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HISTORICAL, MICROANALYTICAL EVIDENCES AND LIMITS OF NON-INVASIVE TECHNOLOGIES IN STUDYING GILDINGS ON 16TH C WALL PAINTINGS

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ABSTRACT

The application of a multi-analytical approach has been adopted for the study of the 16th and 17th century wall paintings decorating the church of St. Alessandro in Lasnigo (Como, Northern Italy). Particular attention has been devoted to the wall painting representing the Crucifixion scene, work of the Master Andrea De Passeri (1514), using portable instruments as XRF, VIS-NIR, Raman spectrometry and IR Reflectography.

Besides the analysis of the pigments' palette used, XRF on the black crusts of the halos detected Au, Sn and Pb; the hypothesis, integrated by VIS-NIR Spectroscopy was that Au foil had been applied on a yellow background (Sn and Pb yellow).

Historical evidences, supported by scientific analysis, showed that was common the application of a tin foil as preparation for the gilded halos on 14th-16th century wall paintings.

Microanalysis on cross sections confirmed the historical background: a 10 µm tin foil was applied on an oil-based missione with the addition of Pb-based pigments as support to the gold foil.

This complementary examination was really crucial because of literature also reports the use of Sn-Pb yellow as preparation layer for the gilding. Furthermore microanalysis shows that traces of Sn-Pb yellow pigments have been added to the oil-based missione.

The concluding remark is that non-invasive analysis should be sometimes integrated at least by historical researches; microanalysis should be carried out when doubts arise on the original technique used.

INTRODUCTION

The recent conservation programme developed in the frame of an Italian-Swiss project called *Past and future of the St. Alessandro Church in Lasnigo (Italy)* has been developed after a detailed analytical campaign using both non-destructive and micro-analytical procedures [1, 2, 3, 4, 5]. The interest on the wall painting representing the *Crucifixion* scene, masterpiece of the painter *Andrea De Passeri* (1514), was due to the elegance of the drawing, to the lights and shadows effects, to the limited palette used and to dark crusts surrounding the halos (Angels, Jesus Christ, the Virgin Mary on the throne, St. Alessandro, the crying Virgin Mary). This wall painting was restored during the seventy years but no information was yet available.

ANALYTICAL AND HISTORICAL BACKGROUND

The materials and pigments used on *Crucifixion* scene have been characterized on the basis of the composition in terms of heavy and medium *Z* chemical elements using a portable XRF and of the spectral visible-NIR reflectance curves using a spectrophotometer working in the range 360-1050 nm [1].

According to the data obtained by means of portable XRF, Au, Pb and Sn have been detected as main elements. The conclusion, supported by VIS-NIR spectroscopy, was that Sn and Pb have been correlated to the Pb-Sn yellow (*giallolino*) used as a preparation layer for the gilding in order to enhance the brightness of the gold foil.

The use of gold, silver and tin foils for decorating wall paintings knows and lives splendour times during the 14th century and the early half of the 15th century, remaining limited up to the 16th century [8].

Old treatises as Eraclio (10th-11th C), St. Audemar (13th C), Jehan Le Begue (15th C), Cennino Cennini (15th C), the *Manoscritto Bolognese* (15th C) mention the gilding techniques and the use of *stagno dorato* (tin gilt). The treatises generally report the introduction of the tin foil coated by coloured varnishes or as support layer for the gold foil; the former is a gilt foil and the latter the composed foil (tin and gold).

The use of the composed foil is more convenient for several reasons: the thickness of the tin foil (generally 15-20 μm) allowed an easier handling then the gold foil (2-4 μm). The resulting composed material was cut in the required shape and than applied on the wall using an adhesive (*missione*). This technical approach allowed the procedures of the final working processes as the burnishing (*brunitura*) and the engraving (*bulinatura*) [6].

Regarding the state of conservation, the tin foil generally reveals altered due to the metal transition from the modification β-Sn to α-Sn or to the oxidation process [6]: the consequence is the colour changing determining the tin darkening (fig. 1). The gold exhibits no altered but the thin foil is fissured and detached from the surface: the consequence is the loss of the gold, remaining in this way limited to traces (fig. 2).

Fig. 1. The tin darkening of the halo (the crying Virgin Mary).

Fig. 2. Particular of the gold traces on the halo.

EXPERIMENTAL

Material and Methods

The samples have been collected from the halos (fig. 2) and preliminary Infra-Red spectroscopy (FTIR) has been carried out for understanding the nature of the adhesive between the metal foils and the plaster. A Perkin Elmer Spectrum One BM has been used; the measurements have been taken over the range 4000-600 cm^{-1}.

