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High energy ion beam analysis of cultural heritage objects, a study of provenance and manufacturing techniques

A. Gillon(1), C. Koumeir(1,2), F. Haddad(1,2), G. Louarn(3), V. Métivier(1), Q. Mouchard(1), C. Pelé-Meziani(4), A. Raimon(4), N. Servagent(1)

Historical context and questions concerning the object

We studied a 12th century Romanesque crucifix. Fire-gilding was used to cover the Christ and his cross. The study of coating thickness can improve the understanding of the manufacturing technique used in the case of fire-gilding on a brass alloy [1].

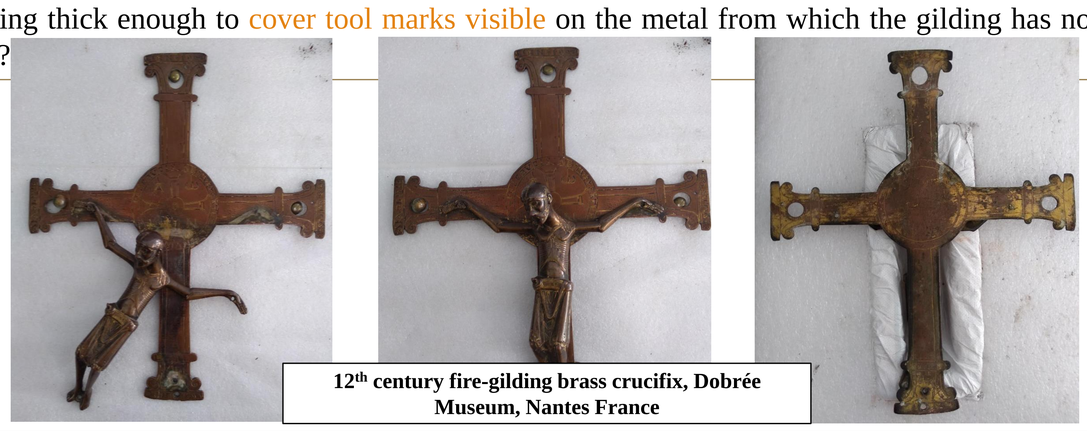
Specific concerns during the restoration process:

Is-there a net distinction of gilding thickness on both element, J-C figurine and his cross ?

Does the nature of the substrate necessitate changing the amount of gold on the surface, increasing gilding thickness ?

Were the figurine and the cross made at the same time ?

Was the gilding thick enough to cover tool marks visible on the metal from which the gilding has now disappeared ?



12th century fire-gilding brass crucifix, Dobrée Museum, Nantes France

Fire gilding technique:

Fire gilding has been performed from 3rd to 19th century to decorate objects mainly bronze and brass statuette. It is a diffusion bonding process. The role of the mercury is to ensure a close contact of substrate and plating. There is a solid-state reaction involving the use of a paste of Au-Hg amalgam (Au2Hg) [2].

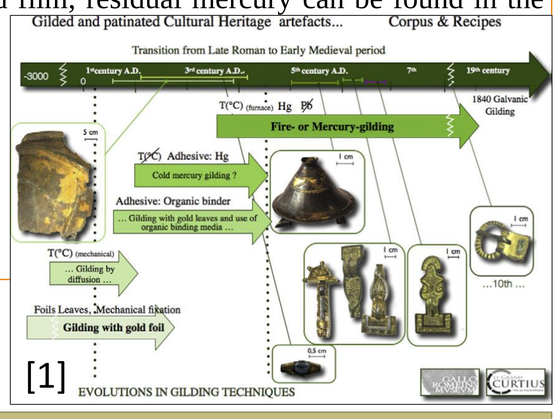
Step n°1 - Grinding gold dust with mercury; it requires a clean and oxide-free metal substrate

Step n°2 - Thermal treatment; it takes a few minutes by heating in air at about 250–350°C (< Hg boiling point at 357°C)

