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

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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 representative 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

Stacks or 3D data cubes of spectra

sample

Be

op
Data treatment by least squares ($\chi^2$) fitting

A selected range of channels $i$ of the measured spectrum $S$ is approximated by model $f$.

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

Motivation: XRF imaging at SR sources

- Background linear intensity factors $a$
- 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)
The easiest way to enhance the sensitivity of an instrument is to enhance the intensity of the primary radiation.

Motivation: XRF imaging at SR sources

Synchrotron:

Magnet

Photon Energy [keV]

5 10 15 20 25 30

Bending magnet

Wiggler

Undulator

commons.wikimedia.org

www.wikipedia.org

Images: www.wikipedia.org

www.photon-science.desy.de

www.commons.wikimedia.org
Next to highly intense primary radiation, synchrotron radiation sources offer other advantages:

- Tunable monochromatic radiation:
  - Reduced spectral background from scattered radiation
  - Easier XRF quantification
  - Necessary for XANES and XRD
  - Allows to vary sensitivity for selected elements
  - Necessary for many X-ray optics

- Polarized primary radiation:
  - Reduces the intensity of the scattered radiation, if the detector is placed 90° to the incident radiation.

\[
\begin{align*}
I_{ijk} &= n \\
> \text{Polari} \\
\end{align*}
\]

\[
\begin{align*}
\frac{\sigma}{d\Omega}_{\text{perp}} \\
\frac{d\sigma}{d\Omega}_{\text{para}} \\
\end{align*}
\]

\[
\sum_{i} \int_{\Omega} I_{ijk} d\Omega = \text{constant}
\]

Motivation: XRF imaging at SR sources


Rh-anode X-ray tube
Outline

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➢ Conclusions
Beamline P06

Beamline P06@DESY, Hamburg, Germany:
• Hard X-ray Micro/Nanoprobe
• 3rd generation Synchrotron Radiation source PETRA III
• operational since 2011.
Si(111) monochromator based on Bragg reflection
Energy resolution: $1.2 \times 10^{-4} \Delta E/E$
Beamline P06

Beam size down to: 300x340 nm²
Rh-coated. Suitable for 5-23 keV

Area detector(s) for tomography and XRD
Beamline P06

Vortex EM SDD

KB mirrors

Sample stage
Beamline P06

Cryostream

Sample
Sample stage

KB mirrors
At beamline P06 a cryo chamber is developed for the investigation of frozen, biological samples by XRF and X-ray (absorption) tomography.
Why use the Maia detector?

The high intensity primary radiation oversaturates the detector and necessitates the attenuation of the primary beam.
More photons are not always better.

- Dead time

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

**Legend:**
- ICR: Incoming Count Rate
- OCR: Outgoing Count Rate
- Source: www.hitachi-hitec-science.us, 2013
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The Maia detector

1 detector element
50 mm² active area
Solid angle: ~0.12 sr
Count rate: 5x10⁵ photons/s
Typical dwell time: 100 ms/pixel

386 detector elements
1 mm² active area/element
Solid angle ~1.3 sr
Count rate: 10⁷ photons/s
Typical dwell time: 1 ms/pixel

Vortex EM SDD

Maia
The Maia detector

1 detector element

50 mm² active area

Solid angle: ~0.12 sr

Count rate: 5x10⁵ photons/s

Typical dwell time: 100 ms/pixel

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.)

XRF: X-ray fluorescence spectrometry

> Solid angle

\[ \frac{I_{\text{recorded}}}{I_{\text{emitted}}} = \frac{A_{\text{detector}}}{4\pi r^2} \]

- \( A_{\text{detector}} \) active area of detector
- \( r \) distance of sample to detector

The solid angle \( \Omega \) is expressed in steradians. (1 steradian = 1 \( r^2 \))
The Maia detector

<table>
<thead>
<tr>
<th>Vortex EM SDD</th>
<th>Maia</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 detector element</td>
<td>386 detector elements</td>
</tr>
<tr>
<td>50 mm² active area</td>
<td>1 mm² active area/element</td>
</tr>
<tr>
<td>Solid angle: ~0.12 sr</td>
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</tr>
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</tr>
<tr>
<td>Typical dwell time: 100 ms/pixel</td>
<td>Typical dwell time: 1 ms/pixel</td>
</tr>
</tbody>
</table>
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$_\alpha$): ~300 eV

Image: © www.axo-dresden.de
The Maia detector

\[ LOD = 3 \cdot c \cdot \sqrt{\frac{I_{\text{back}}}{I_{\text{signal}}}} \cdot \sqrt{t} \]

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

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

The Maia detector

For $i$ pixels do begin
1. Sample is moved
2. Spectrum is acquired
Endfor
The Maia detector

Sample on motorized stage

Motor control

Continuous movement of inner motorized stage

For $i$ pixels do begin

Spectrum is acquired

Endfor

Vortex

xMAP

Experiment control
The Maia detector

Maia

Sample on motorized stage

32-bit events per photon

orders

Maia control

orders

Motor control

Experiment control

motor positions

orders

- Evaluated data
- Raw data saved on hard disc

orders

orders

on hard disc

orders
The Maia detector

Data treatment by least squares ($\chi^2$) fitting

A selected range of channels $i$ of the measured spectrum $S$ is approximated by model $f$.

