Looking for common fingerprints in Leonardo's pupils through non-destructive pigment characterization

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Abstract

Non-invasive, portable analytical techniques are becoming increasingly widespread for the study and conservation in the field of cultural heritage, proving that a good data handling, supported by a deep knowledge of the techniques themselves, and the right synergy can give surprisingly substantial results when using portable but reliable instrumentation. In this work, pigment characterization was carried out on twenty-one Leonardesque paintings applying *in situ* XRF and FORS analyses. In-depth data evaluation allowed to get information on the colour palette and the painting technique of the different authors and workshops. Particular attention was paid to green pigments (for which a deeper study of possible pigments and alterations was performed with FORS analyses), flesh tones (for which a comparison with available data from cross sections was made) and ground preparation.

Keywords

pXRF, FORS, pigments, Leonardo's workshop, Italian Renaissance

INTRODUCTION

"Tristo è quel discepolo che non ava[n]za il suo maestro" - Poor is the pupil who does not surpass his master - Leonardo da Vinci, Libro di Pittura, about 1493[1].

The influence of Leonardo on his peers during his activity in Milan (1482-1499 and 1506/8-1512/3) has been deep and a multitude of painters is grouped under the name of *leonardeschi*, but it is necessary to distinguish between his direct pupils and those who adopted his manner, fascinated by his works even outside his circle. When he first arrived in Milan, the artistic environment was far from his sensitivity and, surely, his pupils had a role for his connection with local artists[2, 3]. In Leonardo's workshop, several young apprentices were present, including Marco d'Oggiono and Giovanni Antonio Boltraffio: when the master left Milan in 1499, the former was a sort of executor of Leonardesque copies, while the latter painted masterpieces of undeniable higher level. Other painters working in Milan in these periods were deeply influenced by the master, although they did not work directly with him. Among them, Andrea Solario, who looked indifferent to Leonardo models until Da Vinci returned to Milan. Closer to Leonardo style is surely the Milanese painter Giampietrino, born Giovan Pietro Rizzoli, who probably had been in touch with the master during his first period in Milan; he contributed to the distribution of the style of da Vinci, copying his masterpieces as well as painting original compositions, often in multiple versions[2]. It is then evident that it was primarily through the work of his pupils and followers that Leonardo's innovative style was disseminated[4]. Leonardo himself, in the *Libro di Pittura*, posthumous collection of cognitive principles and technical precepts, encoded the copy from "the good master" as an essential advice for young artists: "*Ritrai prima i disegni del bono maestro […] poi di rilievo in compagnia del disegno [tratto] da esso rilievo, poi di bono naturale" - The artist ought first to exercise his hand by copying drawings from the hand of a good master […] he should next practice drawing objects in relief of a good style, then from nature* – [1].

Bernardino Luini deserves a separate mention: although there is no sure evidence of a direct contact between Luini himself and Leonardo, Bernardino was deeply affected by Leonardo and adopted the use of *chiaroscuro* and the facial types too. After Da Vinci's death Bernardino Luini embodied Leanardo's manner and played a key role in the great diffusion of *Leonardismo* (Leonardo's style) through his own workshop, mostly after taking possession of some of the master's cartoons[5].

In spite of the undeniable prominent role of Leonardo and his circle in art history, the study of their painting technique through physical and chemical analyses is relatively poor[6-10], even if some systematic studies on the workshop are present[11-13].

In this work, we present the outcome of ten years analyses on easel painting, covering several Leonardo's pupils and followers, trying to identify common features beyond the sole stylistic resemblance, starting from the identification of pigments and pigment mixtures. The integration of different techniques and the possibility of analysing several case studies can give a clarification of the actual artistic situation: for these reason, comparison with published results from the quoted papers and available archive data are integral part of this research work.

In general, the employ of in situ non-destructive analytical methods is a critical matter studying Cultural Heritage. Various non-invasive techniques have been used in recent years, each with its main features and limitations, such as Raman spectroscopy (micro-Raman)[14], micro-X-ray fluorescence (micro-XRF)[15], infrared[16] or visible reflectance spectroscopy[17].

The Renaissance colour palette includes many mineral pigments with known chemical composition: usually, paintings are made of pigment dispersion in a binding media, applied in various layers on with final coating of varnish. The total thickness of the pictorial layer ranges from a few micrometers up to 1 mm and more. For this reason, some difficulties may affect the identification of pigments using only one of the possible techniques, mostly in multiple layer systems, where it can be hardly possible to distinguish information coming from different layers without any sampling. A parallel use of several non-invasive in situ techniques can sometimes help to improve the data interpretation[18-20]. Energy dispersive X-ray fluorescence (EDXRF), in particular, is a widely used tool for examination of paintings, thanks to a number of portable and handheld EDXRF commercial spectrometers, and its total non-destructive character[21-23]. On the other hand, using only EDXRF does not allow to distinguish the information coming from the different layers, even if the introduction of scanning XRF spectrometers recently improved the application of this powerful technique[24, 25].

The combined use of FORS analysis (fibre optics reflectance spectroscopy) is surely useful to overcame the limit: the identification of pigments in the most external layer by reflectance spectra allows us to infer the composition of the underlying layers[18]. Recent research has studied in detail the interaction between light and matter using the radiative transfer equation and the exact solving of the auxiliary function method[10]. The use of the reflectance values recorded over 13 bands by multispectral band pass camera opens new perspective to this analytical method[10].

EXPERIMENTAL

The paintings

Twenty-one easel paintings are considered in the present paper as summarized in table 1; sixteen of them are by Leonardesque painters. Four artworks are from the series of five panels including the Saint Sebastian, formerly entirely attributed to Bernardino Luini, but recently ascribed to the Master of York (Saint Bishop and Saint Mauritius) and to Bernardino Ferrari (Saint Marta and Saint Peter)[5]; these panels have been considered as comparison. The last painting considered is by Aurelio Luini, son and artistic heir of Bernardino Luini; it is a large panel from Milan Cathedral dating 1592.

