Application of Non-Destructive Techniques

Case Study: The *Madonna Del Latte*

Maria Celeste Leuzzi[1], Mila Crippa[1], Giorgio Andrea Costa[1,2]

Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy, celesteleuzzi@gmail.com
[1] *Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy, crippamila@gmail.com*
[1] *Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy, costa@chimica.unige.it*
[2] *CNR-SPIN, Corso Perrone 24, 16152 Genova, Italy*

Abstract – **In the frame of a research project involving a private collection of artworks a panel painting representing the Nursing Madonna (*Madonna del latte*) was studied by means of scientific examination.**
The Department of Chemistry and Industrial Chemistry (DCCI) of the University of Genoa carried out non-invasive exams using reflectance spectroscopy in the visible range (vis-RS), X-ray fluorescence (XRF) and imaging analyses like infrared reflectography (IRR), false colour infrared, UV fluorescence (UVF) in order to better understand the painting technique, from the underdrawing to the artist's palette.
Some of the most interesting results were a well-defined underdrawing, Cu-based pigments, cinnabar, yellow and brown ochre and a Cr-based pigment.
The scientific analyses combined with historical information allow the hypothesis that the *Madonna del latte* was authored by the artist Baccio della Porta, in the early 16th century at the Tuscan School of St. Marco.

I. INTRODUCTION

The *Madonna del latte* is a tempera on wood representing the *Virgo Lactans*, namely the Virgin nursing the Child, which is a traditional iconography of Cristian Art, widely used until the 16th century (Fig.1).

According to historical documents like the painting bill of sale dated 1971, the *Madonna del latte* would belong to the School of the Florentine Mannerism and especially to San Marco's workshop.

In the early 16th century the workshop of the San Marco Dominican friary was a prestigious artistic centre managed by Baccio della Porta (1472-1517), known as Fra' Bartolomeo, one of the most leading Florentine painters in late-fiftteenth-century [1]. Fra' Bartolomeo, as well as the School of San Marco were under the influence of Girolamo Savonarola, a prior who encouraged people to embrace spiritual values through simple artistic forms. In this historical and cultural context, young and minor artists worked under the guidance and supervision of Fra' Bartolomeo and his co-worker Mariotto Albertinelli creating masterpieces for public and private commissions [1].

In this research historical information was combined with scientific investigation in order to carry out an in-depth study of the *Madonna del latte* for the characterization of the techniques and materials applied. The results of the analyses were compared with those of the literature [2,3] concerning Fra' Bartolomeo's artworks and the School of San Marco to better understand the influence of the artistic and cultural atmosphere on the *Madonna del Latte*.

For this purpose observations under a digital microscope, ultraviolet fluorescence (UVF), infrared reflectography (IRR), infrared false colour (IRFC), reflectance spectroscopy in the visible range (vis-RS) and X-ray fluorescence (XRF) were performed.

The data obtained brought to light evidence that gives an important contribution to the knowledge and study of this painting.

Fig. 1. Madonna del latte.

II. MATERIALS AND METHODS

The research methodology was based on non-invasive scientific examination, namely without sample taking. A preliminary investigation with a digital microscope (DinoLite) in visible light was followed by UV fluorescence, infrared reflectography and false colour infrared in order to provide information about the subsurface layers and the nature of pigments with similar optical behaviour in visible light but different reflection in IR light. UVF and IR images were respectively acquired using a mercury vapour lamp with block Wood's glass (maximum emission at 365 nm) and near-infrared LEDs (maximum emission at 980 nm). Infrared images were recorded with a Nikon Coolpix camera professionally modified to remove the infrared filter and then combined with those in the visible light in order to obtain false colour images. Representative points recorded by the imaging techniques were chosen to carry out vis-RS and XRF analyses, aiming at the investigation of the artist's palette. Reflectance measurements (vis-RS) were acquired in the range 400-700 nm with the Minolta CM-2600D spectrophotometer endowed with the software Spectra Magic Nx. Illuminant D65, d/8 geometry, observer angle 10° and the specular component included (SCI) were the experimental conditions adopted. Elemental analysis (XRF) was performed with a Lithos 3000 portable XRF system by Assing and the Lithos software to process the experimental data. The apparatus consists of a molybdenum tube, a zirconium filter and semiconductor silicon (Li) detector, cooled by Peltier effect. The operating parameters were: 25kV, 0.1 mA and 120 seconds of acquisition time.

III. RESULTS AND DISCUSSION

UV-induced fluorescence revealed discontinuities all over the painting surface (Fig.2) which are associated with the reintegration of paint losses and lifted flakes carried out during previous restoration work.
IRR analysis revealed a well-defined underdrawing consisting of soft and fluent strokes that define the figures, the drapery folds and the shadows. The main contours are so sharp that they seem to have been transferred directly from a cartoon. It is also possible that a general sketch was carried out in the cloak of the Virgin and in the architecture but it was not visible because covered by thick and dark layers. Furthermore, the underdrawing showed some *pentimenti*, for example the Virgin's lips in IR appeared bigger and fleshier than those in the visible light. Comparing the images below in Fig. 2, it was evident that the red paint in visible light turned yellow in the infrared false colour, as a result of the paint composition.
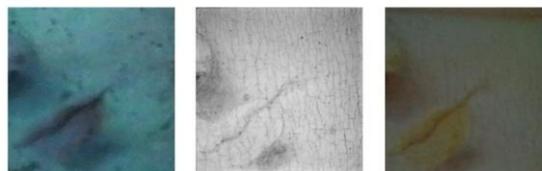

Fig. 2. Set of multispectral images: UVF, IRR, IRFC.

