DIAGNOSTIC - ANALYTICAL STUDY OF THE PAINTING "GIOCONDA WITH COLUMNS"

Salvatore Lorusso,• Chiara Matteucci, Andrea Natali, Salvatore Andrea Apicella, Flavia Fiorillo
Dipartimento di Beni Culturali
Alma Mater Studiorum, Università di Bologna

Keywords: "Gioconda", "Gioconda with columns", Leonardo, authentication

1. Introduction

The painting "Gioconda with columns" (Figure 1) from a private collection, re-proposes a work of art that is "unique" in the art world, in other words, the "Mona Lisa" by Leonardo da Vinci.

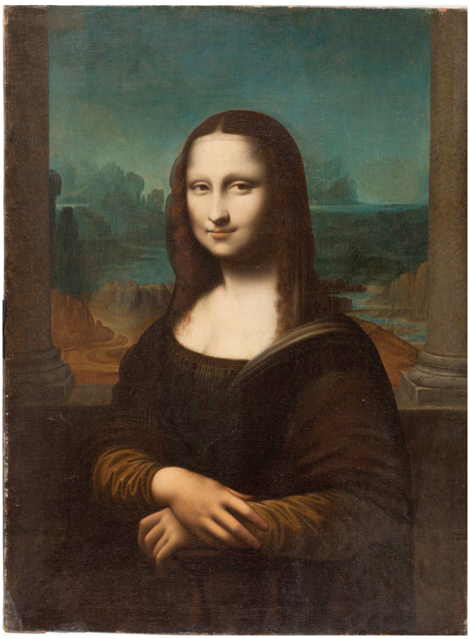


Figure 1. Photograph in the visible of the painting "Gioconda with columns" Saint Petersburg (oil on canvas - 85.2x63.2 cm)

• Corresponding author: salvatore.lorusso@unibo.it

The presence of the columns represents the most significant distinguishing feature when compared to the "Mona Lisa" housed in the Louvre.

According to Federico Zeri "*the work by da Vinci, considered one of the most prestigious of all times, was mutilated, that is, deprived of the two columns that adorned either side to make a "pendant" for a smaller painting: the lateral framing was therefore removed*" but is however present in the painting under examination. This view is shared by Kenneth Clark, Richard Friedenthal and Serge Bramly.

This reduction in size is however refuted by the conservators of the Paris museum: in 2004 the Louvre version underwent a number of scientific and technical examinations, carried out by a group of 39 international experts.

The above-mentioned investigations also demonstrated that the small portions of the columns present on the painting were painted over the background of the sky and the mountains.

Another hypothesis is the existence of a second "Gioconda" by Leonardo da Vinci: in this second version the columns are present. Experts from the "Mona Lisa Foundation" believe that the matrix of the copies with columns is the Gioconda by Isleworth.

Consequently the question arises: "Is the painting "Gioconda with columns" attributable to the genius of Leonardo or one of his followers or is it to be considered a copy of the "Mona Lisa" in the Louvre or the second "Gioconda" or a copy of the latter?"

Thus, the investigation is directed towards identifying the constituent materials and characterizing the pictorial technique in order to artistically collocate its execution and contribute to providing a reliable answer based on both a subjective and objective evaluation.

For this purpose, the study was conducted with the cooperation of an art historian and restorer, as well as a physicist and a technical diagnostician, thus integrating competences that were able to lead to the final results.

The present diagnostic-analytical study was carried out on the painting "Gioconda with columns"(oil on canvas 85.2x63.2cm) (Figure 1) belonging to a private collection. The aim of the investigation is to identify the constituent materials and to characterize the pictorial technique with the purpose of artistically collocating its execution.

Some of the diagnostic-analytical investigations were carried out in the Museum of St. Petersburg where the painting is conserved and others, on samples taken from the work, were carried out in the Diagnostic Laboratory for Cultural Heritage of the Department of Cultural Heritage of the Alma Mater Studiorum University of Bologna (Ravenna Campus) using both portable and non-portable equipment, in compliance with principles of innovation and reliability.

The tests include:
- macroscopic analysis;
- evaluation of conservation state;
- characterization of the support;
- characterization of the binding agent;
- characterization of the preparation and priming of the support;
- characterization of the artist's palette;
- definition of the painting technique;
- definition of the sfumato.

