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Gold leafs in 14th century Florentine painting

Feuilles d'or dans la peinture florentine du XIVe siècle

Giovanni Buccolieri*, Alessandro Buccolieri*, Susanna Bracci**, Federica Carnevale*, Franca Falletti**, Gianfranco Palamà*, Roberto Cesareo*** and Alfredo Castellano*

Abstract: Gold leafs are typically present in paintings and frescoes of the Italian Renaissance in the 13th and 14th centuries. The chemical composition and thickness of gold leafs provide important information toward a better understanding of the technology of that epoch. The present paper discusses the results of non-destructive analysis carried out with a portable energy dispersive X-ray fluorescence (ED-XRF) equipment on the 14th century panel *Annunciation with Saints Catherine of Alexandria, Anthony Abbot, Proculus and Francis* by the painter Lorenzo Monaco.

Résumé : *L'application de feuilles d'or sur des tableaux et des fresques est typique de la Renaissance italienne aux XIIIe et XIVe siècles. Leur composition chimique et leur épaisseur fournissent des informations importantes pour la compréhension des techniques de cette période. Ce travail discute les résultats des analyses non-destructives réalisées avec un système portable de fluorescence X à dispersion d'énergie (ED-FX) sur le panel du XIVe siècle* Annonciation avec Saints Catherine d'Alexandrie, Anthony Abbot, Proculus et Francis *par le peintre Lorenzo Monaco.*

Keywords: Gold leafs; Florentine painting; non-destructive analysis; ED-XRF.

Mots-clés : *Feuilles d'or, peinture florentine, analyse non-destructive, ED-FX.*

1. Introduction

All populations have always used metals to make ornaments, such as leafs, on paintings or other objects of historical art. The most frequent metals employed were gold, silver, lead, copper, tin, and iron (Scott and Dodd, 2002; Duran *et al.*, 2008).

Gold leafs are typically present in paintings and frescoes of the Italian Renaissance in the 13th and 14th centuries, as background, haloes, or decorations. The non-destructive determination of gold leaf composition and thickness in paintings and frescoes is of primary importance for a better understanding of the technological development of the respective epoch. Generally, when a gold leaf is studied by ED-XRF analysis, an X-ray spectrum is obtained, typically containing two Cu-K lines, three Au-L lines and two Ag-K lines. From a quantitative analysis of these lines, the concentrations of Cu, Au and Ag can be determined. Furthermore, the thickness of the Au leaf may be obtained by a detailed study of the internal ratio of the elements. In fact, the X-ray intensity ratios $I_{K\alpha}/I_{K\beta}$, or $I_{L\alpha}/I_{L\beta}$ and $I_{L\alpha}/I_{L\gamma}$, for an element in a multilayer sample, depend on the composition and

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thickness of the layer in which the element is situated, and on the composition and thickness of the superimposed layer (or layers). Multilayered samples are common in archaeometry, for example in the case of pigment layers in paintings or of gilded alloys.

In the present paper, experimental results of an ED-XRF analysis carried out on the panel "*Annunciation with Saints Catherine of Alexandria, Anthony Abbot, Proculus and Francis*" (Fig. 1) by the Florentine painter Lorenzo Monaco (born Piero di Giovanni, c. 1370-1425) are reported.

Lorenzo Monaco (Tartuferi and Parenti, 2006) was an artist whose work bridged the 14th and 15th centuries, between the Trecento art of Duccio and Giotto and the Quattrocento painting of Masaccio and Fra Angelico. His art is considered a synthesis of the Sienese and Florentine Trecento styles and was also one of the most important examples of international Gothic in Italy. In 1391, Lorenzo Monaco took his vows as a monk of the Camaldolese monastery of *Santa Maria degli Angeli*. He rose to the rank of deacon, but in 1402 he was enrolled in the painters' guild with the name of Piero di Giovanni (Lorenzo Monaco means 'Lorenzo the Monk') and was living outside the monastery. The monastery was renowned for its illuminated manuscripts, and several book miniatures, now in the Laurentian Library in Florence, are attributed to him. However, the artist was primarily a painter of altarpieces, examples of which are in the National Gallery in London and at the Uffizi in Florence. His main works in fresco are the scenes of the Life of Mary in the Bartolini Chapel of Sta Trinità, Florence. His style is characterized by a luminous beauty of colouring, and a graceful, rhythmic flow of the line, and is in complete contrast to his great contemporary Masaccio, representing the highest achievement of the last flowering of Gothic art in Florence.

