Determination of gold leaf thickness using X-ray fluorescence spectrometry: accuracy comparison using analytical methodology and Monte Carlo simulations

Sofia Pessanha¹, Ignasi Queralt², Maria Luísa Carvalho¹, Jorge Miguel Sampaio³

¹LIBPhys-UNL – Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação; Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2829-516, Caparica, Portugal

²Dept. of Geosciences, IDAEA-CSIC, Jordi Girona St., 18-26, 08034 Barcelona, Spain

³LIP - Laboratory for Instrumentation and Experimental Particle Physics, Av. Prof. Gama Pinto, n.2 Complexo Interdisciplinar (3is) 1649-003 Lisboa, Portugal

Abstract

In this work, we compared the accuracy of gold leaves thickness determination using X-ray Fluorescence (XRF) setups for different X-ray excitation sources. The sources used consisted on: a) direct *Bremsstrahlung* from an Amptek Mini-X X-ray tube with Rh target, b) partially monochromatized radiation of the same X-ray tube using combination of Al and Ag filters and, c) monochromatic radiation using secondary target, in a portable setup with triaxial geometry. The performance of the used setups was compared using model samples made with gold foil standard reference materials of known thicknesses (1, 2 and 2.5 μm). Thickness determination was based on the selective attenuation that the different energies of a given element of an under-layer undergo in the gilded layer. Ideally, as it can be expected from physics fundamentals, monochromatic radiation is needed for improved accuracy. However, considering the difficulties in using monochromatic radiation in portable instrumentation applicable in Cultural Heritage studies, filtered radiation can also be used for reliable results. Moreover, Monte Carlo simulations of the portable setup with conventional planar geometry were performed for comparison and for future application in more complex samples.

Keywords: XRF; gilding; thickness determination; Cultural Heritage; Monte Carlo simulations

32 1. Introduction

33 When studying gilded artworks, or other kind of stratigraphy, the determination of the
34 gold leaf thickness is, together with the alloy composition, one of the main objectives.
35 Layer thickness determination and compositional analysis of thin coatings and nanolayers
36 of modern and advanced materials can be routinely made by laboratory XRF
37 instrumentation using an adequate software (Roessiger, 2006) which not always can be
38 carried to the museum or archaeological site. Gilding is the deposition of a gold layer on
39 to a surface of another material, and its use has been reported since 3000 BC.

40 Gilding with gold leaf has been applied in several substrates considered of artistic and
41 cultural importance, namely paper and leather (Hayez et al., 2004; Pessanha et al., 2012),
42 clay-based (Wang et al., 2014) or ivory (Rozalen and Ruiz Gutierrez, 2015) sculptures
43 and even wall paintings (Cesareo et al., 2008; Katsibiri and Boon, 2004). There is,
44 however, a great number of artifacts made of copper-based alloys that were entirely gilded
45 to simulate solid gold (Andrade et al., 2005; Cesareo et al., 2010; Trojek and Hložek,
46 2012) or partially gilded for decorative purposes (Veiga et al., 2015). There are several
47 strategies to evaluate gilding of an artwork. Scanning Electron Microscopy (SEM)
48 imaging (Katsibiri and Boon, 2004; Rozalen and Ruiz Gutierrez, 2015; Veiga et al.,
49 2015), and Proton Induced X-ray Emission (Andrade et al., 2005; Ortega-Feliu et al.,
50 2010) are often used to determine the thickness of coatings in art and Cultural Heritage.
51 However, sampling is required in the first technique, while the second only can be applied
52 in small objects that can be moved to the laboratory. X-ray fluorescence techniques are
53 more suitable for this task because they are non-destructive and portable instrumentation
54 is available. Cesareo et al. (Cesareo, 2003; Cesareo et al., 2009) have proven that the ratio
55 of the intensities of the characteristic lines of an element in the substrate depends on and
56 can be used to measure the thickness of gilding. Similar approach was used by Trojek et
57 al. (Trojek and Hložek, 2012) in the study of 18th century Altar decorations and by
58 Pessanha et al. (Pessanha et al., 2014a) in the analysis of an 16th century illuminated
59 manuscript. This method relied on the comparison with the analysis of the substrate
60 without coating, which is, sometimes, not possible. This was the case of the study and
61 comparison of the gold leaf in a set on Namban folding screens, where only the different
62 characteristic lines of Au were determined and compared in order to assess different
63 thicknesses (Pessanha et al., 2014b). Buccolieri et al. (Buccolieri et al., 2018) used the