Observation under the handheld microscope provided preliminary information about the pigments used.
Among the pigments examined in depth were those of the Virgin's cloak, which in visible light were dark blue in the outer part and light green in the inner part. Under the digital microscope the dark blue area showed a blue pigment coarsely ground and mixed with a greenish one, whereas the light green area showed a finely ground green pigment (Fig.3).

Fig. 3. Dark blue (left) and light green (right) by microscope DinoLite.

Starting from this observation XRF combined with vis-RS analyses was performed to gain insight into the pigments possibly used.
Table 1 reports XRF results, where elements with higher concentration are highlighted in bold, whereas Fig.4 illustrates the position of the most representative points selected for the analysis.

Fig. 4. Madonna del latte with indication of the XRF reading points.

Table 1. Elements detected by XRF analysis.

Reading	Colour	XRF detected elements
1	Lacuna	**Cu**, Pb, Fe, Ca, Sr
2	Light green	**Cu**, **Pb**
3	Light green	**Cu**, Pb
4	Light green	**Cr**, **Fe**, **Zn**, Ca, Pb, Cu, Ti, Sr
5	Light green	**Cr**, **Fe**, **Zn**, Ca, Pb, Cu, Ti, Sr
6	Light green	**Cu**, Pb
7	Dark blue	**Cu**, Pb, Fe
8	Dark blue	**Cu**, **Pb**
9	Red	**Hg**, **Pb**, Cu
10	Dark red	**Hg**, **Pb**, **Cu**, Mn, Ca, Fe
11	Red	**Hg**, **Pb**
12	Light red	**Hg**, **Pb**
13	Pink	**Pb**, Fe
14	Yellow	**Pb**, Fe
15	Brown	Pb, Hg, Fe
16	Brown	Pb, Hg, Fe

In a small lacuna XRF detected Ca, Sr, Pb and some amounts of Fe, sometimes present as an impurity. This result allowed to identify calcium sulphate (i.e. natural gypsum), which is typically used in the paintings preparation layer [4,5]. The presence of Pb in all the readings indicates that lead white was used probably for the priming and as white mixed with other pigments to obtain different shades of colour. Readings no. 7 and 8 (dark blue) revealed the presence of a Cu-based pigment. This result combined with the vis-RS absorption band around 640 nm and false colour image (blue turns red-violet), suggests the presence of azurite (Fig. 5, curve 8) [5,6].

Azurite is a basic carbonate of copper, $2CuCO_3.Cu(OH)_2$, widely used throughout the Renaissance as one of the most important blue pigments.

Depending on the degree of fineness to which it is ground, azurite gives a wide range of blues: coarsely ground azurite, produces dark blue, whereas fine grinding produce a lighter tone [7].

The greenish-blue and dark blue shade observed in the Virgin's cloak under the digital microscope, may be explained with the presence of green malachite, a basic carbonate of copper, that is usually associated in nature with azurite, or even developed due to azurite degradation in humid conditions.

Readings no. 2, 3 and 6 (light green) combined with vis-RS result (absorption band around 700-720 nm) suggest the presence of copper acetate (verdigris, $Cu(CH_3COO)_2.2Cu(OH)_2$) usually mixed with yellows or lead white and painted in many overlying layers due to its little covering power (Fig. 5, curves 2 and 6) [5]. This pigment, is one of the most widely used greens by the majority of the 16th century Italian painters, including Fra' Bartolomeo [3,8].

Readings no. 4 and 5 (light green-retouch) indicated the presence of a green Cr-based pigment, like chrome green ($Fe_4[Fe(CN)_6]_3+PbCrO_4$) or chromium oxides (Cr_2O_3), probably mixed with zinc and/or titanium white. These pigments have been used since the 19th century and they are usually found in ancient paintings when restoration has been carried out. This is confirmed by the UV fluorescence images, in which the presence of dark areas that do not fluoresce under UV revealed some retouches. The reflectance spectra recorded in these areas (reflectance peak around 540 nm and absorption band around 630 nm) (Fig. 5, curves 4 and 5), as well as the IRFC image (green in visible light turns red) suggested the use of chrome green [9]. It is interesting to observe that infrared false colour was successfully applied to identify the pigment used in the restoration.

Readings no. 9, 11 and 12 (red) indicated the presence of Hg.

This result combined with vis-RS (shoulder around 600-610 nm) [10] (Fig. 6, curves 9, 11, 12) and IRFC revealed the use of cinnabar (HgS) for the Virgin's dress and for details like lips (Fig. 2) [6].