Author	Year	Title	Museum	XRF	FORS
Boltraffio	About 1500	Portrait of Gerolamo Casio	Pinacoteca di Brera, Milan (Italy)	✓	
Boltraffio	About 1485-1490	Virgin and Child	Poldi Pezzoli Museum, Milan (Italy)	✓	
Marco d'Oggiono	About 1477	Saint Rocco	Accademia Carrara, Bergamo (Italy)	✓	
Marco d'Oggiono	About 1510	The Virgin of the rocks	Castello sforzesco Museum (Milan)	✓	✓
Giampietrino	About 1515-1530	The Magdalene	Accademia Carrara, Bergamo (Italy)	✓	✓
Giampietrino	About 1514-1517	Christ	Bagatti Valsecchi Museum, Milan (Italy)	✓	✓
Giampietrino	About 1535-1540	Virgin and saints	Bagatti Valsecchi Museum, Milan (Italy)	✓	✓
Bernardino Luini	1520	The Calvary ascension	Poldi Pezzoli Museum, Milan (Italy)	✓	✓
Bernardino Luini	1520	Our Lady of Sorrows	Poldi Pezzoli Museum, Milan (Italy)	✓	✓
Bernardino Luini	1510	Saint Antony from Padua	Poldi Pezzoli Museum, Milan (Italy)	✓	✓
Bernardino Luini	1520	Virgin and child	Borromeo Collection, Isola Bella (Italy)	✓	✓
Bernardino Luini	1510	Saint Sebastian	Borromeo Collection, Isola Bella (Italy)	✓	✓
Bernardino Luini	1517	Virgin and child	Crespi Collection, Milan (Italy)	✓	✓
Bernardino Luini workshop	1520-1525	The adoration	Borromeo Collection, Isola Bella (Italy)	✓	✓
Andrea Solario	1515	Escape from Egypt	Poldi Pezzoli Museum, Milan (Italy)	✓	✓
Andrea Solario	About 1503-1505	Ecce Homo	Poldi Pezzoli Museum, Milan (Italy)	✓	✓
The Master of York	1510	Saint Bishop	Borromeo Collection, Isola Bella (Italy)	✓	✓
The Master of York	1510	Saint Mauritius	Borromeo Collection, Isola Bella (Italy)	✓	✓
Bernardino Ferrari	1510	Saint Marta	Borromeo Collection, Isola Bella (Italy)	✓	✓
Bernardino Ferrari	1510	Saint Peter	Borromeo Collection, Isola Bella (Italy)	✓	✓

Aurelio Luini	1592	Saint Thecla	Milan Cathedral, Milan (italy)	✓	✓

Table 1: List of the works subject of the present paper.

Methods

Pigment characterization was performed *in situ*, namely at the owner institution or, in case of restoration in progress, in the restorer workshop. Preliminary information were always gathered by UV light observations and/or IR reflectography: both analyses, in fact, allow to recognize past modified zones prior to the restorer intervention. In this way the punctual analyses were performed knowing the position of possible non-original layers and thus choosing an appropriate area for the spectra acquisition. The ultimate goal was to try to reconstruct the pictorial techniques and to get a rough idea about the stratigraphy sequences of pictorial layers, besides the pigments used. For this reason, we performed two different analytical techniques whose main peculiarity is the different penetration depth[26, 27]. In general, penetration depth depends on the incident and the outgoing radiation wavelength as well as on the material investigated[28].

EDXRF and FORS analyses are both punctual techniques: EDXRF detects the chemical elements of the pictorial layer sequence down to the ground level while visible and near Infrared (NIR) reflectance spectroscopy detects only the spectra corresponding to the pigments of the most external layer. In some simple cases, this makes possible to infer the stratigraphy of pictorial layers without any sampling, taking advantage also of art-history awareness. On the other hand, light elements are not detected by XRF; outgoing characteristic X fluorescence of medium-heavy elements can still pass the whole thickness, while relatively light elements (such as Ca and K) have a higher probability to be absorbed. This means that information related to lowest layers are not always complete. Notwithstanding, even if the grounds for panel paintings is often realized using gypsum, priming is usually made with white lead and its XRF emissions can pass the whole stratigraphy. Moreover, to a first approximation, the element concentration is proportional to its measured intensity, which must be corrected by a ratio correcting for all matrix effects (so called influence coefficients)[29]. Using portable XRF (pXRF) allows to perform *in situ* analyses without taking samples; the qualitative analysis is fast and the elements are simultaneously detected. The association with FORS makes it possible to detect organic pigments and dyes (for instance, lakes) and to recognize some pigments having the same characterizing elements, but different chemical formula (e.g. azurite, malachite and Verdigris). *In situ* non-destructive EDXRF analysis was carried out using Lithos 300 portable spectrometer (Assing, Italy) equipped with a Mo target X-ray tube and a Si-PIN detector. A transmission Zr filter (100 μm thick) allows to have a quasi-monochromatic radiation on the sample (4 mm radius spot size on the sample). X-tube typical working conditions are 25 kV and 300 μA and the measuring time is about 30-60 s. The energy efficiency of the handheld spectrometer is particularly low for elements with $Z<17$ also for the lacking of low energy incident radiation due to the strong absorption by the Zr filter. Short measuring time required by in situ measurements also contributes to lower the sensitivity for low energy characteristic emissions.

FORS is a non-invasive and portable powerful technique for surface pigment characterization, however difficulty in interpretation of spectra can arise from altered surface (presence of dust, yellowing or old varnishes) or from complex mixtures and dark shades[27, 30].

A portable Vis-NIR spectrophotometer (HR4000, Ocean Optics Dunedin, FL, USA) was used for FORS analysis. The spectrophotometer was connected to a tungsten halogen light source (D65, HL2000, Ocean Optics): light was transmitted through a quartz fiber optics bundle 1.5-meter-long (Ocean Opticts), composed by six fibers (400 μm each), to collect reflected light around the single central illuminating fiber (400 μm) using 45°x:45° measuring geometry. The spectrometer was connected to a laptop and calibrated using white and black reflectance standards (Spectralon® 99% and dark trap). Visible-NIR reflectance spectrum from 380 nm to 1000 nm was recorded for each sample with a spectral resolution of 2.7 nm.

RESULTS AND DISCUSSION

The pigments identified in the paintings considered in the present work are unsurprisingly those expected to be found in the Renaissance period: vermillion from cinnabar, lakes, earth in different shades (yellow, brown, red and golden), azurite and natural ultramarine blue from lapis lazuli, lead based yellow. Mixing and applying various layers or *velature* (thin semi-transparent layers) allowed the painters to obtain all the hues and shades. How to use these pigments is described in "The book of the art" of Cennino Cennini[31], which can be effectively considered a "practical treatise on *Quattrocento* Painting", as its subtitle claims, being written as a handbook for the artists. Recipes and solutions must be nowadays read keeping in mind that pigment nomenclature it uses does not univocally corresponds to the modern terminology.

This section presents an overview of the detected pigments along with the speculated stratigraphic sequence of the pictorial layers (see table 2). Painting ground preparation, flesh tones and green shades are instead deeper investigated in the following sections.