For this study the following technologies were applied:

- photography in the visible in diffuse and raking light →photographic camera Canon 650D(18 MPx), Canon objective 18-35, cold light spotlights(5500ºK) Lupo, incandescent spotlights(500 W), tripod, umbrellas;
- microscopy →Zeiss stereoscopicmicroscopeStemis SV11;
- reflectography in UV light →multispectral videocameraMusis MS (multispectral imaging system)(1024x768 px), UV sources Stocker Yale Black Light Blue(365 nm);
- reflectography in IR light →multispectral videocameraMusis MS (multispectral imaging system)(1024x768 px), UV sources Stocker Yale Black Light Blue(365 nm);
- image analysis videomicroscopy →Keyence videomicroscope mod.VH5901, objective (up to 175x);
- spectrophotometric colorimetry →spectrophotometric colorimeter Minolta 2600d;
- X-ray spectrometry→ Electronic Industry Support spectrometer (38kV, 0.5 mA).

The following analytical investigations were also carried out:
- scanning electronic microscopy with microanalysis of the thin section →SEM Inspect S FEI with microprobe Edax Phillips New XL-30;
- FT IR analysis →FT IR diffractometer Tensor 27 Bruker;
- Radiocarbon dating of the support.

Below are shown the diagnostic-analytical findings that are considered significant in achieving the set objectives.

2. Macroscopic analysis

• *Support*

The painting has a support consisting of two canvases mounted on a wooden frame with nails (Figure 2).

The frame can be extended by means of chocks or angular wedges. It has a horizontal crosspiece in the center of two vertical wooden strips (Figure 3). It is in good condition and based on the characteristics of its assembly, its fabrication can be traced back to a period ranging from the late 1800s to the early 1900s[1-2].

The textile support consists of two canvases glued together (lining).

Figura 2. Detail of support

Figura 3. Detail of frame

The original borders of the first canvas on which the painting is found are missing (Figure 4). In fact, along the margins there are no selvages or nail holes from the first stretching of the work onto the original frame.

Figure 4. Detail of canvas edges

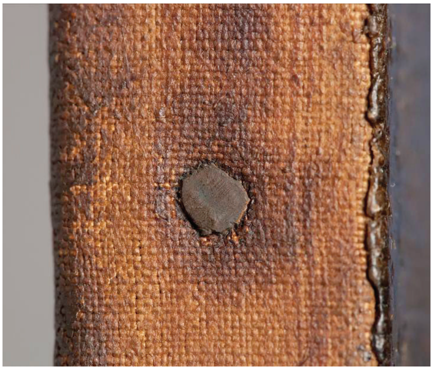


Figure 5. Detail of resinous glue behind canvas used for lining.

The edges, generally frayed or damaged by nails, were cut and removed when the painted canvas underwent lining. In this way, any irksome problems at the time of re-mounting the lined painting onto the new frame, were avoided [3-4].

This practice was common in various parts of Europe among many restorers who worked between the late 1800s and the 1950s, but possibly even later [4].

The negative aspect of this practice is that it prevents the exact measurements of the original painting to be determined.

The canvas used to line the painting has the following characteristics: fine threads and very tight square structured weaving, similar to industrial canvases prepared for painting. It is therefore believed that the lining was executed with wax.

Originally, the canvas was light-colored, but is now brown as a result of the treatment received during the lining with wax [5].

In fact the brown mixture of wax and colophony (rosin) used in the lining when hot has impregnated the plant fibers and passed through the woven cloth with ease, as evidenced by the resinous glue behind the cloth used for the lining (Figure 5).

At present, the two integrated canvases are fitted loosely on the frame.

• ***Surface of painting***

The preparatory layer on which the work is painted is thin and of a color tending towards a red-brown. The limited thickness of the preparation is such that the weaving in the cloth is visible on the surface of the painting. It seems that a preparatory white layer containing white lead is completely missing.

The painting surface has suffered due to the woven cloth below it. The painting is covered with several layers of resinous paint or other material, such as glue or egg albumen used as a final varnish.

This represents a serious obstacle to the examination of the conservation state of the pictorial surface.

3. Evaluation of the conservation state and identification of previous conservation interventions

Examination of the painting proceeded with the aid of diagnostic instruments.

The use of photography in raking light and diffuse light, ultraviolet fluorescence spectrometry and image analysis videomicroscopy allowed an objective evaluation of the conservation state of the work to be made. They also enabled the identification of conservation and restoration interventions that the work has undergone over time[6].

