TEY and FY complementary application for the analysis of Layered Samples with XAS in Cultural Heritage

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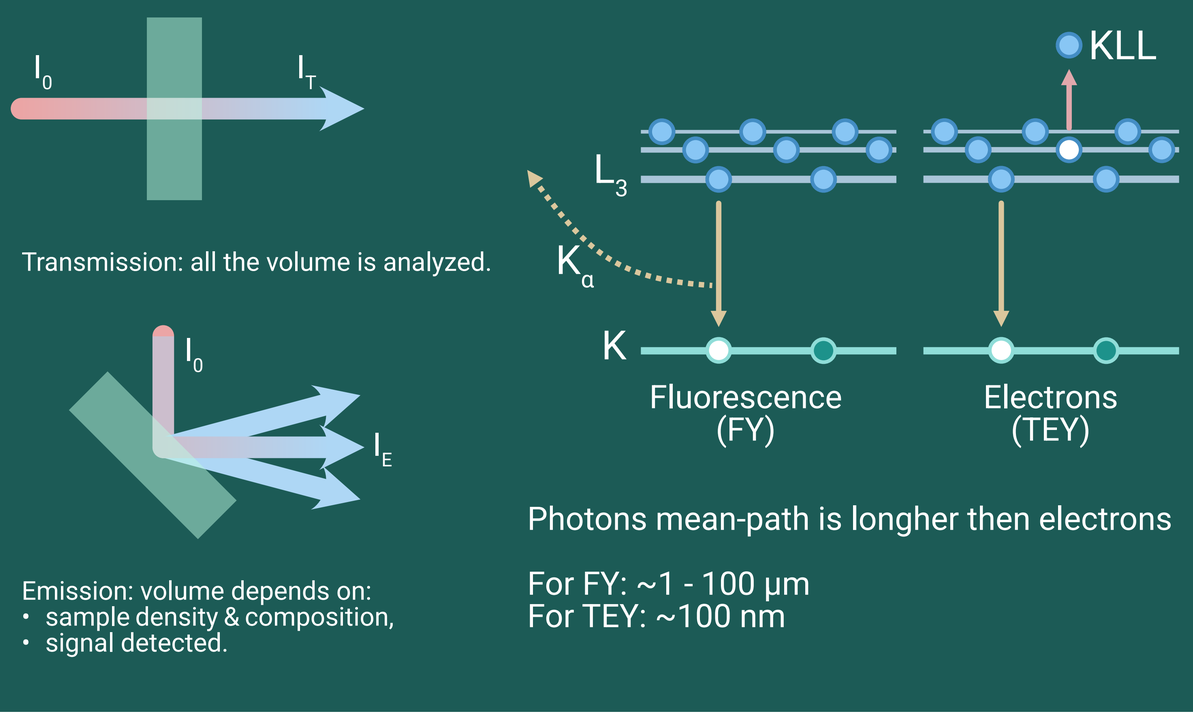
Analysis of Cultural Heritage samples may be extremely complex due to their structural inhomogeneity and the presence of alteration products. To get information on the sample variability, we can collect micro-samples, with the risk of not being representative of the whole artifact, or apply non-invasive analyses, limiting the volume investigated on the surface and losing the layer resolution. Indeed, applying spatially resolved non-invasive analyses is becoming increasingly common (MA-XRF, confocal XRF…). In particular, considering that some phenomena occur from the sample surface to the bulk, for example, the photochemical degradation of paintings, or the presence of oxidized/reduced layers on ceramics, the capability to distinguish the composition of the surface and of the bulk became essential. To obtain these information we performed XAS in Fluorescence and Total Electron Yield at the beamline BM08, LISA at ESRF.

X-ray Absorption Spectroscopy

XAS is an element-specific non-destructive technique that exploits the analysis of the attenuation coefficient to discriminate the oxidation state, coordination and local environment of an element of interest. For this reason it usually applied to analyze the nature and distribution of alteration products, or of the phases produced during the firing process of a ceramic.

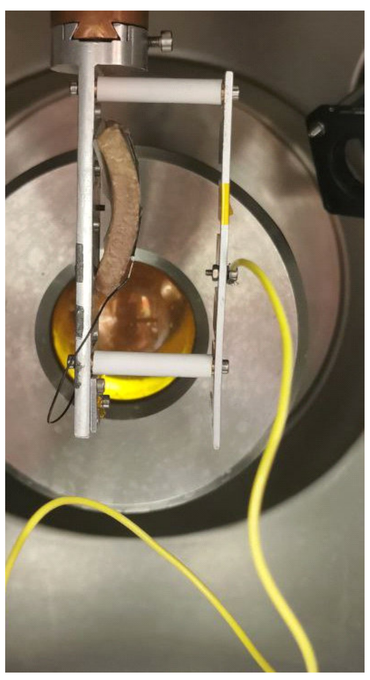
Total Electron Yield and Fluorescence Yield

The volume investigated with XAS depends by the geometry of collection (transmission vs. emission) and the type of signal detected (photons vs. electrons).



