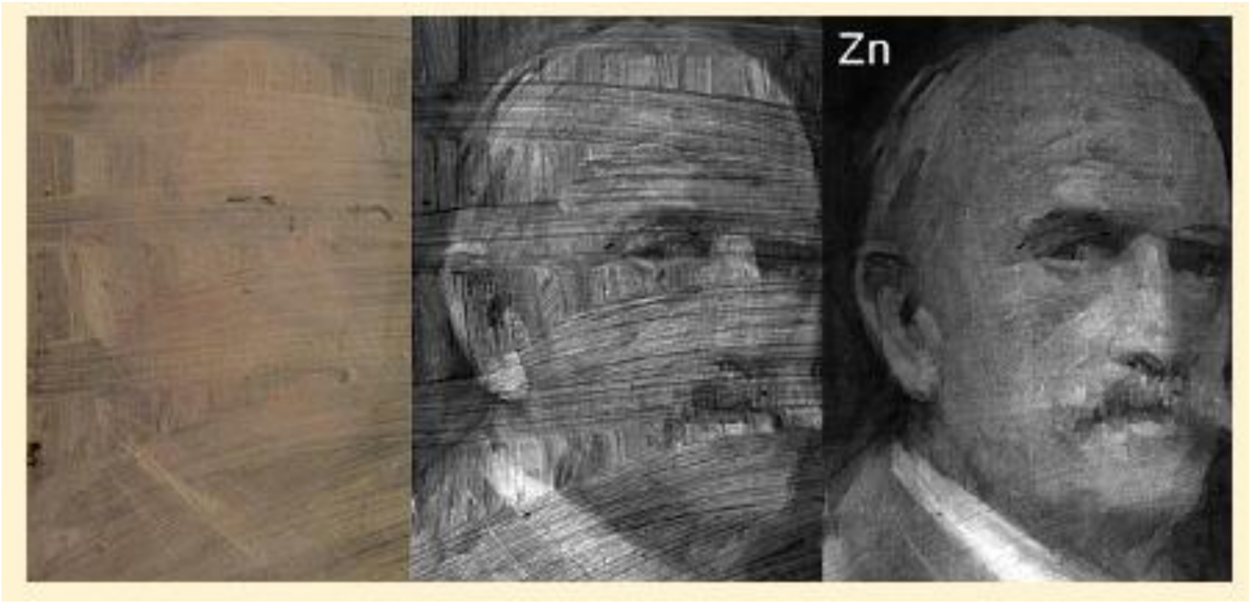
↓

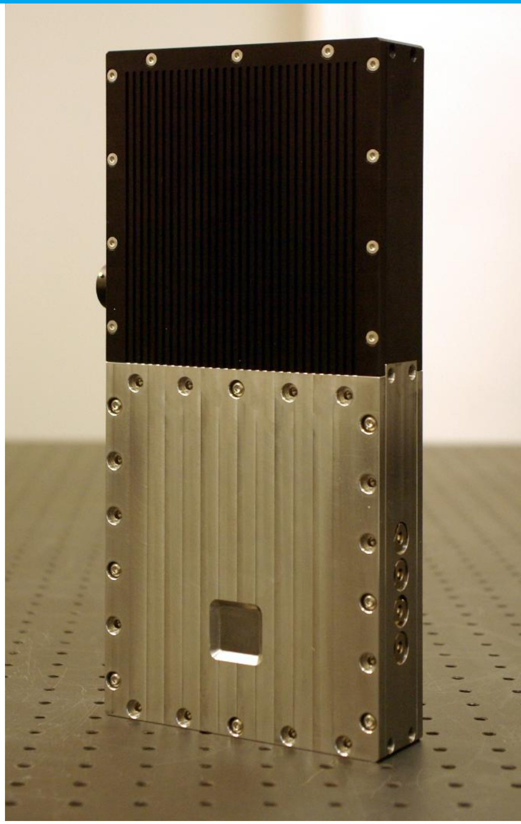
$3PbCO_3.Pb(OH)_2$

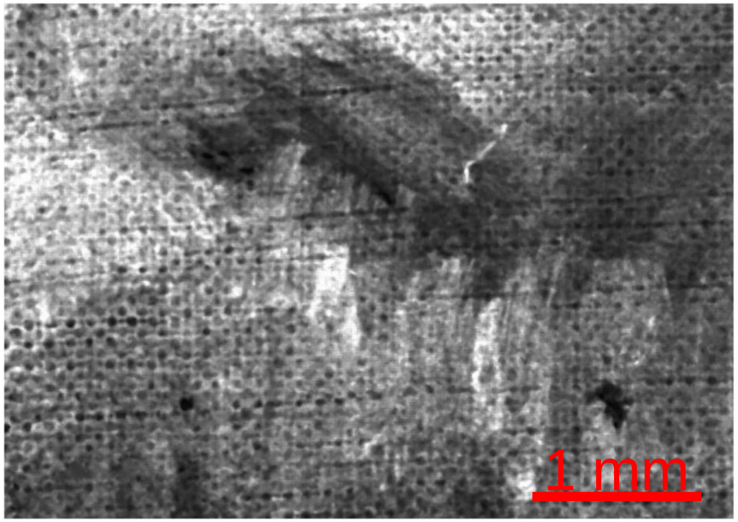
internal oxidizing agent (Pb^{IV} → Pb^{+II})

