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Gilding Thickness Measurements Using EDXRF-Analysis

M.J. dos Anjos [1,2,] J.T. de Assis [1,] R. Cesareo [3], S. Ridolfi [4,] R.T. Lopes [2],
R.S.dos Santos [1,]H.S. Gama Filho[1], D.F.Oliveira [1]

1. Universidade Estadual do Rio de Janeiro, Rio de Janeiro, Brasil;marcelin@uerj.br
2. COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brasil;ricardo@lin.ufrj.br
3. Università di Sassari, Sassari, Italy; cesareo@uniss.it
4. Arsmensurae, Rome, Italy; stefano@arsmensurae.it

Abstract -When a multi layered object such as a gilded material is analyzed by means of energy-dispersive X-ray fluorescence (EDXRF), then one of the most serious problems consists in identifying for each element the correct layer, and in determining the thickness of the various layers, and particularly of the gilding. These questions can be solved, in many cases, by measuring the internal ratio of each element,i.e. the Kα/Kβ or Lα/Lβ–ratios of the various elements below the gilding (Cu, Ag, Pb) and of gold. In facto Kα/Kβ or Lα/Lβ – ratios are tabulated for infinitely thin samples; anomalous values for a given element may depend on the position and thickness of the layer in which the element is located,and on the thickness and composition of the superimposed layer.

In this paper the ratios Kα/Kβ and Lα/Lβ are calculated in the case of gilded artifact as a function of material and thickness of the corresponding layer.

Various examples are described: Gate to paradise on gilded bronze by Lorenzo Ghiberti in the baptistry of Florence; an inscription on gilded bronze on the top of the Trevi fountain in Rome; the carriage of king of Brazil Dom Pedro II on wood with superimposed a lead pigment and gilded.

I. INTRODUCTION

Golding means to apply gold leafs or gold powder to a solid surface such as wood, stone, marble, metal, ceramics painting and so on. The first known gilding process goes back in the 3rd – 4th millennium B.C. in Egypt.

According to the gold thickness d, the term gold foil or gold leaf are employed, when d > 10 μm, or d <10 μm respectively.

Different methods were and are employed to adhere a gold leaf or foil to a solid substrate; in any case the gold can be characterized in terms of thickness and composition. Often, ancient gildings are also covered by a protective layer, giving rise to a multilayered sample.

In this paper, non-destructive and non-invasive methods are described, based on energy-dispersive X-ray fluorescence (EDXRF), and on the use of the different attenuation of X-lines of different energy, produced by the various components of the irradiated sample. These methods are able to "reconstruct" the structure of a multilayered sample in terms of correct location of the chemical elements present in any layer, and to determine the layer thickness.

Ratios of characteristic X-rays emitted by the elements present in the layers are used in two different manners, based on the different attenuation of X-rays (Kα and Kβ or Lα and Lβ) due to their different energy. In the case of gilding:

-self-attenuation of L-X rays emitted by the gilding, due to the different attenuation of the two principal L- gold lines in the gold itself (Lα and Lβ, with energy of 9.7 and 11.8 keV respectively;

-different attenuation of the two K or L-X rays of an element characterizing the more internal layer, by the gold layer; for example in the case of gilded copper, the two Cu-K lines by the gold layer.

Further, also the ratio of the K (or L) X-rays emitted by an element characterizing the internal layer, to the gold L-X-rays can be usefully employed to determine the gold thickness, once the gilding is determined.

In this paper, an improved theoretical description of these methods is given, specialized to gildings, and a large example of applications is described.

In spite of some discrepancy, mainly due to statistical reasons, uncertainty in the determination of some peak area, and to effects of permeation of a layer in another one, all the described methods give satisfactory results, both in the identification of the layers, and evaluation of the gilding thickness.

II. THEORETICAL BACKGROUND

SELF-ATTENUATION

As explained in previous papers [1-8], Kα/Kβ and Lα/Lβ X-rays of any element vary versus thickness according to following equations normalized to 1:

$$\frac{K_\alpha}{K_\beta}/\left(\frac{K_\alpha}{K_\beta}\right)_{thin} = \left(\frac{\mu_{10}+\mu_{12}}{\mu_{10}+\mu_{11}}\right)\left(\frac{1-e^{-(\mu_{10}+\mu_{11})d}}{1-e^{-(\mu_{10}+\mu_{12})d}}\right) \quad (1)$$

$$\frac{L_\alpha}{L_\beta}/\left(\frac{L_\alpha}{L_\beta}\right)_{thin} = \left(\frac{\mu_{10}+\mu_{12}}{\mu_{10}+\mu_{11}}\right)\left(\frac{1-e^{-(\mu_{10}+\mu_{11})d}}{1-e^{-(\mu_{10}+\mu_{12})d}}\right) \quad (2)$$

where:

- $\left(\frac{K_\alpha}{K_\beta}\right)_{thin}$ and $\left(\frac{L_\alpha}{L_\beta}\right)_{thin}$ represent the tabulated and/or measured ratios for infinitely thin samples;
- μ_{10} is the linear attenuation coefficient of the considered elementi (in cm^{-1}), in our case gold, at incident energy E_0 (when monoenergetic radiation is employed) or a "mean incident energy E_0" (when bremsstrahlung radiation is employed) ;
- μ_{11} is the linear attenuation coefficient (in cm^{-1}) of the considered element, at energy of its Kα (or Lα) line ;
- μ_{12} is the linear attenuation coefficients (in cm^{-1}) of the considered element, at the energy of its Kβ (or Lβ) radiation;
- d represents the layer thickness (in cm) of the considered element.

Scheme of principles of self-attenuation and attenuation processes is shown in Fig. 1. Eqs.(1) and (2) are valid when both incident and output beam are normal to the sample surface.

In the case of gilding, and with the experimental conditions explained elsewhere [5], Eq. (2) may be specified as:

$$Au(L\alpha/L\beta) = 0.71\ [(1-e^{-2860\ d})/(1-e^{-2035\ d})]. \quad (2a)$$

It may be deduced, from Eq.(2a), that the method of using Au(Lα/Lβ)-ratio has the maximum sensitivity for Au-thickness of d~ (2-5) μm, and is scarcely useful for d<1μm and for d>10μm.

ATTENUATION OF X-RAYS FROM AN INTERNAL ELEMENT BY AN EXTERNAL GOLD SHEET

When a sheet, supposed thick, and composed by a single element (layer 2, see Fig. 1), is covered by an absorbing layer of a second element (layer 1, see Fig. 1), then the ratios (Kα/Kβ) or (Lα /Lβ) of the internal element (normalized to 1 by dividing to the ratio without covering) is altered in the following manner because of the different attenuation of its Kα and Kβ X-rays (or Lα and Kβ X-rays) by the external element [1-8] :

$$K\alpha/K\beta/(K\alpha/K\beta)_0 = \exp-(\mu_{1\alpha} - \mu_{1\beta})d \quad (3)$$

$$L\alpha/L\beta/(L\alpha/L\beta)_0 = \exp-(\mu_{1\alpha} - \mu_{1\beta})d \quad (4)$$

where:

Kα/Kβ and Lα/Lβ, $(K\alpha/K\beta)_0$ and $(L\alpha/L\beta)_0$ are the ratios of the X-rays of the internal sheet with or without covering sheet respectively;

$\mu_{1\alpha}$ represents the linear attenuation coefficient of the covering sheet at the energy of K_α (or L_α) radiation of the internal sheet;

$\mu_{1\beta}$ is the linear attenuation coefficient of the covering sheet at the energy of the K_β (or L_β) radiation of the internal sheet;

d is the thickness (in cm) of the covering sheet.

In the case of gilding, the external element is gold, and the internal element is, copper, bronze or brass, (which in many cases almost equivalent to copper) or, in many cases of paintings, a lead pigment.

-gilded copper or gilded bronze or brass : in these cases Eq.(3) can be written as:

$$Cu(K\alpha/K\beta)/Cu(K\alpha/K\beta)_0 = \exp-(890 d_{Au}) \quad (3a)$$

By considering Eq.(3a), it may be deduced that the effectiveness of Cu (Kα/Kβ)-ratio to determine the gilding thickness is maximum in the interval d=1-5 μm.