Energy dispersive X-ray fluorescence (ED-XRF) analysis is a common non-destructive method employed in archaeometry for quantitative analysis and for the determination of the thickness of coatings (Nygard *et al.*, 2004; Roldán *et al.*, 2006). ED-XRF analysis generally involves an area of a few mm^2 and a thickness between microns and fractions of mm. Therefore, the analysis is superficial and dependent on surface conditions (Cesareo *et al.*, 2004). In the case of multiple layer samples, it is not possible to rely on the use of standards, and therefore one has to resort to theoretical estimates of the XRF

Figure 1: (See colour plate) *Annunciation with Saints Catherine of Alexandria, Anthony Abbot, Proculus and Francis* (ca. 1410-1415). Panel 210 x 229 cm by Lorenzo Monaco. Galleria dell'Accademia, Florence, Italy. The points on the painting shows the regions analyzed.

Figure 1 : (Voir planche couleur) Annonciation avec Saints Catherine d'Alexandrie, Anthony Abbot, Proculus et Francis *(ca. 1410-1415). Panel de 210 x 229 cm par le peintre Lorenzo Monaco. Galleria dell'Accademia, Florence, Italie. Les points sur le tableau correspondent aux régions analysées.*

intensity. The accuracy of the method can be estimated by using carefully characterized calibration samples.

The aim of the present study is the evaluation of the chemical composition and thickness of gold leafs by using a portable ED-XRF device in order to obtain important information permitting a better understanding of the technology of that epoch.

2. Experimental set-up

The analysis was performed using a portable energy dispersive X-ray fluorescence (ED-XRF) instrument designed and built at the University of Salento (Cesareo *et al.*, 1999). It is composed of an X-ray tube (produced by MOXTEK), with a Pd-anode operating at 15 kV voltage and 3 μA current, a Si-PIN detector, thermoelectrically cooled, with a Be window of 25 μm, a resolution of 190 eV at 5.9 keV and a pocket multi-channel analyzer (both produced by AMPTEK).

3. Results and discussion

ED-XRF spectra of the analyzed paintings show the presence of gold, iron and calcium in the entire painting, while silver, generally present in the composition of gold leafs, was not detected. The presence of iron is due to the use of bolus (iron silicate hydroxide), employed by the artist as a glue to superimpose the gold leafs (Baldinucci, 1681; Cennini, 1971). Calcium is probably used by the artist as priming, as in the case of '*bianco San Giovanni*'. Figure 2 shows the ED-XRF spectra of regions 1, 2 and 3.

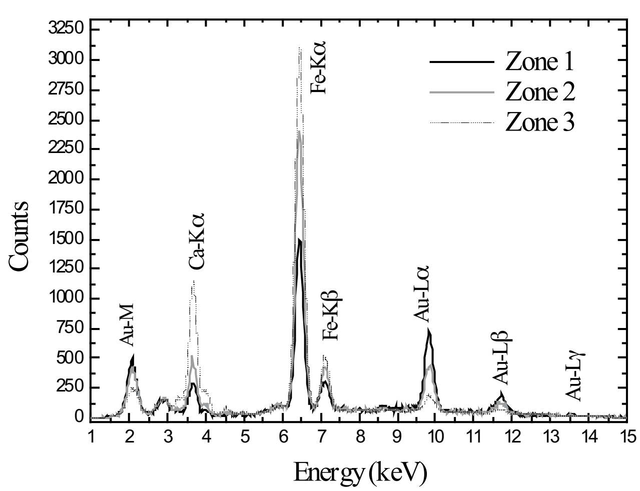

Figure 2: ED-XRF spectra of regions 1, 2 and 3.
Figure 2 : Spectres ED-FX des régions 1, 2 et 3.

A stratigraphic study could be carried out following one hypothesis, where the gold thickness could be approximately evaluated by determining the ratio Fe-Kα/Fe-Kβ, because these lines are differently absorbed by gold. In fact, the Fe-Kα X-rays (with an energy of 6.4 keV) are more absorbed than the Fe-Kβ X-rays (7.0 keV), since the mass attenuation coefficients are $\mu\alpha = 380\ cm^2 \cdot g^{-1}$ and $\mu\beta = 316\ cm^2 \cdot g^{-1}$, respectively.

