Joint ICTP-IAEA School on Synchrotron Applications in Cultural Heritage and Environmental Sciences and Multidisciplinary Aspects of Imaging Techniques

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SR-(micro/T)XRF for environmental and conservation studies

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SR-(micro/T)XRF for environmental and conservation studies

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acknowledgement:
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Florian Meirer - FBK
\[
I(E_{i,j,k}) = \frac{d\Omega_0 d\Omega_1}{4\pi} \int_{E_{\text{edge},i}}^{E_{\text{max}}} I_0(E_0) \exp \left( -\left( \frac{\mu}{\rho}_s, E_0 \right) \rho_s \frac{x}{\sin \psi_0} \right) \exp \left( -\left( \frac{\mu}{\rho}_s, E_{i,j,k} \right) \rho_s \frac{x}{\sin \psi_1} \right) \]
\[
W_i \left( \frac{\tau}{\rho} \right)_{i,E_0} \left( \frac{r_{i,j} - 1}{r_{i,j}} \right) \rho_s \omega_{i,j} p_{i,j,k} E_{i,j,k} dx dE_0
\]
Higher flux:
- faster measurements (scanning)

Natural collimation:
- high brilliance
- micro (nano) spots

Polarisation:
- better peak/background
- magnetism

Wide spectral range:
- selective excitation
- excitation energy vs. sensitivity
- energy scanning
Schematic layout of the ID 18F experimental station. Photodiode 1 is either placed into the sample position if the sample is measured (geometry 1) or in front of the mini-ionisation chamber (geometry 2).

Synchrotron - sources

http://hasylab.desy.de/science/studentsteaching/primers/synchrotron_radiation/index_eng.html

Bending magnet \( I \propto n \)

Wiggler \( I \propto N \)

Undulator \( I \propto N^2 \)

XFel \( I \propto n^2 \)

http://xray.bmc.uu.se/spb/
Spectral modifications

Mirrors – total reflection cut-off, low-pass (focussing)

Crystals – Bragg reflection monochromators
\[ \delta E/E \propto 10^{-3} - 10^{-4} \]

Multilayers – Bragg reflection monochromators
\[ \delta E/E \propto 10^{-2} \]

Gratings – Bragg reflection monochromators
\[ \delta E/E \propto 10^{-3} - 10^{-4} \]
Focussing Optics

reflective: Kirkpatrick-Baez

compound refractive lenses

monocapillaries

decapillaries

zone plates

Flux density gain
Spot size
Energy range
Focal length
Alignment
Silicon Drift Detectors:
- thin (efficiency)
- fast (up to 1 Mcps)
- no LN2

Si(Li) – Ge(HP)
- thick (efficiency)
- not too fast (20-60 kcps)
XAS - detectors

Lytle detector

7 element element

30 element

XRF – detection limits

\[ DL = 3 \sqrt{\frac{\text{Background}}{\text{mass}}} \]

\[ DL \propto \sqrt{\frac{\text{mass} \cdot \text{current}}{\text{time}}} \]

Results usually normalised to 1000 sec measuring time.
Relative detection limits with ID 18F using a 100 component compound reflective lens set at 21 keV at 2μm × 2μm in biological material (NIST SRM 1577a, bovine liver) and NIST 613 glass SRM 613 (live time measurement of 1000 s).

Absolute detection limits with ESRF (ID 13), 21 keV monochromatic radiation at 2μm × 2μm (live time measurement of 100 s). Adapted from Somogyi et al. (2001)
Micro - XRF
- homogeneous sample (assumed – spinning)
- averaged information
- LD: ppm -> ppb

- detect inhomogeneities in sample
- local information -> imaging
- LD: ppm -> ppb ???
- improved signal to background ratio ?
- much more information
  ? data analysis ?
microXRF – example – lead in bone

Most of the work done by Norbert Zoeger for his PhD

Backscattered Electron Image (BE), Patella

Cortical bone

Trabecular bone

Articular cartilage

Calcified cartilage

Tidemark

Subchondral bone

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microXRF – example – lead in bone
microXRF – example – lead in bone

1D scan
mm thick piece
microXRF – example – lead in bone

![Graph showing XRF spectrum with peaks for Ca, Zn, Fe, Pb-La, Pb-Lb, Sr, and scat. with energy range from 0 to 20 keV and cts/cm² on the y-axis.]

