3D MICRO - X-RAY ABSORPTION NEAR EDGE SPECTROSCOPY (3D MICRO-XANES)

Lars Lühl[1,2], Wolfgang Malzer[1], Ioanna Mantouvalou[1], Oliver Hahn[2], and Birgit Kanngießer[1]

Motivation

The combination of 3D Micro-XRF (X-Ray Fluorescence Analysis) and Micro-XAS (X-Ray Absorption Spectroscopy) enables a a **non-destructive and depth resolved chemical speciation**. Hence, this new method 3D Micro-XAS is an excellent tool for the analysis of cultural heritage objects.
Figure 1 shows as an example the determination of copper green pigments of a reverse glass painting.

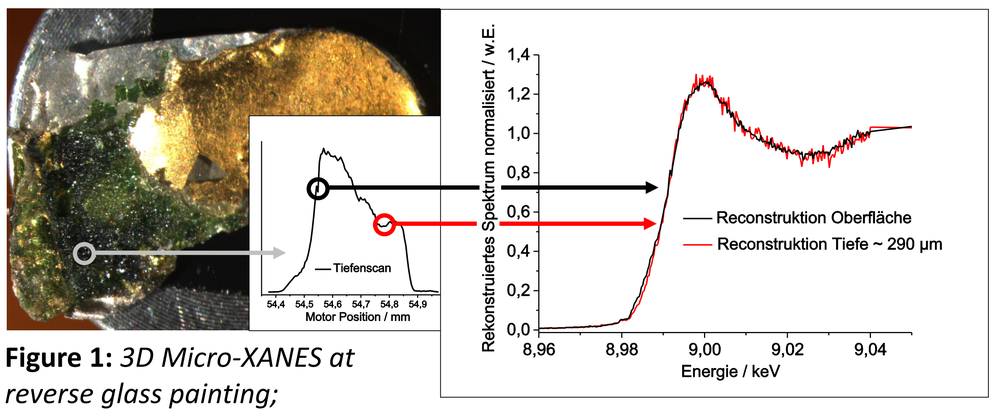


Figure 1: *3D Micro-XANES at reverse glass painting; Latona 16th century provided by Simone Bretz, Oberau*

The **main problem** is to **eliminate the self-absorption effect** of upper layers of stratified samples and upper atom layers in one homogenous sample. This poster provides a short introduction into the principle of 3D Micro-XAS. The problem of the absorption effect will be discussed in detail and a possible quantification approach will be discussed

Methods

XAS:

- Excitation energy is varied in the area of an absorption edge
- Radiation is monitored in fluorescence or in transmission mode
- Structure around the edge jump is typical for the chemical environment of the investigated atom
- X-ray Absorption Near Edge Structure (XANES: energy region shortly before and about 50 eV behind the edge jump) reflects unoccupied electronic states

Following conclusions for chemical properties possible:
→ Oxidation state
→ Number and character of bonding partners

3D Micro-XRF:

Overlapping foci of two polycapillary half-lenses define a probing volume (setup see **Figure 2**). Depth dependent intensity of the fluorescence radiation is achieved by moving the sample step by step through the probing volume. Quantitative 3D Micro-XRF provides layer thicknesses and elemental concentrations. Layers of about >10 µm thickness can be reconstructed.

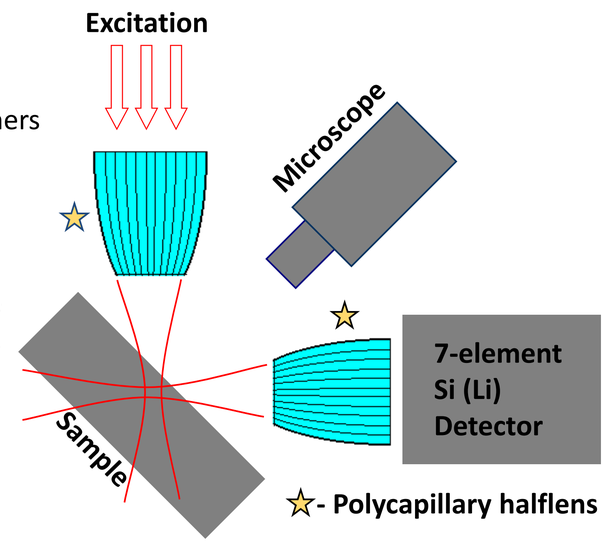


Figure 2: *Confocal setup*

Experimental setup

3D Micro-XANES:

- Measurement of XANES-Spectra in each layer of stratified samples
- Upper layers distort the XANES spectra of deeper layers

Experiment:

Setup at the mySpot beamline @ BESSY II: Depth resolution: **FWHM ≈ 28 µm (9 keV)**; Energy resolution: **E/ΔE ≈ 25000**; Measurement time: **t = 5 s per point**; Step size for XANES measurements: **ΔE** = **0.15 eV**

Samples:
1a) Cu foil, thickness: 2 µm; **1b)** Cu(II)Cl-pellet; **1c)** Cu foil – spacer (kapton foil) – Cu(II)Cl-pellet (see **Figure 3e**); **2)** Stratified lacquer samples with different copper compounds as additives (see **Figure 4 top**)

Challenges in Quantitation:

Example 1 - thin upper layer:
XANES structure of upper layers (see **Figure 3b**) determines the transmission (calculated **Figure 3c**) of this layer. This structure influences the exciting intensity in deeper layers.
Detected fluorescence intensity (see **Figure 3a, green**) is composed of the transmission (see **Figure 3c**) of the upper layers and the XANES structure of the investigated layer (pellet measurement **Figure 3d**).
Example 2 – three thick layers:
Analogue distortion problem

Reconstruction procedure

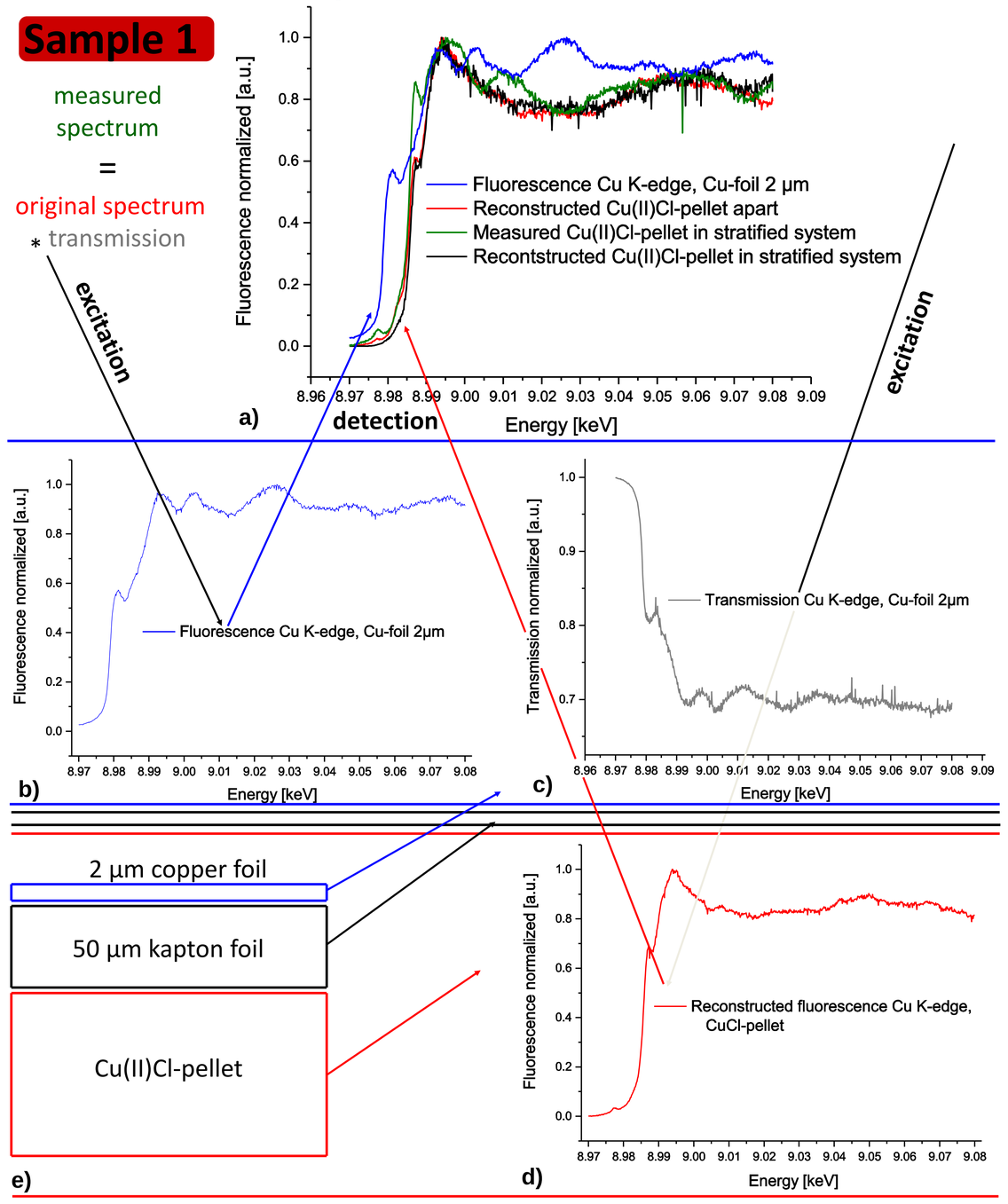


Figure 3: *Interpretation of depth resolved XANES spectra - thin upper layer*

