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Application of Non-Destructive Techniques. The *Madonna Del Latte* Case Study

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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, combining imaging techniques with analytical analyses.
UV fluorescence (UVF), infrared reflectography (IRR), infrared false colour (IRFC), X-ray fluorescence (XRF) and reflectance spectroscopy in the visible range (vis-RS) were used to analyse the painting palette thus obtaining more information on a possible creation date of the painting.
Some of the most interesting results are the identification of a freehand underdrawing and the usage of lead white, cinnabar, iron-based pigments for yellows and browns and copper-based pigments for blue and green colours.
The scientific results, as well as historical information allowed the hypothesis that the *Madonna del latte* was authored in the early 16th century by a Florentine artist, likely a scholar of Baccio della Porta.

Section: RESEARCH PAPER

Keywords: Madonna del Latte; Baccio della Porta and the School of San Marco; Artist’s palette; Imaging techniques; X-ray fluorescence

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1. INTRODUCTION

The Madonna del latte is a tempera on wood representing the Virgo Lactans, namely the Virgin nursing the Child, a traditional iconography of Christian Art, widely used until the mid-16th century when progressively disappeared because the Virgin’s bare breast was considered indecorous by the Council of Trent [1] (Figure 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According to historical documents like the painting bill of sale dated 1971, the Madonna del latte would belong to the School of the Florentine Mannerism and especially to the San Marco School, an artistic workshop within the Dominican convent of San Marco, Florence.

In the early 16th century, this workshop was a prestigious artistic centre headed by the artist and friar Baccio della Porta (1472-1517), also known as Fra’ Bartolomeo, one of the leading Florentine painters in late fifteenth century [2].

Fra’ Bartolomeo, as well as the School of San Marco were under the influence of Girolamo Savonarola, a former prior at the convent of San Marco. Savonarola preached against the hypocrisy and luxury of nobles and popes, encouraging the production of simple artistic forms in order to spread renovated spiritual, political and aesthetic values [3].

In this 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 clients [4].

Extensive researches concerning the production of Fra’ Bartolomeo and the School of San Marco were carried out in the last decades on the occasion of restoration campaigns and exhibitions, allowing more technical assessment of the artists’ paintings [5, 6, 7].

More than thirty works of art were studied combining connoisseurship, technical examination and non-invasive analysis, thus providing new attributions, as well as giving an insight into the workshop’s painting technique.

Figure 1. *Madonna del Latte.*

Starting from art historical and technical information, provided by the painting bill of sale and the literature cited above, a scientific investigation was performed on the *Madonna del Latte*, aiming at studying the painting's materials and technique applied by the author [8].

For this purpose, the painting was examined by using ultraviolet fluorescence (UVF), infrared reflectography (IRR), infrared false colour (IRFC), a digital microscope (DinoLite), X-ray fluorescence (XRF) and reflectance spectroscopy in the visible range (vis-RS).

This paper presents the analyses results on the *Madonna del Latte*, which confirm materials and technique consistent with early-sixteenth century paintings. This finding would give a significant contribution to further art historical studies on who within the San Marco workshop might have contributed to the execution of this painting.

2. MATERIALS AND METHODS

The research methodology was based on non-invasive scientific examination.

A preliminary investigation with ultraviolet light was followed by infrared reflectography (IRR) and infrared false colour (IRFC) in order to provide information about the subsurface layers, such as areas of retouching, the underdrawing and the nature of certain pigments with similar optical behaviour in visible light but different reflection in infrared light.

Furthermore, an examination through a digital microscope (DinoLite, usually around 50 x magnification) showed the sequence of paint and ground layers, as well as coarsely ground pigments and pigments mixtures.

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 XRF and vis-RS analysis, aiming at the investigation of the artist's palette.

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.

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.

3. RESULTS AND DISCUSSION

The painting was firstly investigated under ultraviolet light, revealing several discontinuities throughout the painting surface which show up as dark patches, as visible in Figure 2a representing the Virgin's lips. These black areas correspond to retouching and reintegration of paint losses carried out during previous restoration works.