-lead pigment (white lead or minium) covered by a gold layer; in this case Eq. (4a) can be written: $Pb(L\alpha/L\beta)/Pb(L\alpha/L\beta)_0 = \exp(1130 d_{Au})$. (4a)

which, in the low Au-thickness approximation, may be written as:

$$(L\alpha/L\beta)/Pb(L\alpha/L\beta)_0 \sim 1+1130 d_{Au} \quad (4b)$$

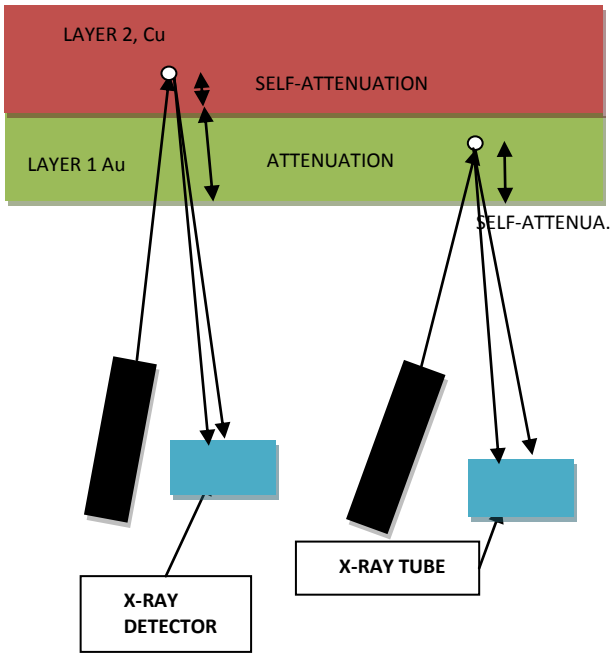

Fig. 1. Example of self-attenuation and of attenuation in the case of gilded copper; from right: photoelectric effect in gold and emission of Lα and Lβ – gold lines which are self-absorbed differently by gold itself (SELF-ATTENUATION); left: photoelectric effect in copper and emission of copper Kα and Kβ – lines which are self-absorbed differently by copper (SELF-ATTENUATION) and also differently absorbed by gold (ATTENUATION).

RATIO OF GOLD L-X RAYS TO Kα OR Lα OF INTERNAL ELEMENT

Another way to experimentally determine the thickness of the external elemental sheet from the X-ray spectrum, assuming that the internal elemental sheet has an infinite thickness, consists in the direct use of the X-ray ratio of the two elements characterizing the two sheet (for example, in the case of gilded copper, the ratio Au-Lα/Cu-Kα) [1-8,9]. Then, following equation (5) may be written:

$$N_1/N_2=P[1-\exp-(\mu_{10}+\mu_{1\beta})d_{Au}]\exp(\mu_{10}+\mu_{1\alpha})d_{Au.}$$

where:

-P is a parameter, which depends on many factors, to be determined from experimental measurements;

-μ_{10} represents the linear attenuation of the element which characterizes covering sheet at incident energy E_0 (covering sheet);

-$\mu_{1\beta}$ represents the linear attenuation of the element which characterizes covering sheet at energy of Kβ-line of internal element;

-$\mu_{1\alpha}$ represent the linear attenuation of the element which characterizes covering sheet of energy of Kα-line of internal element;

-d is the thickness (in cm) of sheet 1, in our case gold.

When the external element is gold, and the internal material copper (or bronze or brass) or a lead based pigment, then following Eqs. (5a) and (5b) may be specialized :

$$N_{Au}/N_{Cu}=P(1-\exp[-2860\ d_{Au}])\exp(4350\ d_{Au})$$

$$N_{Au}/N_{Pb}=P'(1-\exp[-2860\ d_{Au.}])\exp(2410\ d_{Au})$$

At low Au-thickness values, Eqs. (5a) and (5b) may be written as:

N_{Au}/N_{Cu} = P. 2860 d_{Au} and N_{Au}/N_{Pb} = P'. 2860 d_{Au} respectively. This method may be applied when the presence of the two layers is determined.

III. EXPERIMENTAL SET-UP

The experimental set-up for EDXRF-analysis is described in details elsewhere [4]. It is composed of a mini X-ray tube with Ag-anode, working at 40 kV and 200 µA maximum voltage and current, of a Si-drift detector with 135 eV energy resolution at 5.9 keV, and of a notebook. Both X-ray tube and detector can be battery equipped.

IV. RESULTS

First of all, the previous methods were tested, by measuring a gold leaf of 4 µm thickness, located over a sheet of Cu or Pb of infinite thickness. Results are show in Table 1 and show that the three methods to determine a gilding thickness give satisfactory results; however there are large uncertainties, mainly due to lack of adequate standard samples, background under the X-ray peaks and difficulty to evaluate the X-ray peaks integral, and low statistics. Further, the three methods give best results in different intervals of gilding thickness.