- A large part of the mercury volatilize and leaves a gold film; residual mercury can be found in the gold layer due to an incomplete release (8-25%)
- Fire-gilding thickness ranges from 1µm to a few tenths of micron whereas leaf gilding are only 0,1-0,4µm thick
- It stays a well-bounded layer of gold

Step n°3 - Mechanical finishing using burnishers

- It creates a smooth, shiny, gold-like surface
- It avoids uneven and porous layer of gold

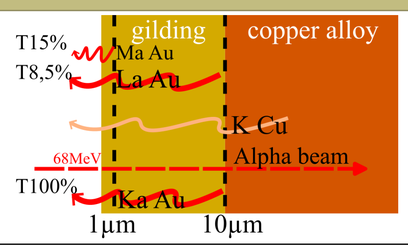


Analytical strategy and methods used, HE-PIXE spectrum

X-Rays Emission Induced by High Energy Particle (HE-PIXE)

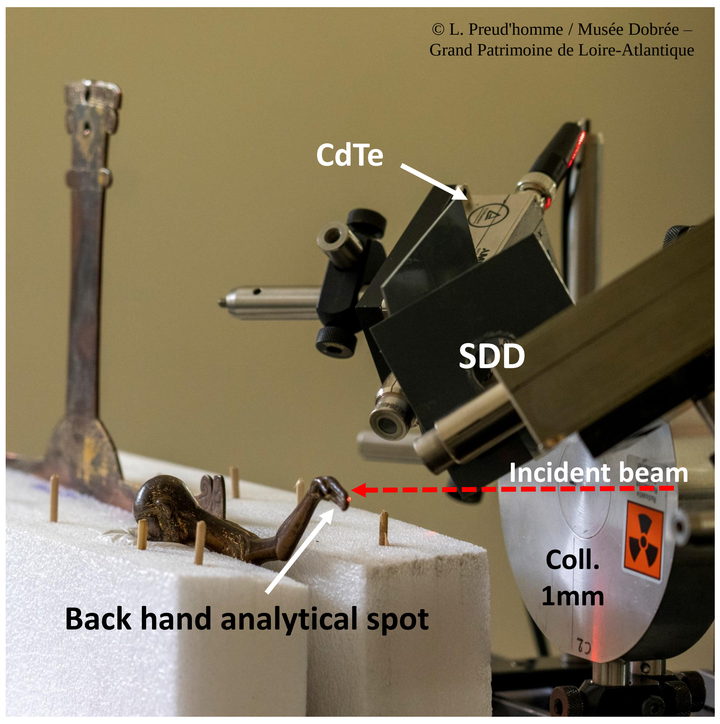
ARRONAX cyclotron allows to perform non-destructive materials analyses with HE-PIXE up to 70MeV [3]. A beam of charged particles ionizes the atoms of the material. When an atom releases its energy to stabilize, it emits a specific X-ray line, characteristic of the irradiated chemical element. Thanks to large K X-ray cross sections production and large particle ranges, it is advantageous to perform HE-PIXE experiments on heritage objects especially for bulk composition analysis of thick targets and for multilayer samples. It has already been used to analyze coins, paintings and metallic artifacts [4,5].