The infrared reflectography revealed an extensive underdrawing (i.e. the artist's preliminary sketch made before the paint layers are applied), done freehand and visible to the naked eye in localised areas where the paint has become more transparent over time. The underdrawing consists of soft and fluent strokes that define the figures, the drapery folds, the shadows and presumably the Virgin's cloak and the architecture, where thick and dark paint layers make the underdrawing not visible in these areas.

Some reworkings have been observed in the sketch of the baby's hands revealing the author's attempts at depicting this detail. The infrared reflectograms exposed other pentimenti (i.e. changes between the initial design and the final painting) in the Virgin's lips which under IR-light appear bigger and fleshier than the depicted one (Figure 2b). This change in the composition can also be observed in the infrared false colour image (Figure 2c), where the Virgin's lower lip is thinner in the final painting than in the underdrawing, that consequently, it remains visible as a curved line on the ground. A close

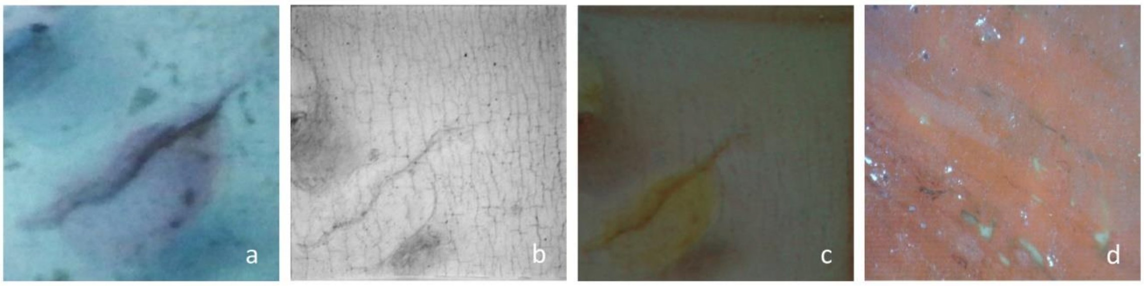

Figure 2. Set of multispectral images of the Virgin's lips: a) UVF, b) IRR, c) IRFC, d) Photomicrograph of the lower lip.

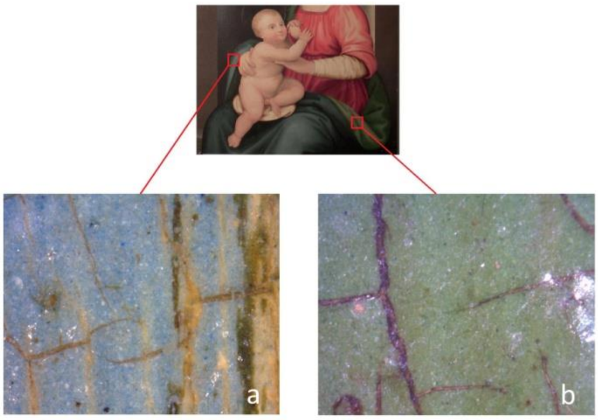

Figure 3. Photomicrographs of the Virgin's cloak: a) Blue pigment from the outer cloak, b) Light green pigment from the inner cloak.

observation of this area with a digital microscope allowed to identify a finely ground red pigment, likely mixed with a white one to obtain pinkish shades, applied over a yellowish ground layer (Figure 2d).

Microscopic examination of the painting surface provided preliminary information about the nature of the pigments used by the artist. Among the pigments examined in depth were those of the Virgin's cloak, which in visible light are dark blue in the outer part and light green in the inner part.

Under the digital microscope, the dark blue area exhibited a blue pigment coarsely ground and mixed with a greenish one (Figure 3a), whereas the light green area showed a finely ground green pigment (Figure 3b).

Starting from this evidence, XRF and vis-RS analysis were performed to gain insight into the painting's palette.

Figure 4 illustrates the position of the most representative points selected for XRF analysis and Table 1 reports the detected elements, where those with higher concentration are highlighted in bold.

In a small lacuna calcium (Ca) and strontium (Sr) were detected. This result allowed identifying the presence of a Ca-based ground, more likely natural gypsum [9], which is typically found in the Italian paintings' ground layer [10].