Colour	Pigments	Author (painting)
White	White lead (in some cases with lakes, copper based green or azurite traces)	All
Blue/light blue	Azurite (in some cases with white lead)	Bernardino Luini (S. Antony, Our Lady of Sorrows, Virgin and Child 1517), Ferrari (Saint Peter), Aurelio Luini
	Ultramarine over Azurite	Bernardino Luini (Our Lady of Sorrows) Bernardino Luini workshop (The adoration) Aurelio Luini, Marco d'Oggiono (The Virgin of the rocks)
Brown	Organic pigment	Bernardino Luini (Saint Antony from Padua)
	Ochre and vermillion in mixture on a white lead ground	Bernardino Luini (The Calvary ascention, Virgin and Child 1517)
	Yellow ochre and red lake	Ferrari (Saint Peter, Saint Marta)
	Ochre	The Master of York (Saint Bishop and Saint Mauritius), Bernardino Luini (Virgin and Child 1520) Oggiono (The Virgin of the rocks)
	Golden ochre	The Master of York (Saint Bishop and Saint Mauritius)
	Dark ochre (with copper based green)	Bernardino Luini (Saint Sebastian)
Red	Vermillion (in some cases with white lead)	Bernardino Luini (Saint Antony from Padua, The Calvary ascention), The Master of York (Saint Mauritius) Aurelio Luini (Saint Thecla)
	Red lake with shares of vermillion (in some cases with white lead)	Bernardino Luini (Our Lady of Sorrows)
	Lake (in some cases with white lead)	Bernardino Luini workshop (The adoration)
	Red lake with shares of vermillion	Bernardino Luini workshop (The adoration)
	Vermillion and lake	Bernardino Luini (Virgin and Child 1517 and 1520) Marco d'Oggiono (The Virgin of the rocks)

	Vermillion and ochre	The Master of YorK (Saint Mauritius)
	Red Lake	Bernardino Ferrari (Saint Martha) Bernardino Luini (Saint Sebastian)
	Ochre and lake	Bernardino Ferrari (Saint Martha)
	Cochineal	Aurelio Luini (Saint Thecla)
	Vermillion, ochre and lake	The Master of YorK (Saint Bishop) Bernardino Luini (Virgin and Child 1517; Virgin and Child 1520)
	Vermillion and lead based yellow	Master of YorK (Saint Mauritius)
Orange/red	Red ochre (in some cases with white lead)	Bernardino Ferrari (Saint Martha)
Yellow	Ochre	Bernardino Luini workshop (The adoration)
	Massicot with ochre	Aurelio Luini (Saint thecla)
	Massicot	Bernardino Luini (Saint Sebastian)
	Lead based yellow	The Master of YorK (Saint Mauritius) Bernardino Ferrari (Saint Peter)
	Lead based yellow with ochre *velatura*	Bernardino Ferrari (Saint Peter)
	Lead based yellow with copper based green	Bernardino Luini (Saint Antony from Padua)
	Ochre with vermillion	Marco d'Oggiono (The Virgin of the Rocks)
Gold yellow	Golden ochre	Bernardino Ferrari (Saint Martha)
Gilding	Gold (copper impurities) probably on a bole ground	Bernardino Luini (Saint Antony from Padua) Marco d'Oggiono (The Virgin of the rocks)
	Copper (no gold)	Bernardino Luini (Virgin and Child 1517, Virgin and Child 1520)

Table 2: Overview of the pigment recognised in the considered paintings. Green and flesh tones are excluded (see next section). Only painting for which both FORS and XRF data available are reported.

As it is well known, it is uncommon to find a pure ultramarine layer due to the high cost of this pigment. For the Virgin mantle, and in some cases also for the sky, the use of ultramarine over azurite is coherent with the Renaissance painting technique and the Leonardesque school. One notable example is, for instance, Leonardo's Virgin of the Rocks held in the National Gallery of London, where the blue mantle shows the ultramarine layer over the azurite one[11]. Brown areas show the presence of the usual mixture of iron oxides based pigments: it is important to note the use of green to get dark shades which is attested in literature on Leonardo's works[11].

Red drapery and clothes highlight a wide combination of the classical pigments used for this purpose, even if it is possible to recognize a homogeneity of materials and hues due to the prevalent adhesion to the Renaissance aesthetic standards and, to some extent, to the symbolic value of materials. The only sharp difference can be seen for Aurelio Luini painting: Aurelio, the last son of Bernardino Luini, worked later in time, already in the Mannerism period of the late 1500.

The analysis of yellow areas needs a preliminary consideration: lead based yellows often reveal a difficulty in being distinguished with the applied techniques: in fact, with the portable XRF spectrometer used in the reported measurements, As and Sn can be hardly seen if present in low quantity. Moreover, FORS spectra features of these pigments depend on the temperature they were manufactured[32, 33]. On these bases, no further consideration can be added to the data summarized in table 2. Experimental XRF data are mainly obtained by using L-lines and K-lines of chemical elements and the used spectrometer does not allow the detection of low Z elements and the use of M-lines of medium/heavy elements in the analysis, as pointed out above. This obviously produces a lack of information in the stratigraphy reconstruction, but this limit can be partially overcame by the joint use of FORS analysis[18].

It is clear that discriminating between the different authors on the sole bases of the used material is hard as all considered painters participated to the Italian Renaissance, where the choice of colour and materials reflected also a symbolic value. However, some particular chromatic areas, detailed in the following, reveal more than expected, starting from the ground preparation.

Ground preparation and priming

It is reasonably almost impossible to get definite indications about preparation and ground of paintings with non-destructive investigations, unless e.g. either differential PIXE[34] or confocal XRF[35] is used, which requires a great effort in term of time and money. Nonetheless, some hints can be inferred by qualitative XRF results[26-28].

In most analysed areas, the ubiquitous presence of Ca and Sr (vicarious of Ca, typically present in calcium minerals) suggests a calcium-based ground (probably *gesso*, $CaSO_4$). The presence of S, that can confirm this hypothesis, cannot be verified as it lies in the lower layers and its characteristic X emission is too low in energy to reach the detector.

It is possible to speculate on the existence of a white lead priming from the presence of Pb also in dark areas: this is linked to the so-called *imprimitura*, made by white lead in linseed oil. Moreover, Ca is normally present in some ochres/earths too, possibly as calcium feldspar, or as calcium carbonate and being Fe and Cu diffusely present, the use of some ochre or earth could be possible. The presence of these elements, typical of dark pigments, are indicators for the *mestica* type of priming that can be deeply coloured.

For all *Leonardeschi* painters, the use of this kind of *imprimitura* plays a key role in the intended tonal modelling, especially for the tone of flesh. See in particular the study of the cross sections taken from Bernardino Luini's "Christ among the Doctors" (National Gallery of London) that allows to confirm the results obtained with non-invasive analyses.