total attenuation of the radiation coming from an ^{241}Am γ -ray source for the determination of the thickness of a wreath of gold leaves from the National Archaeological Museum of Taranto, while Ferreti et al. (Ferretti et al., 2013) derived the thickness of gilded silver using the mass fractions for Ag-K $_{\alpha}$ and Ag-K $_{\beta}$ in the XRF spectra. These methods were designed to be implemented using monochromatic X-ray source, however this is not the case in most circumstances, where only some kind of filtering is used to partially reduce background or even no filtering and the direct *Bremsstrahlung* from the tube is applied for analysis.

In this work, the application of two evaluation methodologies based on the selective attenuation of radiation in a gold foil will systematically compared by using 2 different setups and different incident sources: direct *Bremsstrahlung* from the X-ray tube, partially monochromatized radiation using combinations of filters in the output of the X-ray tube and monochromatic radiation using secondary target on model samples. Furthermore, Monte Carlo simulations of the setup, using filter combinations were performed in order to further evaluate the suitability of this approach to gold leaf thickness determination.

2. Methodology

Two similar approaches have been demonstrated by Cesareo et al. (Cesareo, 2003; Cesareo et al., 2009) and used profusely for the determination of the thickness of gold coatings (Cesareo et al., 2013, 2004; Pessanha et al., 2014a). The first one relates the different characteristic lines of Au due to their differentiated attenuation in the layer regarding the thickness. Considering the L $_{\alpha}$ /L $_{\beta}$ intensity ratio, it would be maximum for an infinitely thin sample and decrease exponentially with increasing thickness until it plateaus for an infinitely thick sample (Sitko, 2009), according to equation 1:

$$\left(\frac{L_{\alpha}}{L_{\beta}}\right) = \left(\frac{L_{\alpha}}{L_{\beta}}\right)_0 \left(\frac{\varepsilon(E(L_{\alpha}))}{\varepsilon(E(L_{\beta}))}\right) \left[\frac{(\mu_0 + \mu_2)}{(\mu_0 + \mu_1)}\right] \left[\frac{1 - e^{-(\mu_0 + \mu_1)d}}{1 - e^{-(\mu_0 + \mu_2)d}}\right] \quad \text{eq. (1)}$$

where,

$\left(\frac{L_{\alpha}}{L_{\beta}}\right)_0$ is the intensity ratio for an infinitely thin sample (Seltzer, 1989);

$\varepsilon(E)$ is the detector efficiency for a given energy;

μ_0 is the linear attenuation coefficient (in cm^{-1}) of Au at incident energy E_0 ;

μ_1 is the linear attenuation coefficient (in cm^{-1}) of Au at energy of L $_{\alpha}$ emission line (9.71

keV);

μ_2 is the linear attenuation coefficient (in cm^{-1}) of Au at energy of $L\beta$ emission line (11.4 keV);

d is path length of the characteristic radiation (in cm) and $d = \frac{x}{\cos\theta}$ where x is the thickness of the layer and θ is the angle between the detector and the normal to the sample. Another technique, used when the gilding under-layer can be assessed, is to compare the characteristic lines of substrate with and without attenuation in the gilding. Considering a substrate of a copper-based alloy covered with gold leaf, the characteristic lines of the substrate are attenuated in the gold layer differently, according to their mass-attenuation coefficient, as can be seen in equation 2:

$$\left(\frac{K_\alpha}{K_\beta}\right) = \left(\frac{K_\alpha}{K_\beta}\right)_{s.a.} e^{-(\mu_1 - \mu_2)\rho_{Au}d_{Au}} \quad \text{eq.(2)}$$

where:

$(K_\alpha/K_\beta)_{s.a.}$ is the intensity ratio of the characteristic lines of Cu in copper due to self-attenuation effects;

μ_1 is the mass attenuation coefficient (in $\text{cm}^2 \cdot \text{g}^{-1}$) of Cu at 8.04 keV;

μ_2 is the mass attenuation coefficient (in $\text{cm}^2 \cdot \text{g}^{-1}$) of Cu at 8.9 keV;

ρ_{Au} is the density (in $\text{g} \cdot \text{cm}^{-3}$) of Au;

d_{Au} is the path length (in cm) and $d = \frac{x}{\cos\theta}$ where x is the thickness of the layer and θ is the angle between the detector and the normal to the sample.