The presence of lead (Pb) in all the measurements indicates

Figure 4. *Madonna del latte* with indication of the XRF measurement points.

that lead white ($2PbCO_3 \cdot Pb(OH_2)$) was probably used in a lower lying layer such as the imprimitura, and in paint layers to change the tonality of other colours and also to improve the drying properties of the paint.

In light green areas (points no. 2, 3 and 6) mainly copper (Cu) was found. A straightforward identification of the pigment used was not possible, as XRF analysis is an elemental technique that does not permit to make the distinction between copper-based compounds. Thus, additional investigation was required.

Vis-RS absorption band around 700 nm suggests the presence of copper acetate ($Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$), verdigris) usually mixed with yellows or lead white, and painted in many overlying layers due to its little covering power (Figure 5, curves 2 and 6) [11, 12]. This pigment is one of the most widely used greens by the majority of the 16th century Italian painters, including Fra' Bartolomeo [7, 13].

Points no. 4 and 5 (light green areas) revealed the presence of a chromium (Cr) based pigment, such as chrome green

Table 1. Pigments identified on the *Madonna del Latte* at each analysis site.

Point	Colour	Description	XRF detected elements	XRF pigments identification
1	White	Lacuna	Ca, Sr, Pb	Ca-based pigment (chalk or gypsum), lead white
2	Light green	Virgin's inner cloak	**Cu**, **Pb**	Cu-based pigment, lead white
3	Light green	Virgin's inner cloak	**Cu**, Pb	Cu-based pigment, lead white
4	Light green	Retouching	**Cr**, **Fe**, **Zn**, Ca, Pb, Cu, Ti, Sr	Cr-based pigment, zinc white, Ca-based pigment
5	Light green	Retouching	**Cr**, **Fe**, **Zn**, Ca, Pb, Cu, Ti, Sr	Cr-based pigment, zinc white, Ca-based pigment
6	Light green	Virgin's shoulder	**Cu**, Pb	Cu-based pigment, lead white
7	Dark blue	Virgin's cloak	**Cu**, Pb, Fe	Cu-based pigment, lead white
8	Dark blue	Virgin's cloak	**Cu**, **Pb**	Cu-based pigment, lead white
9	Red	Virgin's sleeve	**Hg**, **Pb**, Cu	Cinnabar, lead white, Cu-based pigment
10	Dark red	Virgin's dress	**Hg**, **Pb**, Cu	Cinnabar, lead white, Cu-based pigment
11	Red	Collar	**Hg**, **Pb**	Cinnabar, lead white
12	Red	Virgin's dress	**Hg**, **Pb**	Cinnabar, lead white
13	Pink	Cheek	**Pb**, Fe	Lead white, red ochre
14	Yellow	Hair	Pb, Fe	Lead white, yellow ochre
15	Brown	Architecture	Pb, Hg, Fe	Lead white, brown ochre, cinnabar
16	Brown	Architecture	Pb, Hg, Fe	Lead white, brown ochre, cinnabar

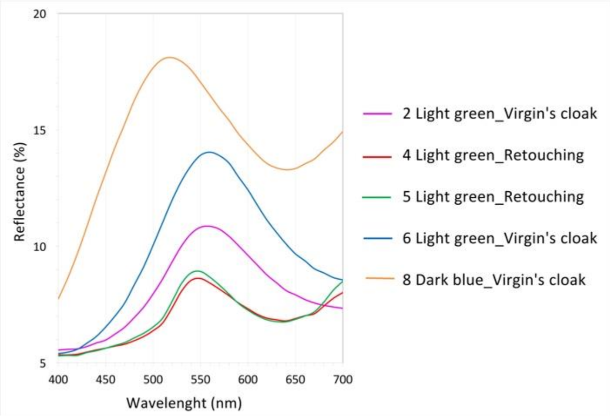

Figure 5. VIS-RS spectra of dark blue and light green pigments. Identified pigments: 8- azurite; 2, 6 – verdigris; 4, 5 – chrome green.

($Fe_4[Fe(CN)_6]_3$+$PbCrO_4$) or chromium oxide (Cr_2O_3) mixed with zinc white (ZnO). All these pigments have been produced in the 19th century and are usually found in ancient paintings as restoration materials [14, 15].