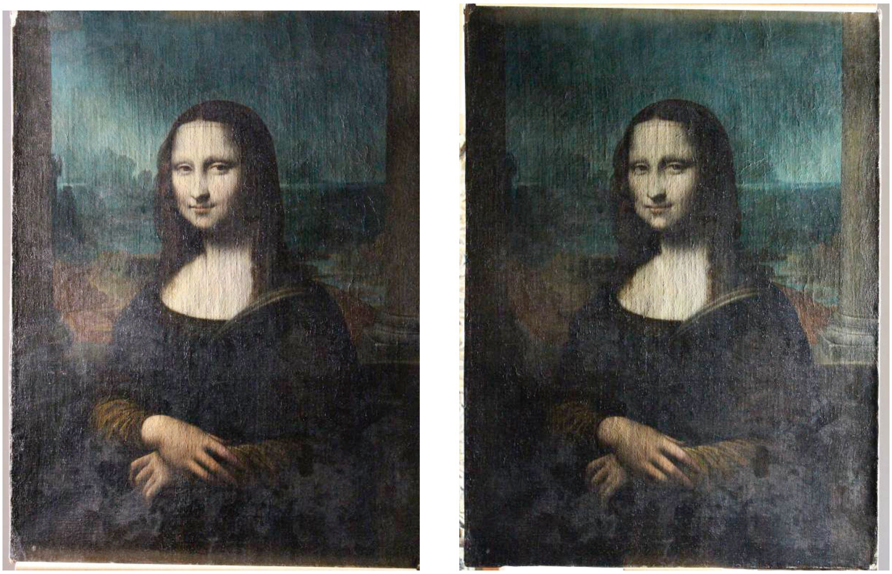
Examination of the painting through the use of the aforementioned diagnostic technologies allowed the following observations to be made:

- the work has undergone restoration work on several occasions which has been discontinuous at times
- the painting has undergone a great many re-integrations (of retouching and re-painting) of various sizes and carried out at different times.

• *Pictorial surface*

The result in raking light in particular (Figure 6) showed the thin layer of paint and consequently the underlying woven texture of the canvas.

The most recent cleaning attempts, successively covered with abundant varnish and coating and identifiable in the UV photo by the brown and black coloring, were found in the lower right hand part, covering approximately a quarter of the painting's surface and small areas along its perimeter at the top (Figure 7).



A B

Figure 6. Image using raking light left (A), right (B).

The images, moreover, highlight the presence of a geometrically selective intervention well-defined by the presence in UV of a vertical line found at the center in the lower part of the painting. In fact this area gives a different UV fluorescence response to that of the remainder of the artifact. Two recent repaintings are present on top of the layer of varnish (in the upper left part and on the woman's forehead close to the edge of the veil) and areas of previous retouching – underneath the layer of varnish – in the area of the cleavage and the sky and landscape on the right of the painting. The use of videomicroscopy shows that the canvas is not orderly and regular. It also appears that in correspondence with several areas with cracking, small pieces of paint tend to come unstuck (Figure 8).

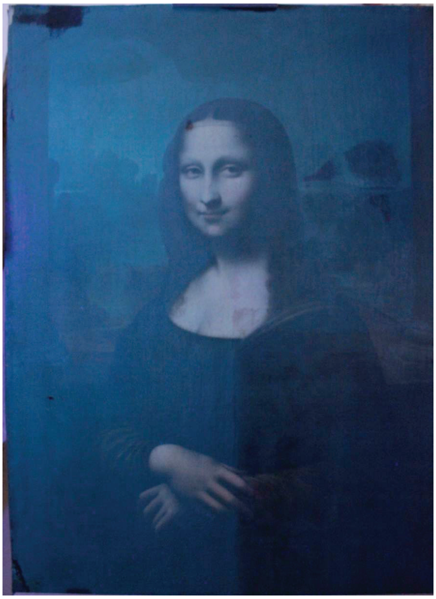


Figure 7. Image using ultraviolet fluorescence.

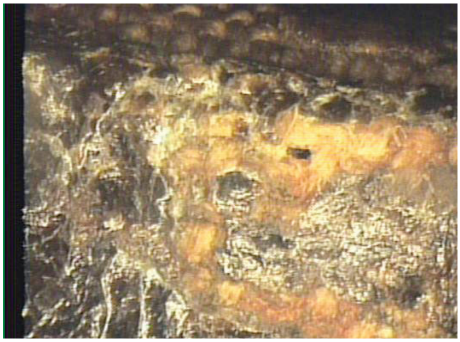


Figure 8. Videomicroscopy (50x) of the pictorial paint layer.

• *Background*

Photography in diffuse light highlights the discontinuity in the sky due to the excessive retouching and cleaning resulting from various interventions (Figure 9).

A great deal of retouching has been done around the head. In the right side of the sky, behind the nape of the neck there is a sign of very evident retouching almost circular in shape, of a light blue color tending toward a dark yellow. There are a great many points that have been retouched in the sky. For this reason many shades of blue are visible. Furthermore, in this same area, in the upper left part, there are some anomalies, due to a different index of refraction in the surface, probably the result of a final varnishing with brushstrokes that have created alternating shiny parts and opaque parts.