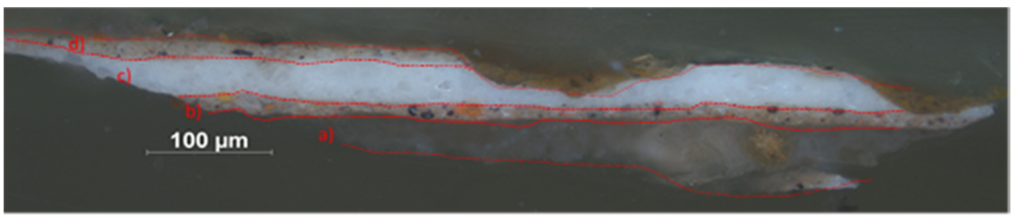

Fig.1 NG18 paint cross section from the Christ's flesh in shadow, showing a ground *gesso* layer (a), a superimposed brownish *gesso* layer with trace of red-orange lead, lead white, ochre, black carbon particle (b) and a pure lead white layer (c). Finally, a surface modelled layer containing lead, ochre and black carbon particle (d). Courtesy of NG laboratory for the (CHARISMA Grant Agreement n. 228330)

In figure 1 the photomicrograph (visible light; magnification 50X) of the cross section with a fragment from the Christ flesh in shadow is shown. It is visible a *gesso* layer with embedded red lead, lead white, ochre and black carbon particles. The thick white superimposed layer is pure white lead

It is worth noting that it is not possible to distinguish between the lead contribute from lead white and the one from red lead on the basis of XRF analysis and, consequently, it is not possible to infer the presence of red lead itself.

Interesting is the case of Boltraffio paintings: the preparation layers are quite different, even if not substantially. By analysing the two panels (Portrait of Gerolamo Casio and Virgin and the Child), the ubiquitous presence of Ca, Pb, Mn, Cu and Fe suggests a sequence of ground and *imprimitura* probably composed by a *gesso* layer and a lead white priming with the presence of darkening pigments (ochres/earths). This hypothesis, made on the base of the sole non-invasive investigation, is confirmed by Keith and Roy work[8]: they observed in a cross section from a dark green colour sampled from The Virgin and the Child (Boltraffio, NG 728, National Gallery of London) a dark blackish-brown under-layer, visible directly over the *gesso* ground.

Flesh tones

We studied the technique used to paint the flesh tones bearing in mind the well-known Leonardo's *sfumato* adopted to render the gradation of flesh tones[7, 10, 11]. As expected, used pigments are easy to recognise: white lead with vermillion, ochres and lakes in different mixture and proportion related to the desired chromatic result. The Milanese painter Giovanni Paolo Lomazzo[36] mentions the use of *terra d'ombra* (umber) to create the shadow of the flesh. This pigment, a translucent brown earth, has been detected in various cross-sections from the Virgin of the Rocks by Leonardo da Vinci (National Gallery of London)[11]. The observed translucent brown particles were found in several paint layers containing iron and organic matter, markers of *terra d'ombra* pigment (umber). Similar results were found in other Leonardo's Mona Lisa[7, 10], while in the paintings here presented, no umber was revealed by XRF in the flesh tints. Going deeper in these evaluations, surprises may arise. In all Bernardino Luini - and his workshop - analysed paintings and only there, the flesh tones show the same elemental composition: lead white with amounts of vermilion and ochre/earth pigments. By considering the intensity of Fe- k_α X-ray line, characterising ochre/earth, and the intensity of Hg-L_α X-ray line, characterising vermillion, a good correlation can be observed (see figure 2). Note that the X line intensities have been corrected by their respective absorption coefficients. For the panel representing "Saint' Antony of Padua" no conclusions can be drawn because there is only one measurement point for the flesh tones.

The evident good correlation between the two elements likely means that the pigments were blended in fixed proportions and then layered with lead white to obtain a common base; the colour modulation could be obtained with subsequent glazes. The different intensities account for the different desired hues; for St. Sebastian, the two point with higher Fe counts (represented with a red square in the diagram) refer to discoloured blood drops under the arrow.

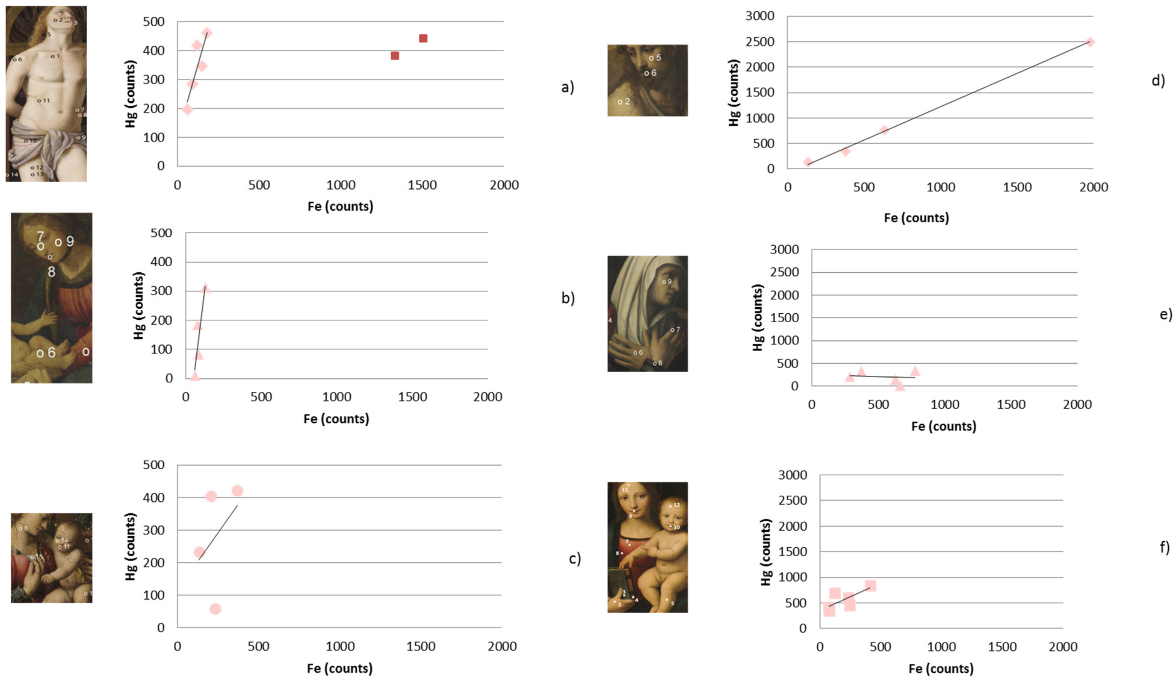

Fig.2 Diagrams reporting Hg Lα peak intensity vs Fe Kα peak intensity for Bernardino Luini paintings. The intensities have been corrected by their respective sensitive factors. (a) Saint Sebastian, b) The adoration; c) Virgin and the child; d) The Calvary ascension; e) Our Lady of Sorrows; f) Virgin and child). Linear fit correlation and measuring points are reported.

FORS testifies that, in the same paintings, brightly coloured shades are obtained by spreading a superficial layer of madder lake. Figure 3 shows the FORS spectrum corresponding to the measurement point 12 (blood drop “San Sebastian” panel), compared with the madder lake reference sample, as an example.