Optical microscopy (OM) on cross section has been employed for studying the stratigraphic succession.

Microanalysis on cross section has been carried out for the elemental composition; a VEGA TESCAN electron microscope coupled to a BSE detector has been used.

Analytical Results

The cross-section examination under incident light showed (fig. 3) a first layer corresponding to the lime-based plaster, a second one corresponding to the preparation layer used to bind the metal foils; on this plaster a third layer grey-blue in colour and a discontinuous fourth one, very bright and very thin corresponding to the gold foil.

The FTIR analysis (fig. 4) shows the following groups.

The presence of linseed-oil is marked by C-H absorptions at 2918, 2845, 1736, 1460, and 1402 cm^{-1}, by C-O absorptions at 1243 and 1100 cm^{-1}, by C-C absorption at 723 cm^{-1}.

The presence of Ca-oxalate is shown by the C=O absorption at 1622 cm^{-1} and the C-O at 1620 cm^{-1} (characteristic peak).

Ca-carbonates are shown by the absorptions at 1410, 873 and 713 cm^{-1}. Other carbonates function at 1046 and 681 cm^{-1}, in addition to the O-H absorption at 3533 cm^{-1}, can be referred to lead white, the basic lead carbonate with formula $2PbCO_3 \cdot Pb(OH)_2$.

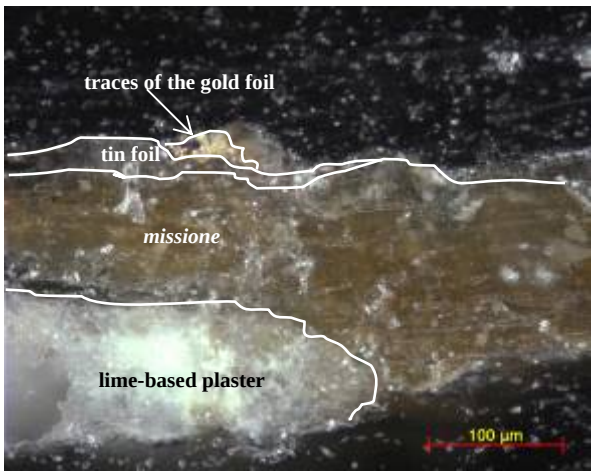

Fig. 3. Stratigraphy of the halo (cross section, incident light) .

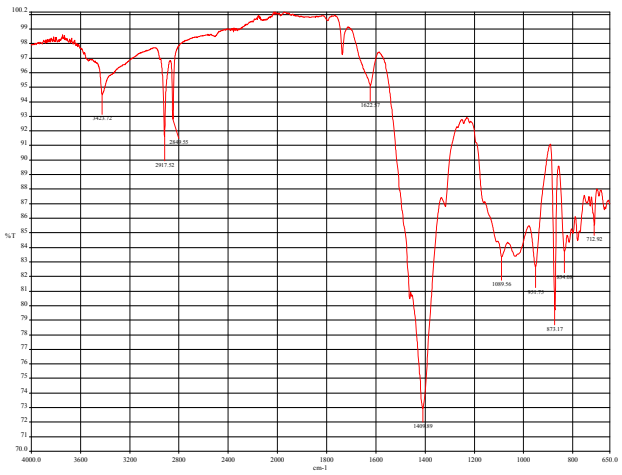

Fig. 4. FTIR on the halo.

The microanalysis on the layers corresponding to the binding media (*missione*) between the plaster and the metal foils is listed in the following table 1. The spots are reported in fig. 5.

Qualitative elemental composition											
	Ca	**P**	**Pb**	**K**	**Na**	**Cl**	**Mg**	**Si**	**Fe**	**Al**	**Sn**
A spot	+ + +	+ +	+	+	+	+	+	+	-	-	-
B spot	+ + +	-	+ + +	+	+	-	+	+	+	+	-
C spot	-	-	+ + +	-	-	-	-	-	-	-	+
D spot	+ +	+ +	+ + +	-	+	-	+	+	+	+	-

Legend: + + + main element; + + secondary element; + minor element..

Table 1. Microanalysis of the second layer (missione).