Summary / Conclusion

Sample 1:
-Correction of the self absorption effect of upper thin layers possible (see consistence between black and red graph of **Figure 3a**)

Sample 2:
-Measurements of intermediate thick layers possible (see **Figure 4** black)
-Correction of the self absorption effect of upper thick layers possible (see consistence of red graph and green dashed graph in **Figure 4**)

First measurements and calculations show the possibility to perform absorption-correction routines of 3D Micro-XANES spectra of stratified samples. With this procedure the reconstruction of XANES spectra originating from the depth of a sample becomes feasible.

This is a first step towards non-destructive, depth resolved chemical speciation.

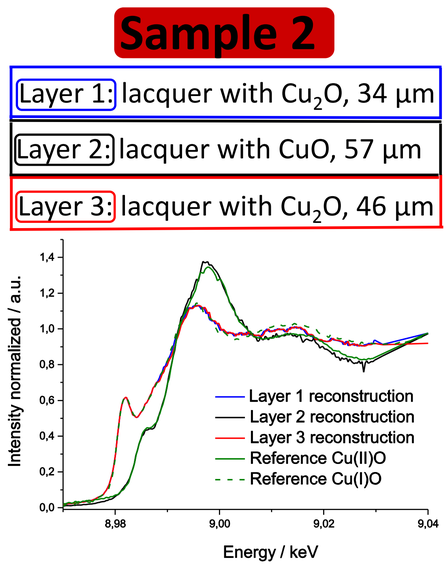
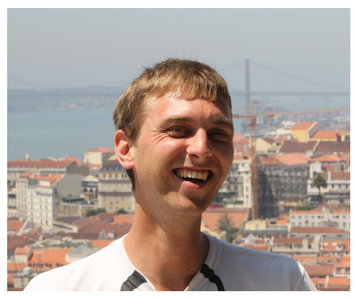


Figure 4: *3D XANES - thick layers*

Contact

Lars Lühl, scientist
lars.luehl@physik.tu-berlin.de



References:

L. Lühl *et al.*, *Anal. Chem.*, 2012, **84**, pp 1907–1914
L. Lühl *et al.*, *Anal. Chem.*, 2013, **85**, pp 3682–3689

[1] Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
[2] Bundesanstalt für Materialforschung und –prüfung, Unter den Eichen 87, 12205 Berlin, Germany