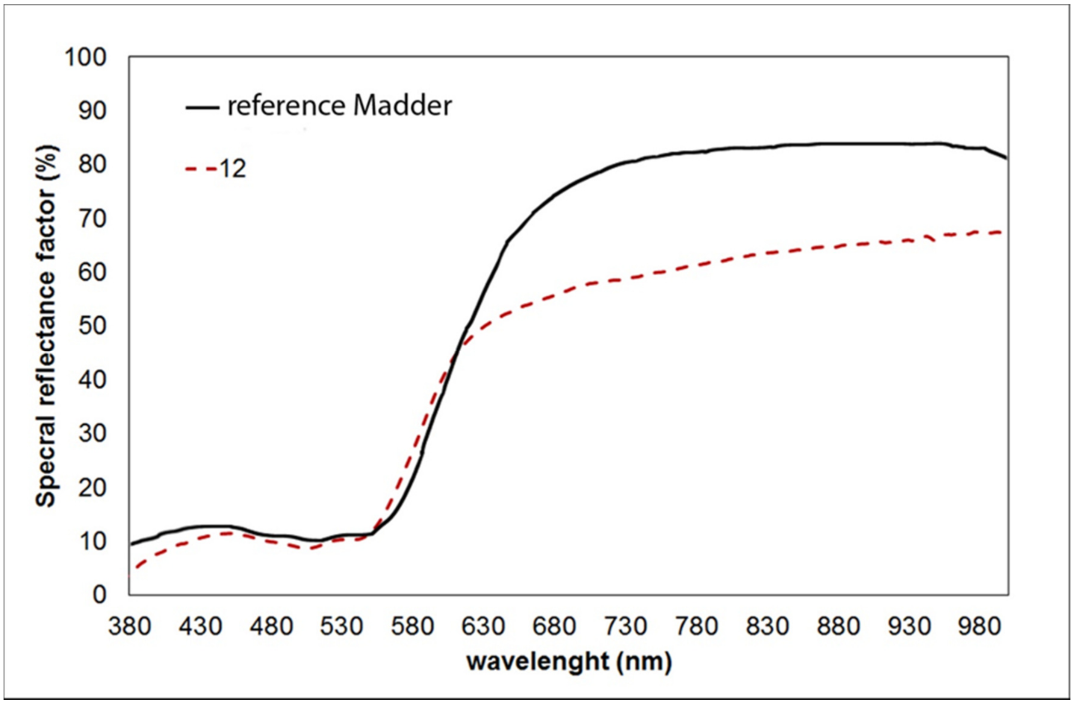

Fig.3 FORS spectrum of point 12 on San Sebastian panel. It is compared with the spectrum acquired from the madder lake reference sample.

It is also interesting to note (see figure 2a) that for the two previously mentioned points (red square in the diagram, corresponding to a faded drop of blood) a higher amount of Fe it is found (XRF spectra in fig. 4) where FORS confirms the presence of an ochre mixed with the madder lake in the outmost layer (figure 5). This hypothesis is based on the shape of the spectra in the NIR region (800-1000 nm). Red ochre has its characteristic peaks at about 450 nm, 600 nm and 770 nm; in the spectra reported in fig 5 peaks are present at 450 nm, 600 and 840 nm. The peak at 840 nm is thus shifted toward longer wavelengths and furthermore the reflectance increase in the NIR range conversely with the typical behaviour of ochre. The shift and the reflectance increase only in this part of the spectrum and cannot be attributed to the sole presence of a white pigment. For this reason, we hypothesize the presence of an organic red pigment like madder that was found in other area of the same painting.

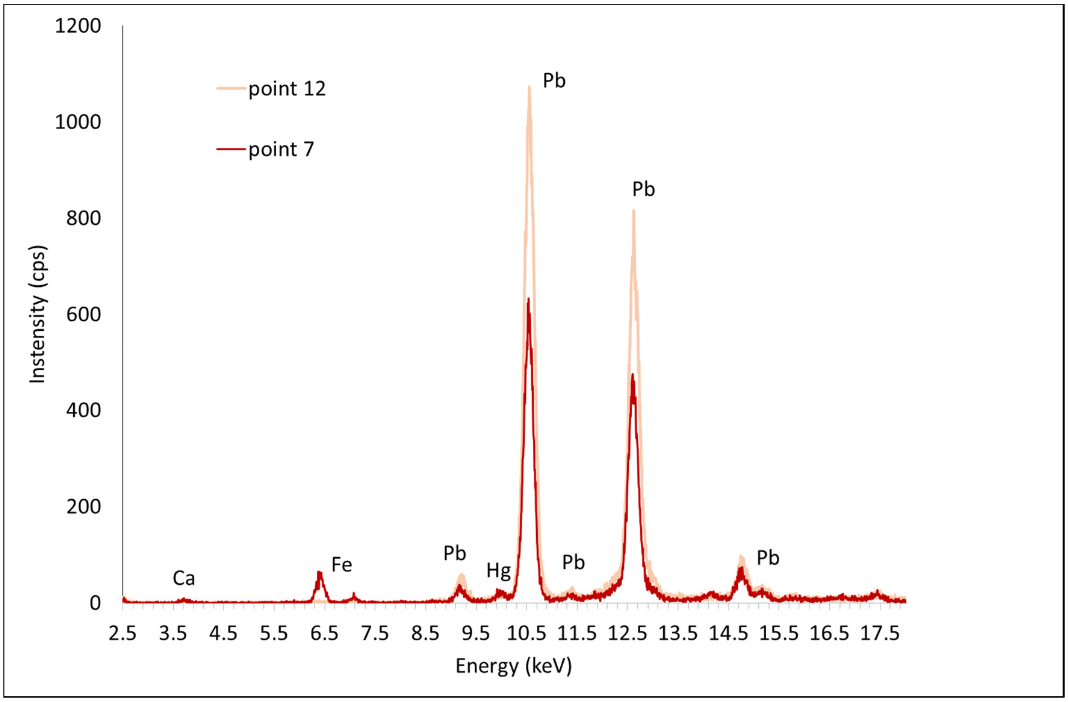

Fig.4 Comparison between XRF spectra from point 7 and 12 (see picture in fig 2a) of San Sebastian panel (see picture in fig. 2a).