This is confirmed by the UVF images, in which the presence of dark areas that do not fluoresce are characteristic of retouching. The reflectance spectra recorded in these two areas (reflectance peak around 540 nm and absorption band around 630 nm) (Figure 5, curves 4 and 5), as well as the IRFC image (light green in visible light turns red in false colour), suggested the use of chrome green [16].

In dark blue areas (points no. 7 and 8) a copper-based pigment was used. Vis-RS absorption band around 640 nm and infrared false colour (blue in visible light turns red-violet in false colour), allowed to identify the presence of azurite (Figure 5, curve 8) [11, 16].

Azurite is a basic carbonate of copper, $2CuCO_3{\cdot}Cu(OH)_2$, widely used throughout the Renaissance as one of the most important blue pigments [17]. As reported in literature, azurite is widely used along with ultramarine by Fra' Bartolomeo 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 produces a lighter tone [18].

The greenish-blue and dark blue shade observed in the Virgin's cloak under magnification, 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.

In In red areas (points no. 9, 11 and 12) a high amount of mercury (Hg) suggested the presence of cinnabar (HgS).

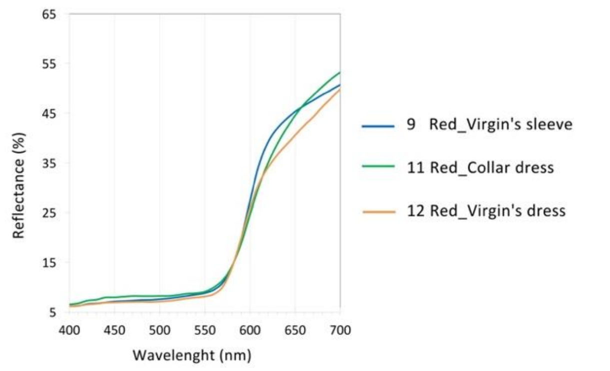

Figure 6. VIS-RS spectra of red colours. Identified pigment: 9, 11, and 12 – cinnabar.

This result was confirmed by vis-RS analysis which shows a shoulder around 600-610 nm, typical of cinnabar (Figure 6, curves 9, 11, 12) [19]. An additional proof of the use of this pigment in red areas was provided by infrared false colour, which exhibits a characteristic yellowish shade, as visible in the Virgin's lips (Figure 2d).

In point no. 10 (dark red) along with mercury, a high amount of copper 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, iron-based pigments or red lakes is reported in literature as a feature of several Florentine paintings, like those of Raffaello, Perugino and Fra' Bartolomeo [12, 13]. Although the presence of manganese (Mn), calcium and iron detected in point no. 10 suggested the use of these compounds, it was not possible to identify univocally their presence.

The last analyses, points no. 13, 14, 15 and 16 indicated the presence of Fe-based pigments. In these areas, both red, yellow and brown ochre, were likely mixed with lead white and cinnabar to depict the flesh tone, the Virgin's hair and the surrounding architecture.

4. CONCLUSIONS

The multi-analytical approach while studying the *Madonna del latte* allowed to assess its condition and gain insight into the painting materials and technique.

Even though several of retouches and repairs were observed throughout the surface by UVF and IRR, the application of non-destructive techniques, such as XFR and vis-RS, gave a crucial contribution to the identification of the painting's palette. It comprises lead white, azurite, verdigris, cinnabar, red and brown ochre. These traditional pigments have been historically used by Italian painters for centuries and were found in several masterpieces of Fra' Bartolomeo and paintings of his scholars at the San Marco School.

The results concerning the features of the underdrawing, especially its freedom and the evidence of changes made between the first sketch and the finished painting, suggests that the *Madonna del Latte* is an original work and not a copy of an existing model.

This finding may confirm the belonging of the *Madonna del latte* to a Florentine workshop of the early 16th century and possibly as work of a minor artist, as reported by historical documents. The evidence provided by scientific examination together with a more comprehensive historical and artistic research about the Florentine painters of the first Mannerism would allow the more specific definition of the author of the *Madonna del latte.*

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