In Figure 3, the symbol *x* ($g\ cm^{-2}$) indicates the radiation paths of Fe-Kα and Fe-Kβ into gold, and the symbols I_0 and I indicate the intensity of the radiation before and after the layer of gold, respectively.

$$I_\alpha = (I_\alpha)_0 e^{-\mu_\alpha x},\ I_\beta = (I_\beta)_0 e^{-\mu_\beta x} \Rightarrow \frac{I_\alpha}{I_\beta} = \frac{(I_\alpha)_0}{(I_\beta)_0} e^{-(\mu_\alpha - \mu_\beta)x}$$

$$x = \frac{1}{\mu_\alpha - \mu_\beta} \ln \frac{\frac{(I_\alpha)_0}{(I_\beta)_0}}{\frac{I_\alpha}{I_\beta}} \qquad \text{(eq.1)}$$

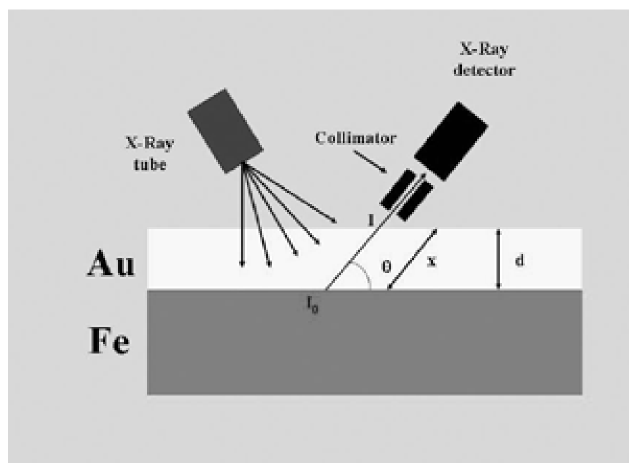

Figure 3: Simulation for determining the thickness of the coating of gold on iron.
Figure 3 : Simulation pour l'évaluation de l'épaisseur de la couche d'or sur le fer.

In region 3 (Fig. 2), there is a single leaf (of thickness x), while in the near region 2 there are two leafs (of thickness 2x). Therefore, by using equation 1 on these areas, the ratio $(I_\alpha/I_\beta)_0$ was calculated for iron. This value is equal to 7.42 and it has been used for the determination of the gold thickness in different regions of the painting; the values obtained are reported in Table 1. The gilding technique employing gold leafs uses the superposition of several layers of gold leafs, particularly in areas where covering with one

Region	Total thickness (µm)	No. of layers	Thickness (mm)
1	3.5	4	0.9
4	3.1	3	1.0
5	2.3	2	1.2
6	1.6	2	0.8
7	2.0	2	1.0
8	1.1	1	1.1
9	0.9	1	0.9
10	2.8	3	0.9
11	1.1	1	1.1

Table 1: Determination of gold thickness.
Tableau 1 : Détermination de l'épaisseur des feuilles d'or.

single layer is difficult to carry out. The gold leafs were glued on the substrate with bolus, a compound containing iron (Cennini, 1971).

Experimental data obtained by ED-XRF measurements on a single layer showed that the thickness of the gold leafs used by the artist is between 0.9 and 1.1 µm. Measurements carried out on apparently thicker areas led us to hypothesize that these areas are made by superimposing several layers of equal thickness. The thicknesses analyzed show the remarkable technological capacity of the artists of the time (*batiloro*). As shown above, it was possible to obtain gold leaf thicknesses of about one micrometer from a gold coin. Assuming that the *batiloro* used an Italian florin coin (3.54 g), from one such coin it was possible to obtain gold leafs with an area between 1500 and 2000 cm^2.

4. Conclusion

Experimental results show the presence of gold, iron and calcium all over the surface of the painting. The presence of iron may be due to the use of a layer that contained a pigment of iron under the gold leaf, while calcium was probably used by the artist as priming. Moreover, the reported data show that the thickness of a surface gold leaf may be determined by a differential absorption of deeper elements.

Thus, energy dispersive X-ray fluorescence appears as a powerful, fast, inexpensive, non-destructive and portable method of analysis that can be used successfully in archaeometry in order to determine the chemical composition and the thickness of gold leafs on paintings or other objects of historical and artistic interest.

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