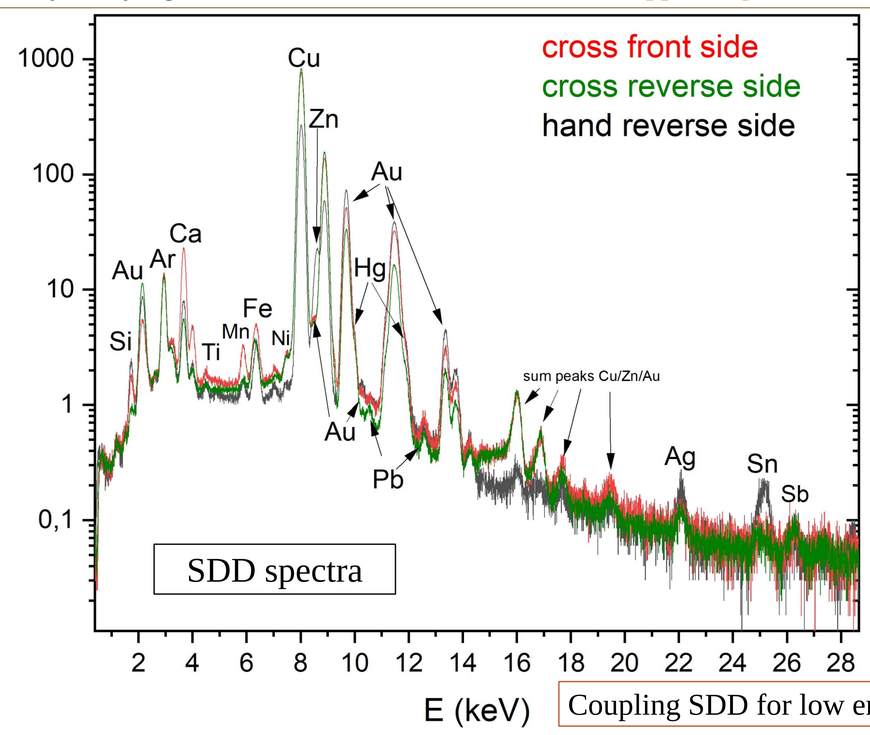
For our purpose, coating thickness measurement can be done with the net intensity of Au K-X ray line (because self attenuation is negligible, see diagram beside). Furthermore, the gilding quality was evaluated by studying the variation of the ratios Ka/Kb of copper in gold.

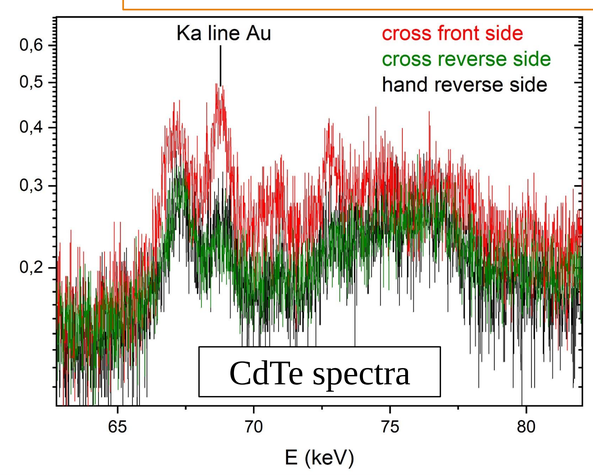


Specific X-ray lines attenuated through gilding layer and copper matrix

Component identification	
Cu/Zn	brass
Sn/Pb/Sb/Ti/Mn/Fe/Ni	alloying additions
Au/Hg/Ag	gilding
Si	SDD detector
Ar	air
Ca	surface contaminant