In reading no. 10 (dark red) along with Hg, a high amount of Cu was detected probably due to the use of azurite to underline the drapery folds and to create shadows. The use of combine reds with azurite, Fe-based pigments or red lakes is reported in literature as a feature of several Florentine paintings, like those of Raffaello, Perugino and Fra' Bartolomeo [2,3]. Although the presence of Mn, Ca and Fe detected in reading no. 10 suggested the use of these compounds, it was not possible to identify univocally their presence. The last analyses, reading no. 13 (pink) and readings no. 14, 15 and 16 (yellow and brown) indicated the use of both yellow and brown ochre, mixed with lead white and sometimes with cinnabar to create different shades of colour.
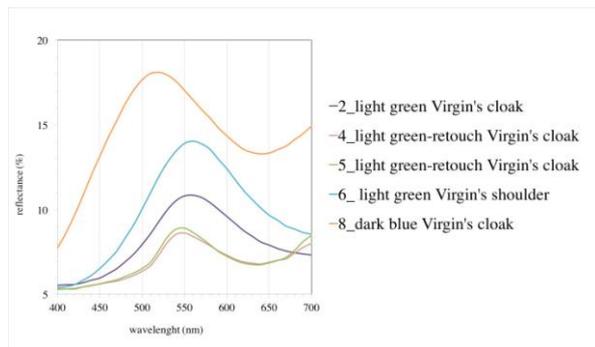
Fig. 5. VIS-RS spectra of dark blue and light green pigments. Identified pigments: 8- azurite; 2,6 – verdigris; 4,5 – chrome green.
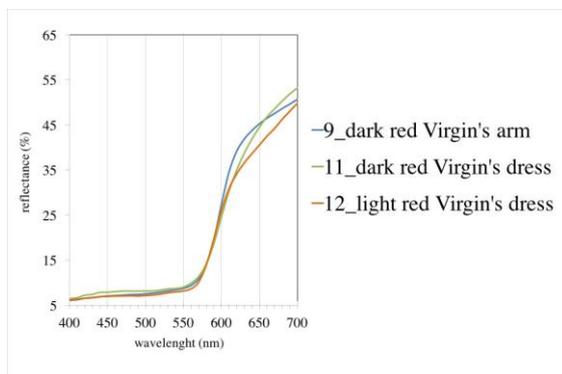

Fig. 6. VIS-RS spectra for reds. Identified pigment: 9,11,12 – cinnabar.

IV. CONCLUSION

The multi-analytical approach while studying the *Madonna del latte* was crucial in gain insight into the painting technique and assessing the condition of the painting. Even though several of retouches and repairs were observed on the paint layers by UVF and IRR, it was possible to identify the artist's palette, composed of: lead white, azurite, verdigris, cinnabar, red and brown ochre. These pigments have been historically used by Italian painters for centuries and according to the literature [2,3] they were employed by Fra' Bartolomeo in several masterpieces. The results concerning the composition of the surface and the features of the underdrawing may confirm the belonging of the *Madonna del latte* to a Florentine workshop and possibly as work of a minor artist, as reported by historical documents. Further investigations may be planned on the basis of the non-invasive results to understand the painting stratigraphy as well as the nature of the binders. This information combined with a wider historical and artistic research about the Florentine painters of the first Mannerism will allow the more specific definition of the author of the *Madonna del latte.*

REFERENCES

[1] AA.VV., "Rinascimento. Fra' Bartolomeo: sacra famiglia a modello", 1st edition, Sagep editori, Genova, Italy, 2014.

[2] P.Moioli, C.Seccaroni, F.Persia, "Applicazione di tecniche non distuttive: l'Adorazione del Bambino di Fra' Bartolomeo," ENEA-INN-ART RT-3/007.

[3] P.Moioli, C.Seccaroni, Analisi di fluorescenza X su sei dipinti di Fra' Bartolomeo in "L'età di Savonarola. Fra' Bartolomeo e la Scuola di San Marco", Venezia, Italy, 1996, pp. 314-316.

[4] E.Franceschi, F.Locardi, "Strontium, a new marker of the origin of gypsum in cultural heritage?", JCH, No. 15, 2014, pp. 522-527.

[5] M.L.Amadori, P.Baraldi, S.Barcella, g. Poldi, "New studies on Lorenzo Lotto's pigments: non-invasive and micro-invasive analyses", Proc. Of 7th national congress of Archeometry, 2012, vol.1, pp. 1-23.

[6] A.Cosentino, "Identification of pigments by multispectral imaging; a flowchart method", Heritage Science, vol.2, No.8, March 2014, pp. 1-12.

[7] Cennino Cennini, "Il libro dell'arte", 5th edition, Neri Pozza, Vicenza, 2009

[8] P.Moioli, C.Seccaroni, "Pigmenti a base di rame: fonti storiche e analisi scientifiche, OPD Restauro, vol.7, 1995, pp. 216-252.

[9] https://oceanoptics.com/fiber-optic-reflectance-spectroscopy-pigment-identification/

[10] G.Poldi, " La scienza del colore del giovane Lotto: pigmenti e analisi non invasive", https://www.academia.edu/5402806/G._Poldi_La_scienza_del_colore_del_giovane_Lotto_pigmenti_e_analisi_non_invasive.