† Electronic Supplementary Information (ESI) available:

[Characterization of the LouX^{3D} set-up

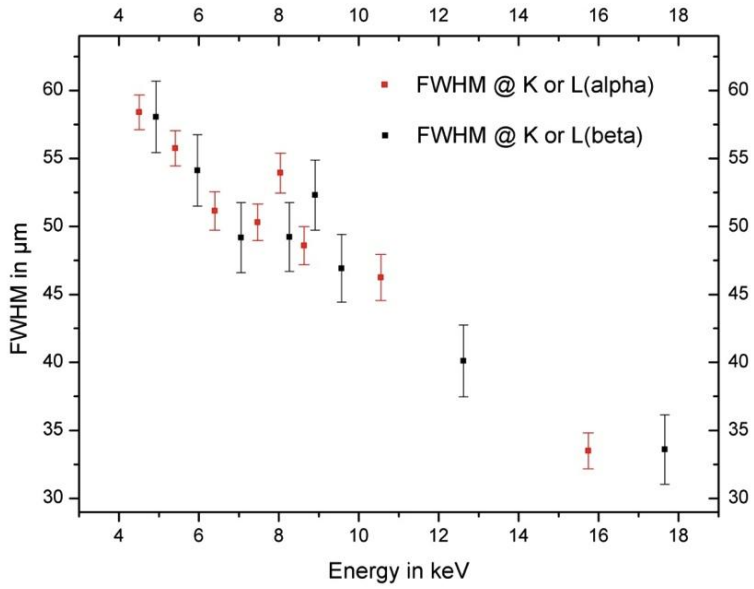

Figure 1) Full Width at Half Maximum (FWHM) of the intensity curves of the corresponding Kα and Kβ radiations of the various elements in dependence of the respective X-ray energy. Thin metal foils (Ti, Cr, Fe, Ni, Cu, Zn Pb, and Zr, respectively 2µm thin) were scanned with the LouX^{3D} spectrometer with steps of 5 µm in the depth direction. This graph shows the decrease of the probing volume with higher fluorescence energy. These values can be regarded as a measure of the spatial resolution of the set-up for the respective energy.

Spatial resolving capabilities and effective penetration depth of the set-up

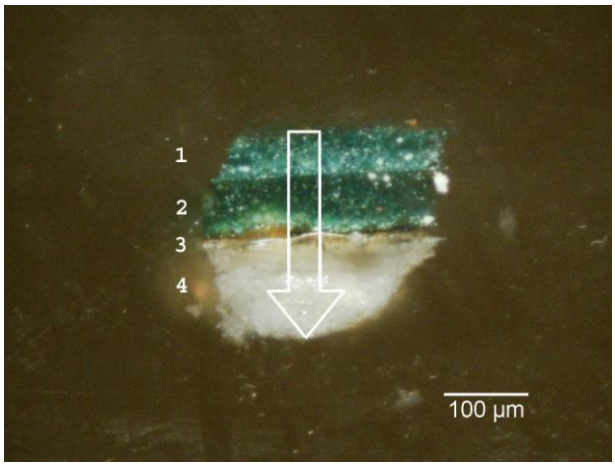

Figure 2.a) Optical micrograph of cross section n° 5318 taken from the Virgil portrait of the Famous Men series (F3322, MI 645, Louvre museum) with numbered paint layers and the measured profile indicated.

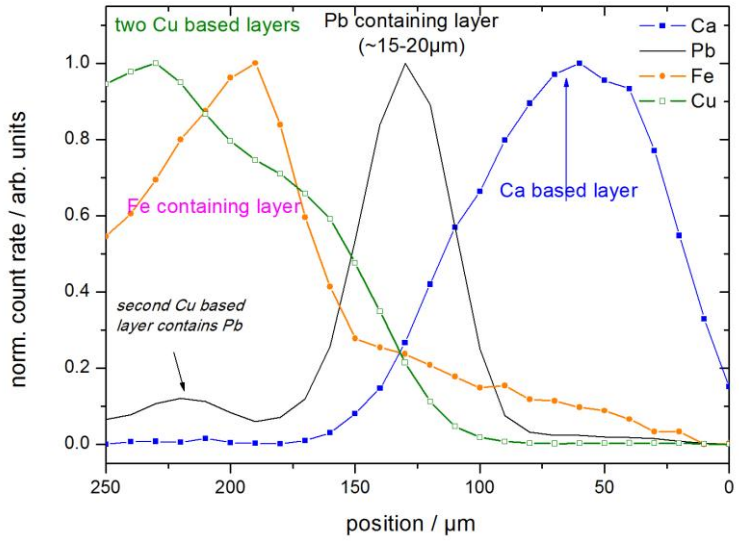

Figure 2.b) Normalized lateral elemental profiles of Ca, Pb, Cu and Fe at the surface on the cross section n° 5318. One vertical scan at the surface of the cross section and one scan at 30 µm depth were performed with a step size of 10 µm and a long acquisition time of 420 s per spectrum in order to provide good spectrum statistics. This scan reveals in accordance with SEM-EDX and microscopic observations four different layers: two white layers, one composed of a Ca-and the second of a Pb-based pigment, as well as two green paint layers, one consisting of a Cu-based pigment with the presence of a minor Fe phase and the other composed of a Cu-based pigment mixed with a Pb-based phase. The comparison of the elemental depth profiles with the microscopic paint layer analysis enables to evaluate the spatial resolving capabilities of the set-up. Obviously, paint layers of a thickness down to 15-20 µm can be identified using elemental profiling with a step size of 10 µm.

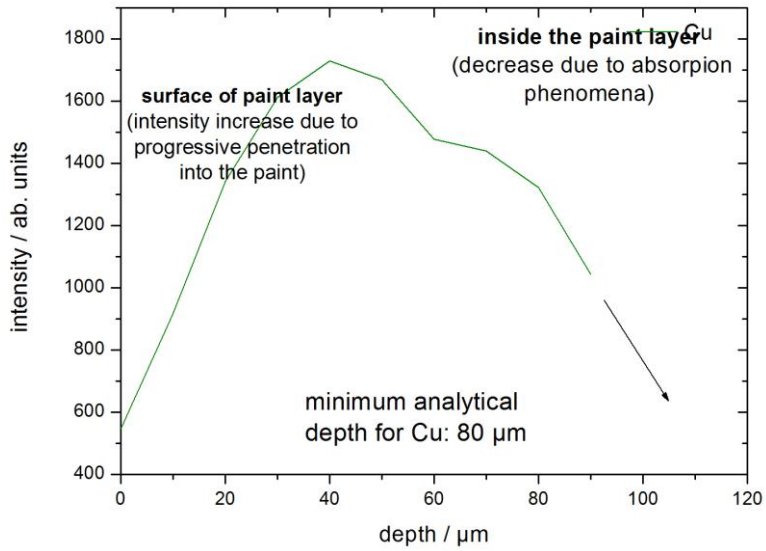

Figure 2.d) Depth profile measured on the 3rd layer (green Cu-based layer) performed in order to evaluate the effective penetration depth of the set-up in this special application. According to the measured depth profile an approximate analytical depth of about 80 – 100 µm was evaluated by using the values at half intensity maximum of the depth profile. Certainly, the penetration depth strongly depends on the chemical composition and it is difficult to predict an exact penetration depth.].