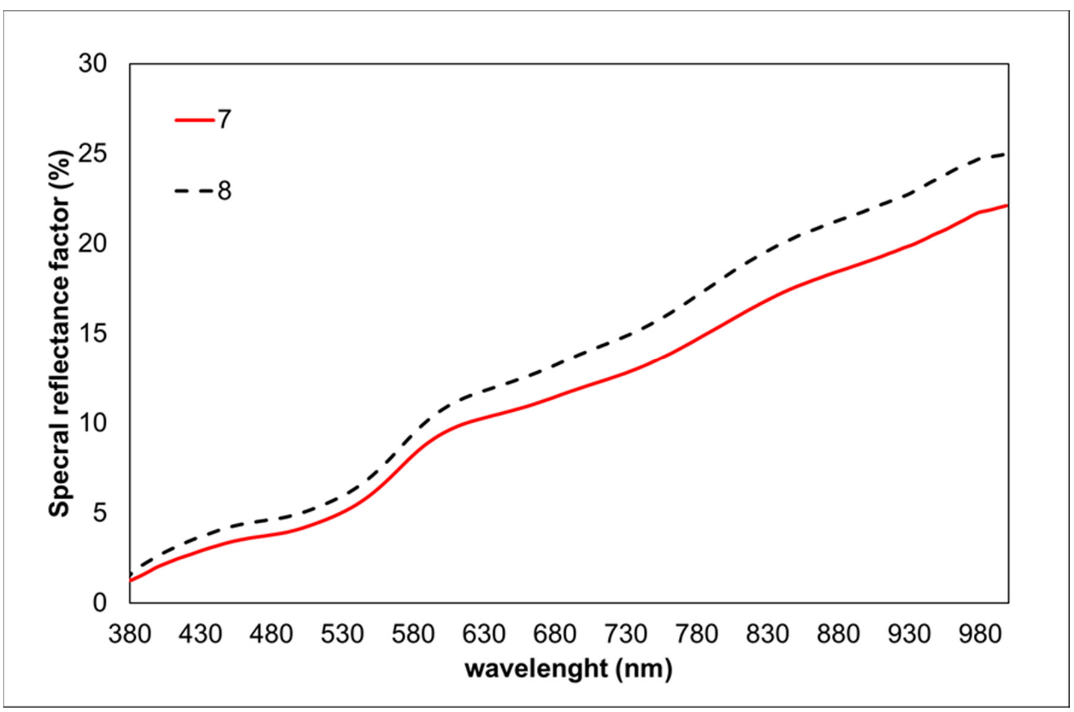

Fig.5 FORS spectra of measurement points 7 and 8 of San Sebastian panel (see picture in fig. 2a).

Observing at the optical microscope a cross section from Bernardino Luini's "Christ among the Doctors" board (National Gallery of London, NG18, hand of the doctor on the right side), it's possible to deduce that the flesh tone consists of red earth, vermillion, some red lake with a few black particles added for the shadow (see figure 6). This confirms the non-invasive results presented in this work.

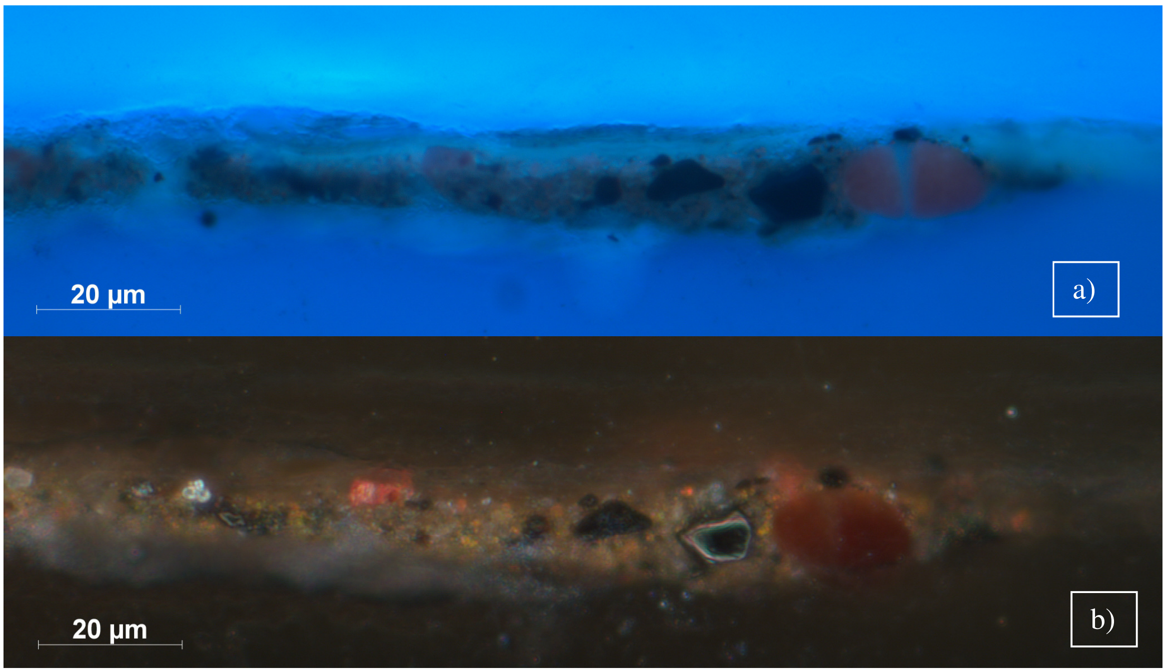

Fig.6 NG18 cross section from the shadow on the hand's doctor on the right. (a) visible light; b) ultraviolet light). Red earth, black particle, vermillion and trace of lake on the right corner are evident. Courtesy of NG laboratory for the (CHARISMA Grant Agreement n. 228330)

For all the other investigated Leonardesque authors, the palette for the flesh tones is consistent with the pigments adopted by Bernardino Luini (lead white, vermillion, ochre/earth pigment and madder lake), but no correlation between Hg and Fe has been observed.

Green shades

Three green pigments were mainly used in the Renaissance colour palette.

The first one was green earth, a natural pigment of varying tones, complicated in composition, but made up chiefly of glauconite and celadonite, hydrous iron, magnesium and aluminium potassium silicates[37]. Green earth was popular with early Renaissance painters in Italy, who used it also as an under-paint for middle and shadow flesh tones. It can be easily distinguished by XRF because of Fe presence, while FORS spectrum shows two weak reflectance maxima at about 560 (visible region) and 830 nm (IR).

The second green pigment was malachite, distinguished by its bright green shade and obtained by the mineral, basic carbonate of copper[38]. In this case, XRF can only detect Cu, without giving any further information to differentiate it from the third type of green used in the Renaissance: verdigris, a synthetic blue-green, which was the most vibrant green available. Its transparency made it been frequently mixed with lead white or lead-tin yellow, or used as a glaze.

Modern technical literature uses the term verdigris to refer exclusively to copper salts of acetic acid, but as late as 18th century, it encompassed a range of copper corrosion products that painters considered to be the same pigment[39]. The different methods for the production of verdigris, in fact, may lead to a number of different copper-containing compounds, including basic or neutral copper acetate, copper chlorides, copper carbonates as well as copper oxide, copper sulphate and copper nitrate[40]. When dealing with original materials, it seems then appropriate to use the term in this broader sense, as Renaissance artists had few means to distinguish the various corrosive products of copper.