- spectrum at 350 µm
- spectrum at 1200 µm
microXRF – example – lead in bone

1D scan
200 μm thick piece
**microXRF – artifacts**

Incident beam

(17 keV
~15μm)

Microscope

To detector

Information depth:

Ca ~ 40μm
Pb ~ 300μm
Sr ~ 600μm

homogeneous sample

Ca, Sr, Pb
Information depth:

Ca $\sim 40\mu m$

Pb $\sim 300\mu m$

Sr $\sim 600\mu m$

Microscope

Incident beam

(17 keV ~15\mu m)

heterogeneous sample

Ca, Sr, Pb

To detector

200\mu m

200\mu m
Why 3D?

Because 2D projection can be misleading.
Confocal set-up – hasylab L

Figure 7.16: Scheme of the confocal setup at HASYLAB, beamline L.

20 x 22 x 14 μm³ (lateral x depth x height) for Au La
Confocal set-up – hasylab L

Detection volume

spatial resolution

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Confocal set-up – hasylab L
all (2601) fluorescence spectra from the area scan (red) compared with the single spectrum at the maximum of Pb (black), obtained in 5s measuring time
Confocal set-up – hasylab L

Three-dimensional element distribution in human patella
Tomo set-up – ANKA
Tomo set-up – ANKA

Ca

Ca μ(E₀)

Ca μ(E₁)

Zn

Zn μ(E₀)

Zn μ(E₁)

Pb

Pb μ(E₀)

Pb μ(E₁)
**Figure 6:** Comparison of XANES spectra recorded at different tidemark (TM) positions and different regions in the trabecular bone (TRB) of the human patella (G3776) and femoral head (A3753) sample [2].

**Figure 7:** Comparison of bone XANES spectra (black) - because TM and TRB spectra of Fig. 6 show no differences they have been merged for further evaluation - with spectra of reference compounds [2].
Pb XANES – ANKA

March 2011

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Sample PR11

Polycapillary micro-XRF

confocal micro-XRF
TXRF
Total Reflection X-Ray Fluorescence
Total external reflection

\[ n (\text{x-ray range}) = 1 - \delta - i\beta \]

\[ \delta \sim 10^{-6} \quad \beta \sim 10^{-8} \]

\[ \phi \text{ critical} \approx \sqrt{2} \delta \]

\[ \phi \text{ critical} \]
(Si, 17.5 keV) \approx 0.1^\circ \approx 1.75 \text{ mrad}

(Si, 500 eV) \approx 3.7^\circ \approx 64.6 \text{ mrad}
Idea: - analyse impurities-contamination of polished surfaces

- deposit sample on a reflector and carry out analysis of the sample
• background reduction
• double excitation of sample by both the primary and the reflected beam
• small distance sample - detector (\(\sim 1\)mm) : large solid angle
• small sample amounts required
• detection limits in the pg range with X-ray tube excitation
• detection limits in the fg range with Synchrotron radiation excitation
• “no” matrix effects ?
TOTAL REFLECTION
X-RAY FLUORESCENCE SPECTROMETRY -
A VERSATILE TOOL FOR ULTRA - MICRO ANALYSIS
OF OBJECTS OF CULTURAL HERITAGE

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TXRF – critical thickness/mass

![Graph showing critical thickness and critical mass vs. energy (keV)]
TXRF – cultural heritage studies - sampling
TXRF – cultural heritage studies
### TXRF – cultural heritage studies

<table>
<thead>
<tr>
<th><strong>White Pigments</strong></th>
<th><strong>Red Pigments</strong></th>
<th><strong>Blue Pigments</strong></th>
<th><strong>Green Pigments</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony white</td>
<td>Cadmium red</td>
<td>Azurite</td>
<td>Basic copper sulfate</td>
</tr>
<tr>
<td>Lithopone</td>
<td>Cadmium vermilion</td>
<td>Cerulean blue</td>
<td>Chromium oxide</td>
</tr>
<tr>
<td>Permanent white</td>
<td>Chrome red</td>
<td>Cobalt blue</td>
<td>Chrysocolla</td>
</tr>
<tr>
<td>Titanium white</td>
<td>Molybdate red</td>
<td>Cobalt violet</td>
<td>Cobalt green</td>
</tr>
<tr>
<td>White lead</td>
<td>Realgar</td>
<td>Egyptian blue</td>
<td>Emerald green</td>
</tr>
<tr>
<td>Zinc white</td>
<td>Red lead</td>
<td>Manganese blue</td>
<td>Guignet green</td>
</tr>
<tr>
<td>Zirconium oxide</td>
<td>Red ochre</td>
<td>Prussian blue</td>
<td>Malachite</td>
</tr>
<tr>
<td>Chalk</td>
<td>Vermilion</td>
<td>Smalt</td>
<td>Verdigris</td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
<td>Ultramarine</td>
<td></td>
</tr>
</tbody>
</table>