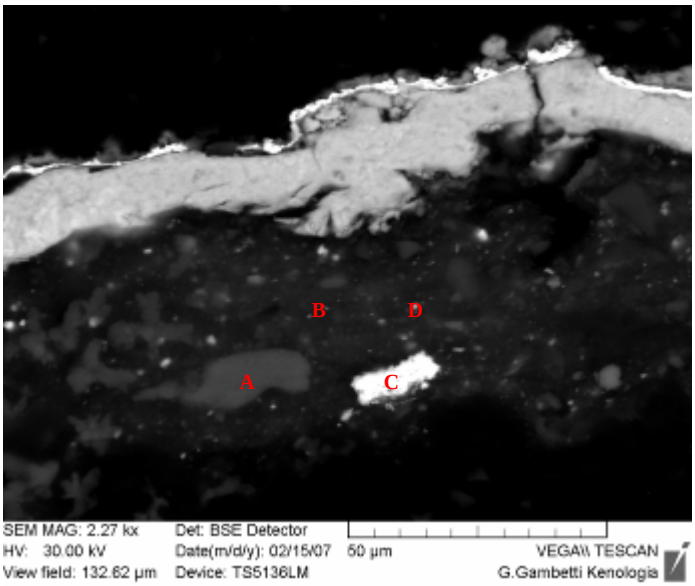

Fig. 5. BSE image with indication of the spots for microanalysis.

The microanalysis of the metal foils (fig. 6) is reported on fig. 7.

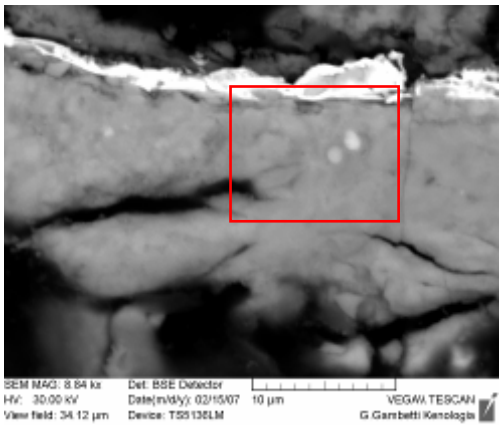

Fig. 6. BSE image of the metal foils.

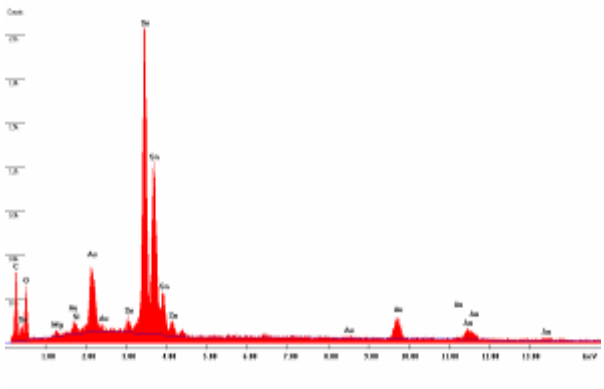

Fig. 7. Microanalysis of the metal foils (square area in fig. 6).

DISCUSSION AND CONCLUSIONS

The optical examination of the samples collected from the halos, integrated by micro-analysis and FTIR, allows to represent the complete stratigraphic succession, the materials and the techniques used.

The first layer, corresponding to the support plaster of the gilding, is a lime based mortar (*intonachino*).

The second layer is composed of an organic binder (linseed oil) with the addition of inorganic pigments. The pigments used are, in order of relative abundance, bone white $Ca_3(PO_4)_2$ (see the A spot) and lead white $2PbCO_3{\cdot}Pb(OH)_2$; (see FTIR analysis and microanalysis on B and D spots), other subordinate pigments are yellow Pb oxides, Fe oxides (yellow ochers) as from microanalysis (spot B and D); traces of lead and tin oxide Pb_2SnO_4 have been detected too (microanalysis, spot C).

The third layer is a Sn foil, the thick is about 10-15 μm; the fourth layer is an Au foil and the thick is about a few microns.

Looking at fig. 5, the contact between the two foils is discontinuous and this creates conditions for the detaching of the fragile gold foil.

The unsolved problem regards the binding material between the two foils. It is possible, as suggested by Matteini and Moles [6], that animal glue has been used for binding Au on Sn foil. The presence of Ca-oxalates resulting from FTIR could be related to the presence of denatured proteins.

The results obtained from micro-analytical studies are in accordance with the historical treatises and in contrast with the data interpretation coming from the non-destructive techniques [7, 8].

The main difference regards the interpretation of the technique used for the gilding of the halos. On the basis of EDXRF and VIS-NIR spectroscopy [1], the gold foil was applied on a yellow preparation layer obtained using Pb_2SnO_4; micro-analysis showed that Sn is correlated to the metal foil and not to a pigment, except for the presence of a few grains of lead-tin oxide.

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