Verdigris is the most reactive and unstable of copper pigments, but under very favourable circumstances it can be durable[37]. Besides, green glazes were commonly used in oil painting between 15th and 17th century; copper resinate, an amourphous green of copper salts of resin acid, is often identified in these green areas. It has been suggested that copper resinate was intentionally obtained by dissolving verdigris in hot varnish, or by dilution with turpentine[41], but none of the numerous instructions for glazing with verdigris recommends the heating; they always advice cold oil or varnish. The presence of resinate should therefore be seen as a degradation process in relation with different chemical composition of verdigris[39] which can react with the binder to form metal soaps[42].

FORS spectra of the three copper-based historical pigments quoted above are shown in figure 7, reporting reflectance from pure pigment layers spread with linseed oil. Malachite shows a broad band with maximum at about 540 nm, while verdigris (in this case copper acetate) spectrum has a strong maximum at about 500 nm and a soft slope from the near IR region. Copper resinate shows maximum reflectance at about 570 nm and an upward slope from the far IR region (about 670 nm) to longer wavelengths in IR.

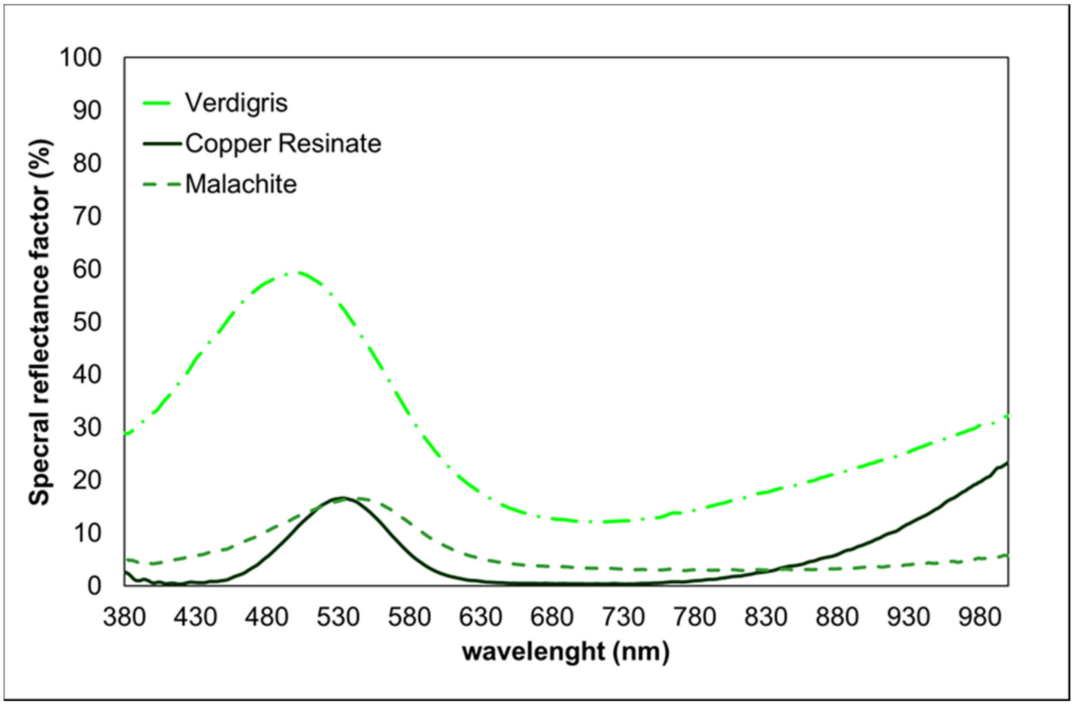

Fig. 7: FORS spectra of verdigris, copper resinate and malachite spread in oil; experimental set up is the one described in the experimental session of the present paper.

Indeed, verdigris spectra can be slightly different depending on the used recipe. A colorimetric study [43], has detected a shift of the reflectance maximum wavelength from about 490 nm to 550 nm following the different chemical composition of the pure synthetic pigments spread with linseed oil and comparable results were found for the specific case of green pigments mixed with white lead where the verdigris undergo to 40 nm shift of the reflectance maximum wavelength when mixed with the white lead[44].

It is clear that it can be hard to distinguish malachite and verdigris on the basis of the position of their maximum in reflectance spectra, especially when they are mixed with yellow pigments or yellowed by the ageing. In fact, ageing cause a shift through higher wavelengths and a broadening of the bands; the mixture with yellow pigments, frequent in the Renaissance paintings, causes a shift to higher wavelengths. However, the spectral behaviour in the near IR region allows to discriminate the three pigments. In particular, the ratio between the maximum reflectance peak in the green region and the reflectance at 950 nm can be used for this purpose, being about 2 for Verdigris, 3 for malachite and less than 1 for copper resinate when pure pigments are spread in oil and no ageing is present. The defined ratio slightly changes for mixture with yellow pigments, never going below 1 for Verdigris and malachite (mixture in oil 2:1, 1:1, 1:2 respectively). Mixtures in oil with white lead uniformly increase reflectance, without affecting the ratio.

In the Leonardesque paintings considered in this work, FORS analysis was essential to recognize green pigments as reported in table 3. All the cases show the presence of copper based pigments and their behaviour in the IR makes it probable to confirm the presence of verdigris/copper resinate – sometimes in mixture with yellow pigments - more than malachite. In most cases, copper resinate seems to be the best answer on the basis of reflectance trend in the near IR region, but the presence of a complex mixture of copper compound must also be taken into account, together with the effect of ageing.

AUTHOR	**TITLE**	**DESCRIPTION**	**FORS RESULTS (Peak/950nm)**
Marco D'Oggiono	Virgin of Rocks	Angel mantle	Copper resinate (0.6)
Bernardino Luini	Saint Antony from Padua	Leaves	Probable verdigris with lead based yellow. The slope in the IR region excludes malachite.
Bernardino Luini	Virgin and child (1520)	Grass	Copper based green with green ochre. The slope in the IR region excludes malachite.
Bernardino Luini	Saint Sebastian	Grass 16	Verdigris (0.6)
Bernardino Luini	Virgin and child (1517)	Mantle	Copper Resinate (0.4)
Bernardino Luini workshop	The adoration	Mantle and veil	Copper Resinate (0.4) Copper Resinate with green ochre
Andrea Solario	Ecce Homo	Cane	Green Earth
Aurelio Luini	Saint Tecla Martyrdome	Mantle	Copper based green in mixture withe lead based yellow. The slope in the IR region excludes malachite.
Bernardino Ferrari	Saint Marta	Mantle	Copper resinate with yellow
Bernardino Ferrari	Saint Peter	Book	Copper resinate probably in mixuture with yellow

		Mantle, after cleaning (dark)	Copper reasinate possibly in mixture with ochre
The Master of York	Saint Bishop	Mantle (dark)	Verdigris (0.7)
The Master of York	Saint Maurizio	Mantle	Verdigris probably in mixture with yellow
		Mantle, clean area (dark)	Probably copper resinate (0.2)

Table 3: List of green pigment recognized by FORS in the studied paintings. In brackets, the indicative ratio between the peak intensity and the reflectance value at 950 nm is reported when a pure pigment is supposed.