- **As₂S₃**
- **As₂S₄**
- **CdS**
- **CdS + CdSe**
- **Cds + HgS**
- **Cu₄(SO₄)₂(OH)₂**
- **Cu₅(SO₄)₂(OH)₂**

<table>
<thead>
<tr>
<th><strong>Yellow Pigments</strong></th>
<th><strong>Blue Pigments</strong></th>
<th><strong>Black Pigments</strong></th>
<th><strong>Black Pigments</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Auripigmentum</td>
<td>2Cu₂O₃ x Cu(OH)₂</td>
<td>Antimony black</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td>Cadmium yellow</td>
<td>CoO x nSnO₂</td>
<td>Black iron oxide</td>
<td>FeO x Fe₂O₃</td>
</tr>
<tr>
<td>Chrome yellow</td>
<td>CoO x Al₂O₃</td>
<td>Carbon black</td>
<td>C (95%)</td>
</tr>
<tr>
<td>Cobalt yellow</td>
<td>Co₃(PO₄)₂</td>
<td>Cobalt black</td>
<td>CoO</td>
</tr>
<tr>
<td>Lead-tin yellow</td>
<td>CaO x CuO x 4SiO₂</td>
<td>Ivory black</td>
<td>C + Ca₃(PO₄)₂</td>
</tr>
<tr>
<td>Massicot</td>
<td>BaSO₄ x Ba₃(MnO₄)₂</td>
<td>Manganese oxide</td>
<td>MnO + Mn₃O₃</td>
</tr>
<tr>
<td>Naples yellow</td>
<td>Fe₃[Fe(CN)₆]₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strontium yellow</td>
<td>Co-glass (K₂O + SiO₂ + CoO)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium yellow</td>
<td>Na₈₋₁₀Al₅Si₇O₂₄S₂₋₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow ochre</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc yellow</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **SrCrO₄**
- **Sr₂O₃ x 20TiO₂**
- **NiO x Sb₂O₃ x 3H₂O**
- **Fe₂O₃ x nH₂O (20% - 70%)**
- **K₂O x 4ZnO x 4Cr₂O₃ x 3H₂O**
TXRF – cultural heritage studies

Iron gall ink

Red ink

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TXRF – cultural heritage studies

Figure 11. Scroll of a Cello made by L. Maugin, 19th century and TXRF spectrum of the original varnish.

Figure 12. TXRF spectra of an original and retouched violin varnish from a violin made by Th. & S. Thompson, London, about 1780.
The measurement: Example – TXRF-XANES of As droplet sample on Si reflector

- Variation of excitation energy
- Spectrum at each energy
- Spectrum evaluation (peak area; e.g. As-Ka ROI)

**EXAFS**

\[ W_{ij} = \frac{2\pi}{\hbar} \left| \langle \Psi_i \mid \hat{H} \mid \Psi_f \rangle \right|^2 \rho(E_f) \]

EXAFS equation, Fingerprint method (XANES)
Example I

Arsenic speciation in cucumber (*Cucumis sativus* L.) xylem sap by K-edge TXRF-XANES

**Giancarlo Pepponi**

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J. Broekaert, U. Fittschen

and G. Falkenberg

Application of synchrotron-radiation-induced TXRF-XANES for arsenic speciation in cucumber (*Cucumis sativus* L.) xylem sap


*X-Ray Spectrometry, Volume 36, Issue 6, pages 408–412, 2007*
• Arsenic is contained in groundwater in Eastern Hungary in concentrations that can exceed 50 μg/L

Source: National Public Health and Medical Officer Service, Hungary
Cucumber xylem sap – motivation