3. Experimental

3.1. Materials

A set of three 99.9% pure Au square foils (from Goodfellow Inc., Huntingdon, UK) with 25 x 25 mm in size and thickness of 1, 2 and 2.5 μm ($\pm 25\%$) were used.

The under layer consisted of a plate, ~3 mm thick, of uncertified nearly pure copper metal. Quantification of XRF spectra, obtained with a benchtop commercial setup M4Tornado, using Fundamental parameter method for bulk samples (Pessanha et al., 2015), determined 99.9% Cu with traces of Fe and Pb.

3.2. Portable setup with triaxial geometry – p3XRF

An experimental setup was assembled using a sided window X-ray tube with a Mo anode, OXFORD XTF5011 (max 50 kV, 1 mA) and a Silicon Drift Detector, thermoelectrically cooled (60EX, Vortex) (FWHM at 160 eV at Fe-K α), with an active area of 50 mm² and a 25 μ m thickness Be window. Monochromatization and reduction of the *Bremstrahlung* from the tube was obtained using a secondary Yttrium target disk (99% purity, 1.0 mm thickness, 25.0 mm diameter, GoodFellow Inc., Huntingdon, UK) in triaxial geometry as it was described in a previous work (Pessanha et al., 2017). The spot size was measured with a radiographic film producing an ellipsoid image with 17 mm $\times$ 12 mm. Spectra were acquired using PI-SpecA[®] software and the X-ray generator was operated at 50 kV, 1 mA during 300 s.

3.3. Portable XRF setup with conventional geometry

The XRF portable setup consists of an X-ray generator (Mini-X, Rh target, 50 kV, 200 μ A, max. from Amptek Inc., Bedford, USA) and silicon PIN detector (XR-100CR, 7 mm² detection area, 500 μ m thickness and a 12.5 μ m Be window, from Amptek Inc., Bedford, USA).

The angle between the incident and the emitted beam is 90° in order to obtain high reduction of the background due to Compton scattering. The energy resolution is 190 eV at 5.9 keV. Spectra were acquired using PocketMCA software and the X-ray generator was operated at 40 kV and 40 μ A during 200 s. Partial monochromatization was achieved using a combination of filters provided by Amptek (2 x 1 mm Al + 250 μ m Ag). Knife edge method determined a spot size of 1.1 mm.

Spectra analysis, for both spectrometers was performed using the LabSpec[®] software package (5.58 version). Intensities were determined by integrating the full area under the curve. Efficiency curves for SDD and SiPIN detectors were taken from the manufacturer's datasheets.

3.4. Monte Carlo simulations

The modeling of the portable spectrometer with filters was done by means of Monte Carlo simulation using PENELOPE (Penetration and ENergy LOss of Positrons and Electrons) code (Baró, 1995), 2011 version. In order to reduce computing time and improve

statistics, instead of simulating the whole setup since the acceleration of electrons into the anode, a direct measurement of the X-ray tube's spectrum after filtering was used as input in the simulation file after deconvolution with the detector's efficiency. The absorption energies, elastic scattering parameters and cutoff energies were set as the default recommendation considering the maximum energy of particles in the simulation (EPMAX) of 40 keV. The output spectra were then convoluted with the efficiency of the detector and an energy dependent Gaussian function for the broadening of the peaks obtained by determining the Full Width at Half Maximum (FWHM) of several mono-elemental samples.

4. Results and discussion.

Figures 1 and 2 represent the theoretical plots of equation 1 for the different setups. Furthermore, they present the experimental results for Au (L_{α}/L_{β}) intensity ratios determined for the 3 Standard Reference Materials, with the different combination of excitation sources, corrected for the efficiency of the detector and absorption in air (Söğüt, 2004). As can be seen, the experimental results obtained for the setup with monochromatic radiation are within 1 standard deviation of the theoretical curve.

Regarding the results obtained for the other setup, the use of direct excitation from the source, without filtering produces higher intensity ratios and presents challenge to correlate with the theoretical curve. This divergence from the theoretical curve occurs because it was also plotted considering the anode's incident energy of Rh- K_{α} , which does not correspond to the real incident spectrum. Full monochromatic radiation with the filters was not achieved, and additionally, incident X-rays will be hardened as the thickness of the layer increases.