(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681

Investigation of historical paintings



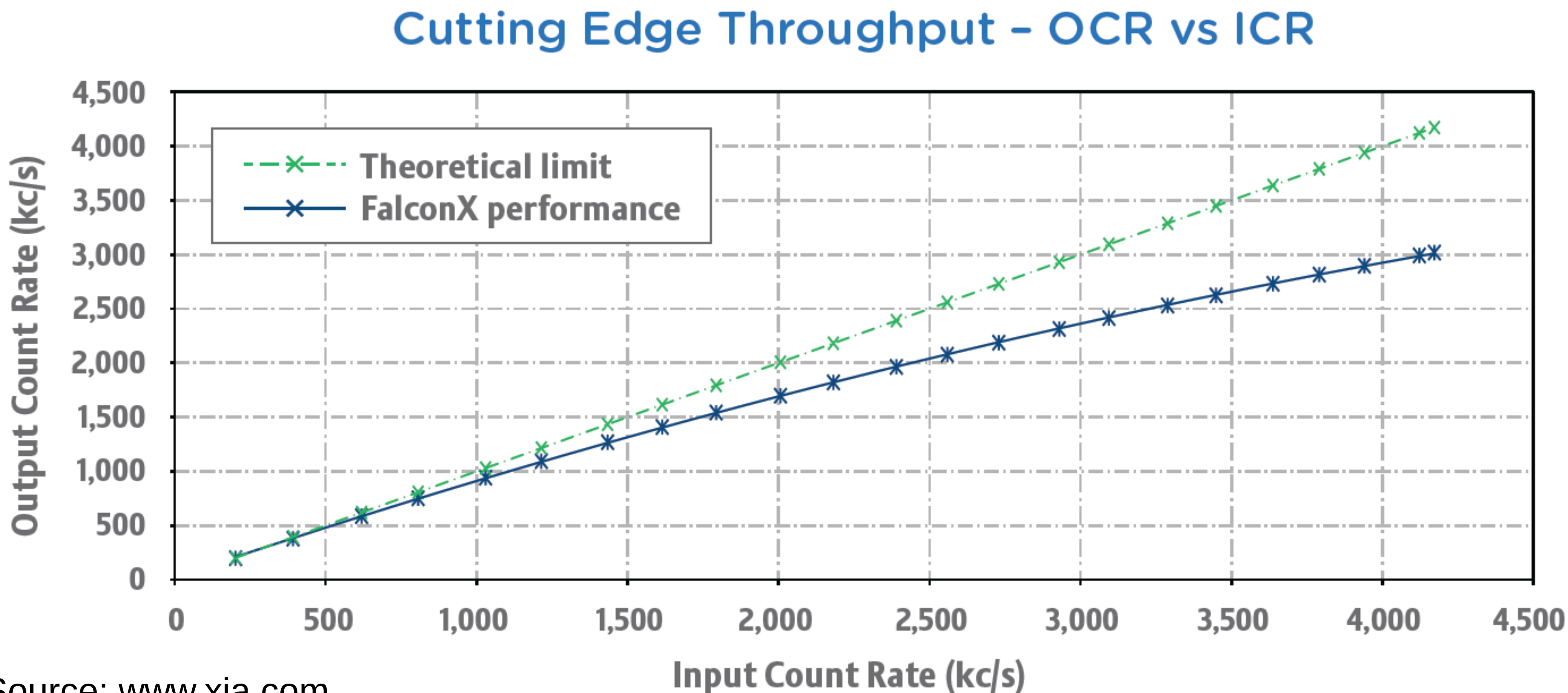




Set-up with a Maia at the Australian Synchrotron.
3 ms/pixel dwell time, 50 µm pixel size, 25 Mpixel image
total time 22.5 hours.
See: Howard, D. L. et al., *Anal. Chem.* (2012). **84**, 3278-3286.

Alternatives to the Maia system

- Recent developments brought up fast Multi Channel Analyzers, such as the FalconX (XIA) and the Xspress3 (Quantum detectors), which



Source: www.xia.com

Conclusions

- With the Maia Beamline P06 features:
  - An high intensity sub-micron beam
  - A very sensitive detector
  - A flexible sample environment
- This allows for:
  - The fast acquisition of high resolution elemental distribution images
  - High resolution XRF tomography
  - XANES imaging
  - XRD imaging and XRD tomography
- These capabilities are suitable for the investigation of samples from a wide range of scientific fields, including cultural heritage.
- The beamline is available to outside users. Deadline for beamtime application is in SeptemberXXX.
- The Maia system was quickly integrated in the beamline environment and available for user operation.

Acknowledgements

Financial Support:
The German Federal Ministry of Education and Research (BMBF) - Verbundprojekt 05K2012. (2013-2015)

Former colleagues at P06:
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Ulrike Bösenberg
Christian Schroer
Walter Schröder
Juliane Reinhardt
Maria Scholz
Andreas Schropp
Mateusz Czyzycki
Thorsten Claussen
Preety Bhargava

Users of P06:
Koen Janssens
Geert Van der Snickt
Frederik Vanmeert
Letizia Monico
Seema Mishra
Hendrik Küpper
Simone Cagno
Ole Lind
Brit Salbu
Gert Nuyts

Maia detector development:
D. Pete Siddons (BNL)
Chris Ryan (CSIRO)
Robin Kirkham (CSIRO)

You – Attention!