- different species of As have different toxicity

<table>
<thead>
<tr>
<th>Compound</th>
<th>LD$_{50}$ mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$O$_3$</td>
<td>20</td>
</tr>
<tr>
<td>Na$_3$AsO$_3$</td>
<td>60</td>
</tr>
<tr>
<td>Na$_3$AsO$_4$</td>
<td>120</td>
</tr>
<tr>
<td>CH$_3$AsO(OH)$_2$ (MMA)</td>
<td>700</td>
</tr>
<tr>
<td>CH$_3$AsO(ONA)$_2$</td>
<td>1800</td>
</tr>
<tr>
<td>(CH$_3$)$_2$AsO(OH) (DMA)</td>
<td>1600</td>
</tr>
<tr>
<td>(CH$_3$)$_2$AsO(ONA)</td>
<td>2600</td>
</tr>
<tr>
<td>(CH$_3$)$_3$As$^+$CH$_2$COO$^-$ (As-betaine; AsB)</td>
<td>4500</td>
</tr>
</tbody>
</table>
Cucumber xylem sap - motivation

Occurrence of As species in plants, lichens, fungi, algal species and microorganisms


\[
\begin{align*}
\text{AsO}_3^- & \quad \text{AsO}_4^{3-} \\
\text{arsenic (III) arsenite} & \quad \text{arsenic (V) arsenate} \\
\text{H}_3\text{C}\text{AsO}_2\text{H} & \quad \text{H}_3\text{C}\text{AsO}_2\text{OH} \\
\text{arsenous acid} & \quad \text{arsenic acid} \\
\text{Methylarsonate} & \quad \text{Methylarsonic acid} \\
\text{H}_3\text{CAsO}_2\text{H} & \quad \text{H}_3\text{CAsO}_2\text{OH} \\
\text{dimethylarsinate} & \quad \text{dimethylarsonic acid}
\end{align*}
\]

Speciation of the As is important to . . .

- understand how plants metabolise and transform As
- assess the health risk caused by As entering the food chain

In aerobic soils arsenate [As(V)] is the most stable form
• At two leaf stage: transferred in solution with arsenic compounds and diminished phosphate concentration

• After 30 days from germination (17 d arsenic):
  - stem cut 2 mm above root neck
  - sap collected with micropipettes for 1 hour into PE vials immersed in ice salt bath

Flow Injection Analysis (FIA)  
HPLC-HR-ICP-MS  
TXRF-XANES
Cucumber xylem sap - experimental

- Water is "pulled up" through the xylem.
- Water is taken in through the roots.

Source:
http://www.fairchildgarden.org/EduProfDev/Leaf_anatomy.html

Source:
Cucumber xylem sap - experimental

Solutions were

pipetted onto quartz reflectors
vacuum dried
sent in inert atmosphere (Ar)

<table>
<thead>
<tr>
<th>reflector</th>
<th>sample</th>
<th>oxidation number</th>
<th>concentration [ppb]</th>
<th>volume [μl]</th>
<th>mass As [ng]</th>
</tr>
</thead>
<tbody>
<tr>
<td>117</td>
<td>standard solution</td>
<td>3</td>
<td>10000</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>122</td>
<td>nutrient solution</td>
<td>3</td>
<td>150</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>101</td>
<td>nutrient solution</td>
<td>3</td>
<td>150</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>124</td>
<td>xylem sap</td>
<td>3</td>
<td>50</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>121</td>
<td>standard solution</td>
<td>5</td>
<td>10000</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>123</td>
<td>nutrient solution</td>
<td>3</td>
<td>150</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>115</td>
<td>xylem sap</td>
<td>5</td>
<td>30</td>
<td>10</td>
<td>0.3</td>
</tr>
</tbody>
</table>
HASYLAB L - setup

Beamline L
bending magnet

double crystal
monochromator
Si (111)

ionisation
chamber

sample

Si (111) sample

ionisation
chamber

1m resolution
17keV beam

reflect - wedge

detector

beam

cross slits

chamber

slits

camera

detector

translation

rotation

beam monitor
As standard solutions - XANES

standard solution As(III)
standard solution As(V)
Fluorescence signal extraction

Results:

- Speciation of As was possible down to the 30ppb level
- As(III) in nutrient solutions oxidises easily to As(V)
- Cucumber roots convert As(V) to As(III)