The determined thicknesses of the three foils using the second approach (equation 2), again using both setups, as exhibited in table 1.

As expected, the determined thicknesses are less accurate when using unfiltered radiation. The most accurate results were obtained using the p3XRF setup, with monochromatic radiation, with a maximum deviation of 5% respect to the certified value.

Regarding the use of filters, as employed in most published case studies mentioned in the introduction section, the deviation to the certified thickness is less than 12%, with underestimated values. Regardless these deviations and considering the uncertainties, the obtained values are reliable and in accordance with the discrepancies found elsewhere (Lopes et al., 2016; Ortega-feliu et al., 2017).

In Fig.3 are displayed the obtained results for $\text{Cu}(K_{\alpha}/K_{\beta})$ intensity ratios considering simulated samples of varying thicknesses of 100% Au (0.1 to 2.5 μm) over an infinitely thick layer of Cu (500 μm). The uncertainty contemplates the statistical uncertainty of the output simulated spectrum and uncertainty of the fitting of the curve using Labspec®. After fitting of the obtained curve considering equation 2, the value for $\text{Cu}(K_{\alpha}/K_{\beta})$ intensity ratio due to self-attenuation in the Cu layer was determined to be 6.87 ± 0.03 .

Conclusion

The use of a non-destructive approach for gilding analysis is of utmost importance when dealing with Cultural Heritage and delicate objects of artistic value. This paper described the systematic comparison of two simple analytical approaches for the determination of the thickness of gildings using XRF instrumentation, for different excitation sources and instrumental design. As anticipated, the use of monochromatic radiation is paramount when great accuracy is needed in the calculations. However, in practice, most portable instrumentation for XRF does not comply with this requirement. Considering the obtained results, the use of filters for background reduction and partial monochromatization can be used as an alternative, quite accurate approach, for thickness determination when the characteristic lines of an element of the under-layer can be assessed and compared with and without gilding. On the other hand, performing these calculations without filtering the X-ray source would lead to deceptive results.

The modeling of this setup using Monte Carlo method also proved suitable for reproducing such simple stratigraphy as pure gold of varying thicknesses over a layer of infinitely thick copper. This approach can, hence, be used for the simulation of more complex samples and determination of gilding thickness without sampling or without the need for assessing the underlayer.

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Figure captions:

Fig. 1 - Comparison of the theoretical dependence of Au (L_{α}/L_{β}) intensity ratio and the thickness of Au layer for the p3XRF setup and the experimental results. The incident radiation for theoretical curve was set to 14.9 keV (Y- K_{α}). Vertical error bars correspond to 1 standard deviation for 6 measurements.

Fig. 2 - Comparison of the theoretical dependence of Au (L_{α}/L_{β}) intensity ratio and the thickness of Au layer for the portable setup with planar geometry considering (considering incident energy of Rh - K_{α} (20.2 keV)), the experimental results (vertical error bars correspond to 1 standard deviation for 6 measurements) and Monte Carlo simulations of the setup (vertical error bars correspond to the uncertainty of the method).

Fig. 3 - Comparison of the simulated dependence of Cu (K_{α}/K_{β}) intensity ratio and the thickness of Au layer for the portable setup with conventional geometry (vertical error bars correspond to the uncertainty of the method) and the experimental results (vertical error bars correspond to 1 standard deviation for 6 measurements). Fitted curve using exponential function is also presented.

Table 1. Mean thicknesses (μm) determined for the different configurations. The uncertainty corresponds to one standard deviation over 6 measurements. Δ corresponds to the relative deviation to the certified value (in %).

Thickness (μm)	Portable				p3XRF (Monochromatic)	Δ (%)
	No filter	Δ (%)	filter Al/Ag	Δ (%)		
1.00 ± 0.25	1.5 ± 0.2	40	0.9 ± 0.1	10	1.0 ± 0.1	<1
2.0 ± 0.5	2.2 ± 0.2	10	1.8 ± 0.2	10	2.1 ± 0.1	5
2.5 ± 0.6	3.0 ± 0.3	20	2.2 ± 0.3	12	2.4 ± 0.2	4