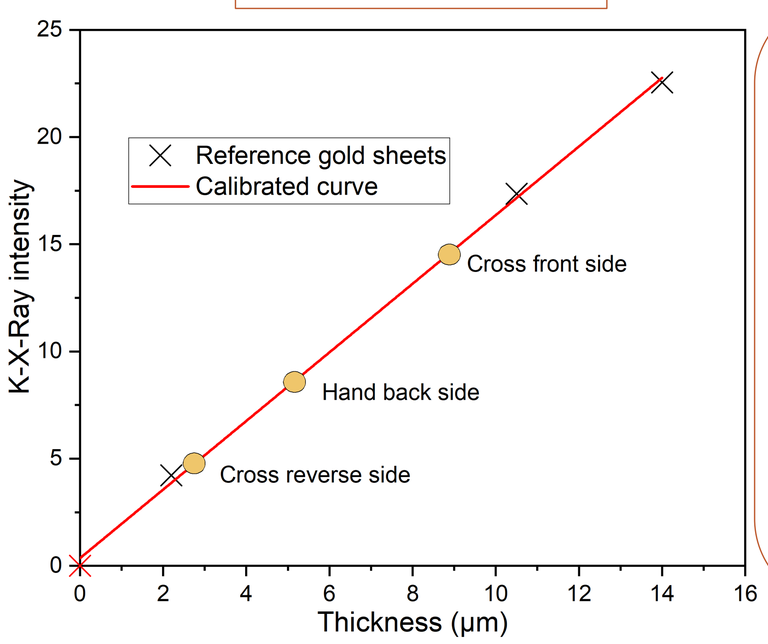




Coupling SDD for low energy X-rays (<15keV) with CdTe for higher energies up to 100keV.

Results

Gold layer thickness



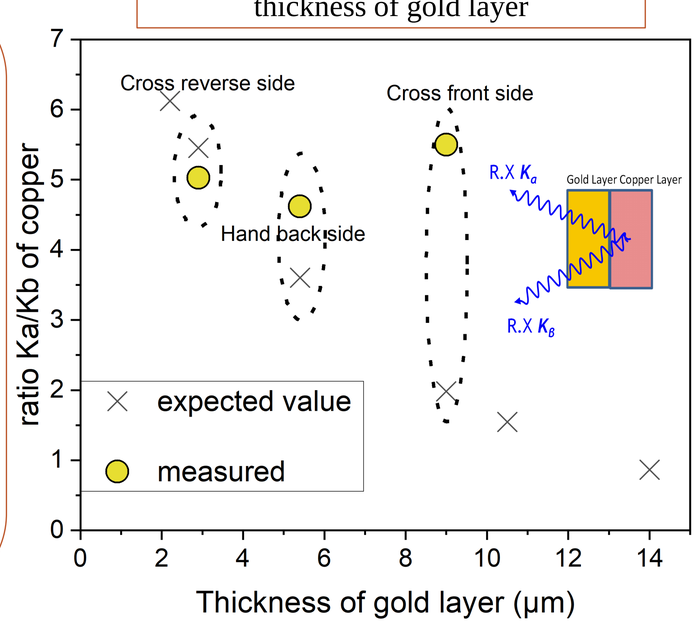
3 reference gold sheets were used, they have a thickness of 2,2, 10,5 and 14µm.

The CdTe detector was used to measure the intensity of the Au Ka lines, X-ray attenuation in Au is negligible so the intensity of the lines is directly proportional to the thickness of gold crossed by the beam.

The thickness of the gilding is different at each point of analysis

- Cross reverse side = 2.9
- Christ'hand back side = 5.4µm
- Cross front side = 9µm

Ka/Kb copper ratio corresponding to thickness of gold layer



The SDD detector was used to measure the K lines intensity of copper coming from behind the gilding thickness.

Expected values are calculated using mass attenuation coefficient of gold at Ka and Kb energies of copper.

They show the logical behavior of the ratio Ka/Kb, since Ka is less energetic thus more attenuated than Kb, the ratio decreases when the thickness increases.

Experimental values do not fit exactly to the expected ones, this can be explained by a surface heterogeneity of the gold layer. Currently, the gold thickness is an average measurement over the irradiated area and the ratio of the copper K-lines depends strongly on the actual thickness fluctuation.

Conclusion and Outlooks

- Gilding thickness measurements are in agreement with the historical data collected during the study of comparable objects. Fire gilded bronze are mainly associated with thicknesses of 1 to 10µm.
- HE-PIXE is well suited for coating layer thickness measurements using K X-ray lines even if XRF could also be performed with L and M lines.
- Since the HE-PIXE analysis, object has been restored. Gold area are now mush more visible than before.
- Further analyses need to be done with an handheld XRF device to cover all the gilded zones to conclude and say whether the Christ necessitates a thicker layer of gold than the cross.
- Other questions relating to the quality of the gilding and the work done during the elaboration of the object remain to be answered.

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