<table>
<thead>
<tr>
<th>Sample</th>
<th>As(III) [%]</th>
<th>As(V) [%]</th>
<th>R-factor</th>
<th>( \chi^2 )</th>
<th>Reduced ( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>xylem sap (As(III))</td>
<td>88 ± 3</td>
<td>12 ± 3</td>
<td>0.0155</td>
<td>1.09</td>
<td>0.0115</td>
</tr>
<tr>
<td>xylem sap (As(V))</td>
<td>83 ± 3</td>
<td>17 ± 3</td>
<td>0.0143</td>
<td>1.06</td>
<td>0.0112</td>
</tr>
<tr>
<td>As(III) nutrient solution</td>
<td>100 ± 3</td>
<td>0 ± 3</td>
<td>0.0103</td>
<td>0.68</td>
<td>0.0072</td>
</tr>
<tr>
<td>As(III) nutrient solution after 48h</td>
<td>71 ± 3</td>
<td>29 ± 3</td>
<td>0.0080</td>
<td>0.60</td>
<td>0.0063</td>
</tr>
<tr>
<td>As(V) nutrient solution</td>
<td>2 ± 2</td>
<td>98 ± 2</td>
<td>0.0065</td>
<td>0.63</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

A strange result

nutrient solution As(V)
standard solution As(V)
Self Absorption

\[ I(x) = I_0 \exp(-\mu x) \]

Sample (droplet) size becomes thickness, i.e. path that the primary beam crosses

⇒ Large or highly concentrated samples: penetration depth of incident beam < sample size
Self Absorption

Self Absorption – grazing exit

- GE setup suffers minimally from self-absorption effects
- Shows lower sensitivity than GI-setup
  ⇒ difficult to apply to XAFS analysis of trace amounts (few nanograms) of samples

Speciation of copper and zinc in size-fractionated aerosol samples using TXRF-XANES

J. Osán1, F. Meirer2,3, S. Török1, D. Ingerle2,
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Christina Streli, Giancarlo Pepponi

Speciation of copper and zinc in size-fractionated atmospheric particulate matter using total reflection mode X-ray absorption near-edge structure spectrometry

Particulate matter - motivation

- Health effects of aerosol depend on the size distribution and the chemical composition of the particles
- Heavy metals of anthropogenic origin are connected to the fine (PM$_{2.5}$) aerosol fraction
- Determination of copper and zinc speciation in size-fractionated aerosols from a short sampling period
- Relation of the size distribution of Cu and Zn speciation to the aerosol sources
Particulate matter - experimental

Size fractioned aerosol sampling

- 7-stage May-type cascade impactor
- cut-off diameters: 16, 8, 4, 2, 1, 0.5, 0.25 μm for stages 1–7 at 20 lpm flow rate
- sampling 20–3200 l air depending on stages and aerosol concentration

The deposited aerosol particles form a 200-500 μm wide strip in the middle of the Si wafer of 20x20 mm²
Particulate matter – self absorption
**Particulate matter – Zn XANES**

**Fig. 5.** Zn–K edge TXRF-XANES spectra of the aerosol sample set collected at the airport of Budapest on 12 01 2006; zinc sulfate and carbonate standard spectra are plotted for comparison.
**Fig. 6.** Cu–K edge TXRF-XANES spectra of the aerosol sample set collected at the airport of Budapest on 12 01 2006; standard spectra of Cu(II) sulfate, Cu(II) oxide and Cu(I) oxide are plotted for comparison.
Particulate matter – conclusions

The combination of TXRF-XANES and direct sampling of aerosol particles onto Si wafers using a May-type cascade impactor was found to be well applicable for non-destructive speciation of transition metals in atmospheric particulate matter.

Cu and Zn chemical forms could be identified from air concentrations as low as 140 pg/m³ for a collected air volume of 1 m³ (50 min sampling time).

Speciation of metals with air concentrations in the ng/m³ range is possible in the time scale of a few minutes, allowing the tracing of mobile sources variable in time.

Cu and Zn were found to be bound to secondary aerosol particles in the form of sulfates and nitrates in the fine fraction.

Sources of soil resuspension and brake pad wear erosion could be distinguished based on the chemical form of copper in the coarse fraction (2μm).
TXRF XANES conclusions

TXRF XANES good for:
- small sample amount (mass)
- diluted samples
- solutions/suspensions
- particulate matter

Speciation performed down to:
- 30 ng/ml (xylem sap)
- 140 pg/m$^3$ (fine particulate matter)

Weaknesses:
- self absorption in “highly” concentrated samples (standards)
- alignment can be time consuming