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

linear intensity factors $a$

background

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

$$ \chi^2 = \sum_{i=0}^{i} w_i (S_i - f(a_0, a_1, \ldots, p_0, p_1, \ldots))^2 $$
Data treatment by linear least squares ($\chi$) fitting

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

- Peak profile, dependent on non-linear parameters $p$.
  (e.g. energy calibration and detector settings)
Dynamic analysis replaces the least squares fitting of a data set with a matrix multiplication (a fast operation).

\[ S \Gamma C = \sum (k_i \cdot y_{Baf}) \]

If \( \Gamma \) was correctly calculated concentrations are obtained, otherwise the integrated peak area is yielded.


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 occasion, 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.

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-Kα)
- Enhanced scatter contribution (compensated by enhanced sensitivity)
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
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 mm² 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)
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???
XRF tomography

Distribution of As in *Ceratophyllum demersum*

- *Ceratophyllum demersum* was grown in 0 to 5 μM As solution.
- After harvesting leaves 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:
XRF tomography

- Cryostream
- Maia detector
- KB mirrors
- Sample
- Sample stage
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
XRF tomography

elastic

Zn

As

200 μm

200 μm

200 μm
The P06 Microprobe with the Maia allows for the acquisition of high resolution, quantitative tomograms. No beam damage was observed (but sample drifts and vibrations).
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)
XANES: X-ray Absorption Near Edge Structure

Photoelectric cross section

\[ \tau [\text{cm}^2/\text{g}] \]

Primary energy [keV]

\[ 10^1 \quad 10^2 \quad 10^3 \quad 10^4 \quad 10^5 \]

Fe, Ni, Pb
XANES: X-ray Absorption Near Edge Structure

Fluorescence [a.u.]

Energy [keV]

Cr(VI)
XANES: X-ray Absorption Near Edge Structure

![Graph showing XANES spectra for Cr(III) and Cr(VI)]
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

![Graph showing fluorescence vs. energy for Cr(III) and Cr(VI)]

Energy [keV] 0.2 0.4 0.6 0.8 1 1.2
Fluorescence [a.u.] 5.95 6.0 6.05 6.1

Cr(III)  Cr(VI)

5.992 keV  6.003 keV

5.992 keV  6.003 keV
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.

52 artificially 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

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:

1. Scanning XRPD
2. Data reduction
3. Average/Maximum
4. Bragg peak intensity maps (ROI's)
5. ROI map correlations

Hematite (Fe$_2$O$_3$)
Goethite (FeO(OH))
Prussian blue (Fe$_4$[Fe(CN)$_6$]$_3$·14H$_2$O)
Cinnabar (HgS)
Unidentified

(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678–3681
Sample Van Gogh F563

μ-XRF

Ca-K 
Cr-K 
Fe-K 
Co-K 
Ni-K 
Cu-K 
Zn-K 
Hg-L 
Pb-L 

Cerussite 
Minium 
Zincite 
Pb-L 
Minium 
Cerussite 
Hydrocerussite 
Zn-K 
Zincite 
Ca-K 
Gypsum

41 x 51 pixels (h x v) 
5 x 5 µm² step size 
200 x 250 µm² scan size 
1 sec exposure

41 x 47 pixels (h x v) 
5 x 5 µm² step size 
200 x 235 µm² scan size 
1 sec exposure

(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681
41 x 58 pixels (h x v)
2 x 2 μm² step size
80 x 114 μm² scan size
1 sec exposure

Minium
Cerussite
Zincite

Minium
Cerussite
Unknown

(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

181 pixels; 91 projections
180 μm; 180 degrees
1 sec exposure

Minium
 Pb₃O₄

Plumbonacrite
6PbCO₃.3Pb(OH)₂.PbO

Cerussite
 PbCO₃

Hydrocerussite
2PbCO₃.Pb(OH)₂

Zincite
 ZnO

Unknown 7
(unknown 4 - 2D maps petra0213)

Similar distribution as plumbonacrite

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

\[ \text{PbO}_2 \cdot 2\text{PbO} \rightarrow \text{unknown phase} \]

\[ \rightarrow 3\text{PbCO}_3 \cdot \text{Pb(OH)}_2 \cdot \text{PbO} \]

\[ \rightarrow 3\text{PbCO}_3 \cdot \text{Pb(OH)}_2 \]

Previously unknown intermediate product

Internal oxidizing agent \((\text{Pb}^{IV} \rightarrow \text{Pb}^{II})\)

(c) K. Janssens; F. Vanmeert, G. Van der Snickt, K. Janssens, Angew. Chem. 2015, 127, 3678 –3681
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. 
Recent developments brought up fast Multi Channel Analyzers, such as the FalconX (XIA) and the Xspress3 (Quantum detectors), which feature count rates of several million counts per second. These MCAs can, in combination with other hardware, be used to construct instruments of similar sensitivity to the Maia system. However, to my best knowledge, there is no instrument that combines acquisition speed, sensitivity AND online data evaluation of the Maia system.

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 September).

> The Maia system was quickly integrated in the beamline environment and available for user operation.
Acknowledgements

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Walter Schröder
Juliane Reinhardt
Maria Scholz
Andreas Schropp

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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!