In figure 8, the FORS spectra of different measuring points in green areas on the same panel (Saint Marta attributed to Bernardino Ferrari), both cleaned and not cleaned, are reported. It is possible to note that the maximum reflectance is about 550 nm and 575 nm for cleaned areas, and 570 nm for un-cleaned zones, confirming the unreliability of pigment determination only through the position of the band, mostly if a mixture with yellow in the presence of varnish is possible.

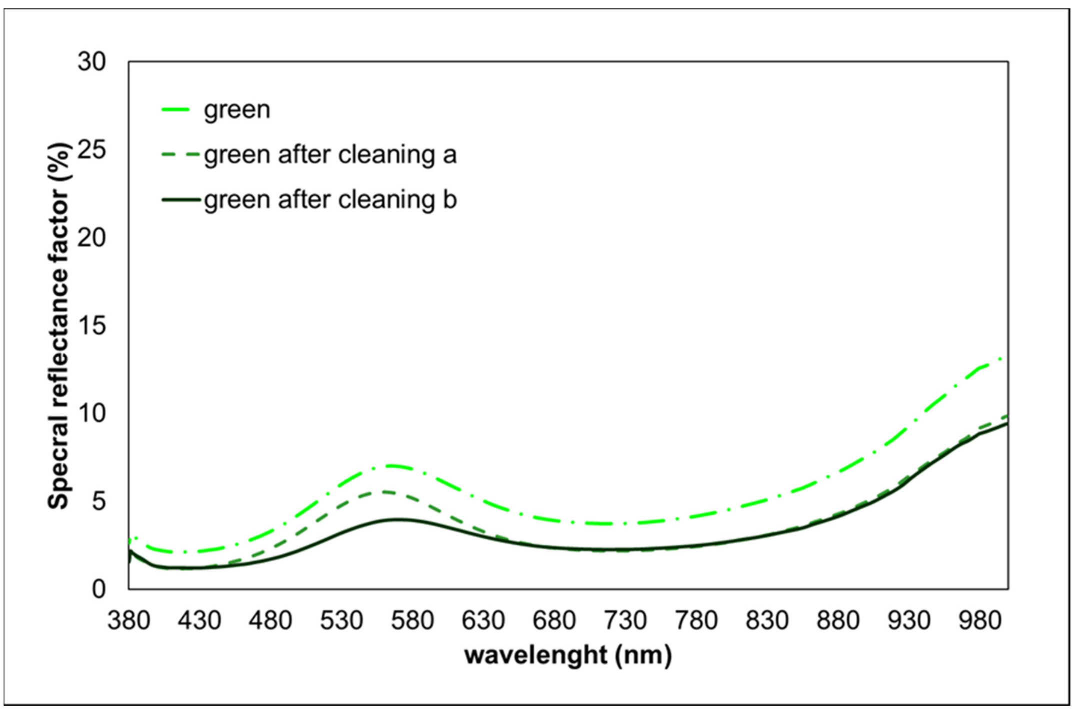

Fig. 8: FORS spectra of three different green area on Saint Marta panel attributed to Bernardino Ferrari: “green” indicates a green area before any intervention, “green after cleaning” refers to two different areas, (a) and (b) respectively, already cleaned by the restorer.

Actually, Leonardo wrote around 1492 in his *Libro della Pittura* about “the green colour made of rust of copper” that “even when this colour is mixed in oil, its beauty goes away like smoke if it is not quickly varnished.” This implies that he had obtained even worse results with glue or egg tempera[39]. Moreover, he added that “if it is washed with the sponge made wet in simple, ordinary water, the Verdigris will be removed” from the painting (“*Of green colour made of copper, even when this colour is mixed with oil, its beauty goes away like smoke if it is not quickly varnished. It not only goes up in smoke, but if it is washed with the sponge made wet in simple, ordinary water, the verdigris will be removed from its panel on which it has been painted, especially in humid weather. This comes about because the verdigris is necessarily made from salt, which re-dissolves easily on rainy weather, and especially when it is made wet and washed with the sponge mentioned earlier” (II, 211)*[45]). In this way, Leonardo gives some hints about the green colour made from copper rust, and not only to his peers. We can argue that the material in use in Italy in that period was highly unstable and ready to react with the medium.

Our hypotheses are supported by the available data on other paintings by Bernardino Luini, in which the use of copper resinate (cross-section observation and SEM analysis)[46] and copper acetate with lead based yellow (XRF, FORS and False Colour imaging)[47] is detected. Leonardo’s Vergin of the Rocks held in London shows the use of Verdigris[11] for the dark green foliage and all the Leonardesque panels reported in the National Gallery bulletins[8, 12, 13] are typified by the presence of Verdigris, alone or in mixture with lead white and lead-tin yellow. Only in one work by the Pala Sforzesca Master[13] malachite and copper sulphate are reported, but this is the case of an egg tempera painting.

CONCLUSIONS

A systematic study on twenty-one paintings from authors close to the Leonardo workshop was carried on using only low cost non-invasive techniques such as XRF and FORS with the clear aim to recognize, beside the used pigments, the painting execution technique.

The identified palette includes the classical Renaissance pigments (vermillion, lakes, earth, azurite, natural ultramarine blue, lead based yellow, Verdigris) mixed and applied in various layers. In details, the clear identification of the green pigment required an in depth investigation on copper based green pigments and their behaviour in FORS spectra, namely in the near IR region. Challenging has been the reconstruction of layer sequence for the flesh hues, for which the comparison with available stratigraphic results was essential. As expectable, even if some fingerprints can be seen, it is impossible to distinguish the single author.

Surely, a good data handling allows to get the most from simple techniques, but a correct interpretation of scientific data should require a complete reading of the artworks through the synergic intersection of human science (art-history, archive research on both the painting and the author and so on) and diagnostic analytical methods. Besides, the availability of archive data and a systematic measuring session on masters of the same artistic tendency can guide to the correct data interpretation.

Acknowledgments

The author would like to thank all the Museums and Institutions for giving us the opportunity of carry out this research. We are grateful to Carlotta Beccaria for her trusting support. Andrea La Bella has collaborated to the data processing. Financial support by the Access to Research Infrastructures activity in the 7th Framework Programme of the EU (CHARISMA Grant Agreement n. 228330) is gratefully acknowledged by Anna Galli and Letizia Bonizzoni.

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