Sample and Analytical Methods

Thanks to being deeply studied in the early 2000s and their layered structure, luster ceramics can be employed as benchmark samples



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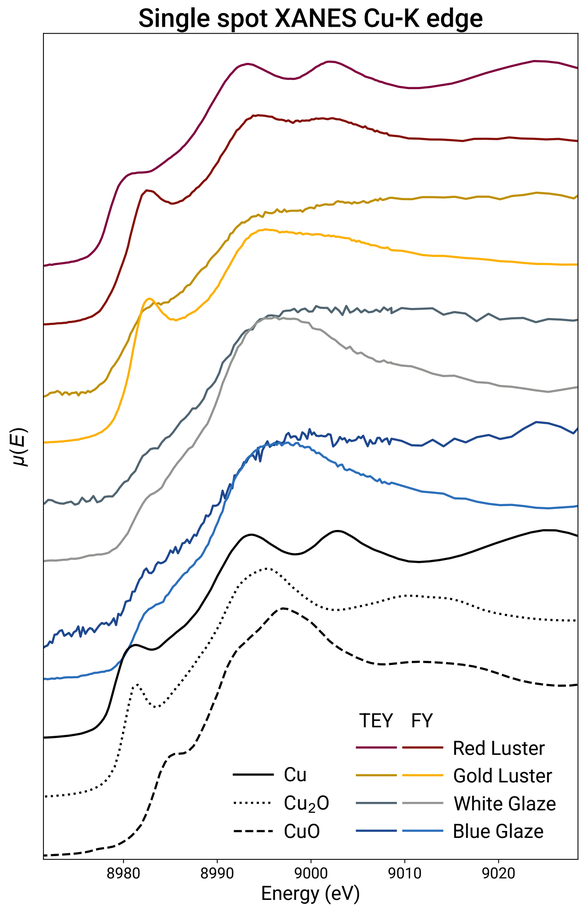
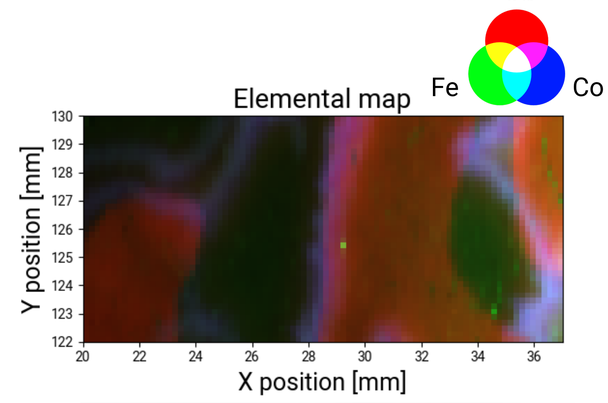
Results





- Investigated area: 8 ×17 mm^2
- Vertical step: 0.2 mm
- Horizontal step: 0.2 mm
- Dwell time: 3 s
- Atmosphere: 200 mbar He

For this sample the TEY signal is very low pssibly due to the topmost silical layer. No phase difference is observed in blue and white glaze, always a mixture of Cu^{I} and Cu^{II}.

In the luster area we observe mostly Cu^{I} in fluorescence, ad a strong metallic component in TEY. Metal is mostly visible in the red luster, where the signal aso affects the fluorescence spectrum.

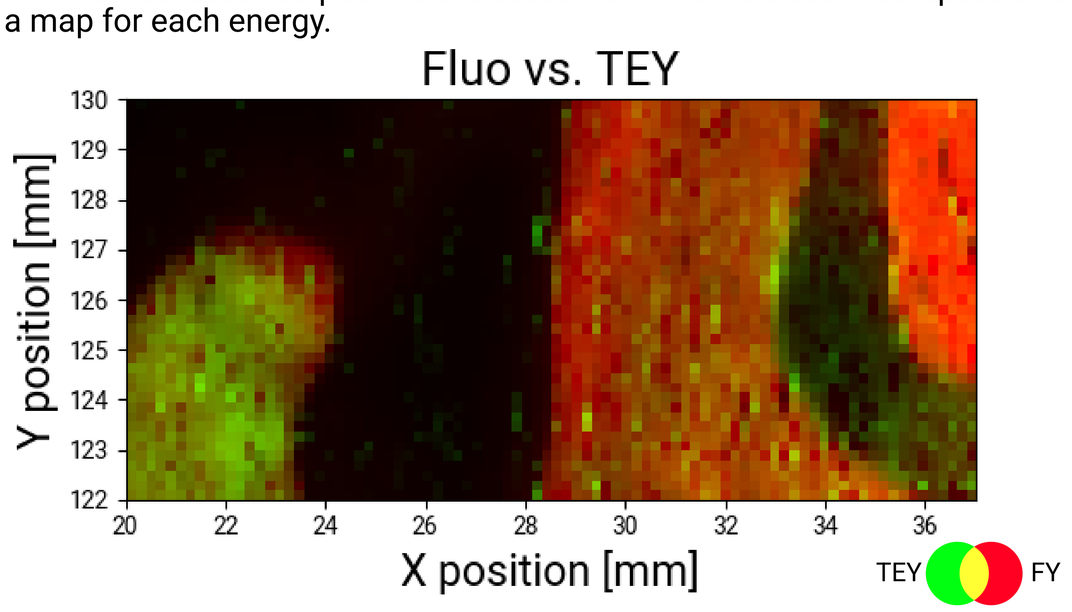
This can be due to:

- red luster layer is thicker
- red luster layer more concentrated of metallic nanoparticles.

A map at different energies is then collected:
- M_0: before the edge (9800eV)
- M_i: on the energies of interest (9400eV)

$M_F = M_i - M_0$

A ROI on the fluorescence peak is extracted from the fluorescence spectra to create a map for each energy.



Conclusions

TEY and FY can be employed to evaluate the different phases present on the surface and bulk of the sample, this is particularly useful when investigating layered samples. The image on top is similarly created registering the TEY and FY signal collected after the Cu edge (subtracting the same intensity collected before the edge). The signal of TEY is particularly intense in the red luster where a higher concentration of metallic copper is observed, and less intense in the yellow luster.

A limit is given by the low TEY signal, which increases the noise and requires a longer acquisition time.