Then, practical examples are discussed in the following:

Gate to paradise

The panel "Abraham" of the east door of the Baptistry of Florence, on gilded bronze, was systematically analyzed during restoration, by using a portable EDXRF equipment.

The east door of the Baptistry of Florence, also known as "Gates to Paradise" (Fig. 2), was done by Lorenzo Ghiberti between 1426 to 1452 [10]. It is composed of 10 panels made on gilt bronze.

The gilding was produced with an amalgam of gold. Today, models of the doors hang on the Baptistry, while the originals are on display at the "Museo dell´Opera del Duomo". At the

time of measurements, it was under restoration at the "Opificio delle Pietre Dure" in Florence.

The aim of the analysis was to determine again, with a modern equipment, the bronze composition and the gilding composition and thickness. Following bronze composition was measured, in agreement with previous measurements [11]: Cu=92.4%; Sn=1.8%; Pb=0.7%; Zn=3.8%; Sb=0.9%; As=0.2%; Ag=0.2%. The door is, therefore, almost on copper.

Following results were obtained for the gilding thickness:

Fig. 2. The panel "Gate to Paradise" by Lorenzo Ghiberti, on gilt bronze.

Fig. 3. Trevi fountain, Rome.

Trevi fountain in Rome

The famous Trevi fountain in Rome was designed by architect Nicola Salvi and completed in 1762 by Pietro Bracci and Giuseppe Pannini [12]. Standing 26 m high and 49 m wide, it is the largest Baroque fountain in the city and one of the most famous fountain in the world (Fig. 3). The fountain has appeared in several notable films, including Fellini's *la dolce vita* and the eponymous *three coins in the fountain.* The fountain was under restoration in 2013 and 2014, when analyses were carried out.

At the top of the fountain there is following inscription: *PERFECIT BENEDICTUS XIV PONT. MAX.*, which may be translated into *Benedict XIV pontifex maximum made perfect.* Benedict XIV was pope in the years 1740-1758. The big inscription was supposed to be on gilt bronze and was under restoration when the measurements were carried out.

Following results were obtained:
-the gilding background is brass, and its composition is: Cu=81%, Zn=15.5%, Sn=1%, Sb=0.5%. Pb=0.8%.
-the gilding composition is: Au=99.5% , Ag=0.5%.
-the gilding thickness, calculated on the basis of Au(Lα/Lβ) and (Au-Lα/Cu-Kα)-ratios, is: 3.4±0.5 µm.

Carriage of "dom Pedro II"

Dom Pedro II was the second and last emperor of Brazil, reigning for over 58 years (1833-1891). A special gilded carriage was constructed by the royal firm Pearce & Countz in 1837 for his coronation in 1841. The carriage, restored several times (the last one in 2011) is now in the imperial museum in Petropolis [13] (Fig. 4). It is made on wood, covered by a lead-pigment, possibly minium (Pb_3O_4) and gilded.

Fig. 4. Carriage of brasilian emperor "dom Pedro II", on gilded wood

During the restoration process, the gilded elements received chromatic reintegration with gilded mica coating diluted with paranoid-B72. Mica thickness was measured to be 65±µm. A large number of measurements were carried out, in order to determine the composition of the components above the wood structure, and to measure the gilding thickness. From all the EDXRF-spectra following could be deduced:

-following chemical elements are present: Ti,Fe,Au,Pb.

-the gilding is too thin to use the Au(Lα/Lβ) or Pb(Lα/Lβ) – ratios to determine the gilding thickness; only the ratio Au-Lα/Pb-Lα may be usefully employed, which gives following result: Au-Lα/Pb-Lα = 0.027±0.007, corresponding to a thickness of 0.13±0.02 µm. By considering the presence of mica, which has a mean thickness of about 65 µm and absorbs more gold Lα-rays (9.7 keV) than lead Lα-rays (10.5 keV), the corrected thickness will be: d = 0.14 µm.

V. CONCLUSIONS

The sensitivity of the three described methods to determine the gilding thickness mainly depends on the its thickness, and is resumed in Table 1, assuming that the gilding composition corresponds to almost pure gold.

Table 1

Gilding thickness (µm)	Self-attenuation	Attenuation	Au-Lα/Cu-Kα or Au-Lα/Pb-Lα
0-1	No	No	Yes
1-2	No	Yes	Yes
2-6	Yes	Yes	Yes
>6 and <8	No	Yes	Yes
>8	No	Yes	No

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