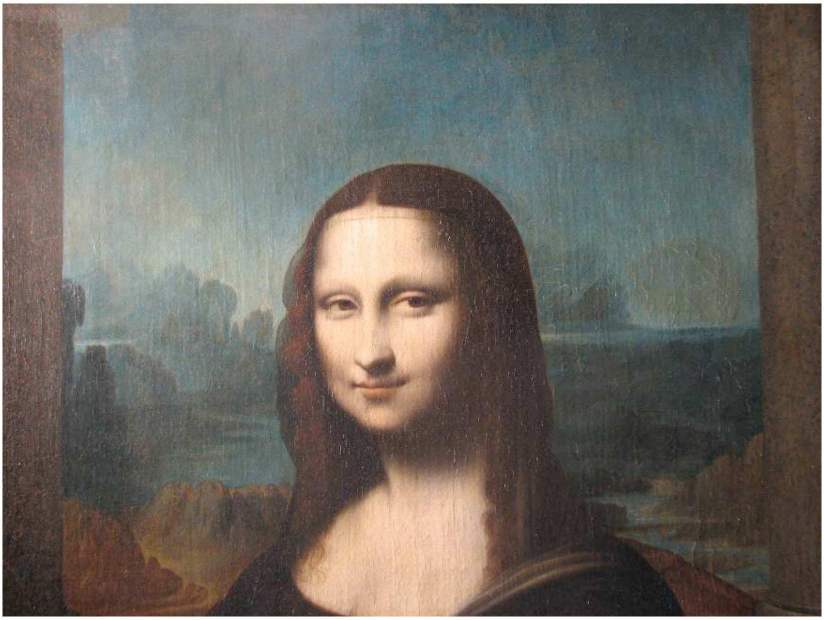


Figure 9. Detail of background in diffuse light

Figure 10. Detail of right-hand column in diffuse light

The landscape is full of retouching. On the right-hand column colors have been used to produce light effects (Figure 10).

• *Figure*

Diffused light technology reveals, on the other hand, that the outline of the figure (head and shoulders) is marked by a strong, dark and clear sign (Figure 11). Between the color and the shade of the two flesh tones, in fact, there is a difference: the hands are more rosy and soft compared to the rest that has few chromatic vibrations. The hands, moreover, have some very small points which have been retouched and some tiny dark spots (Figure 12).

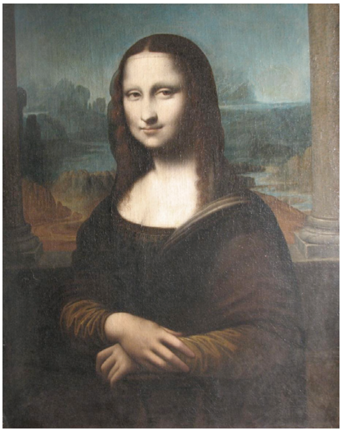


Figure 11. Detail of the figure in diffuse light

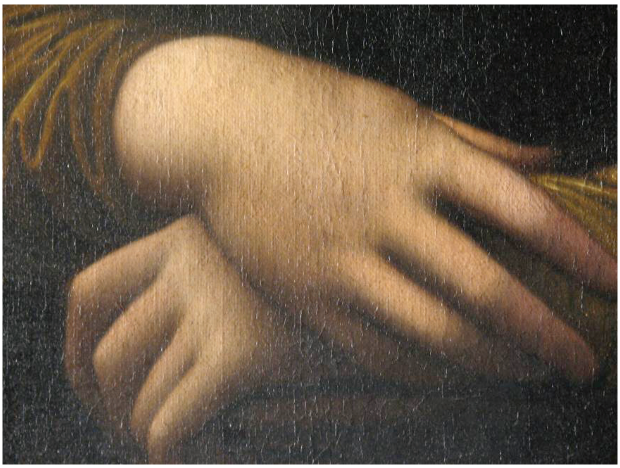


Figure 12. Detail of the hands in diffuse light

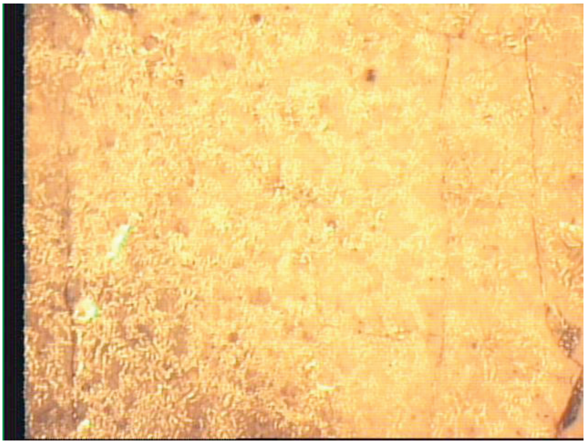


Figure 13. Videomicroscopy image of the flesh tones

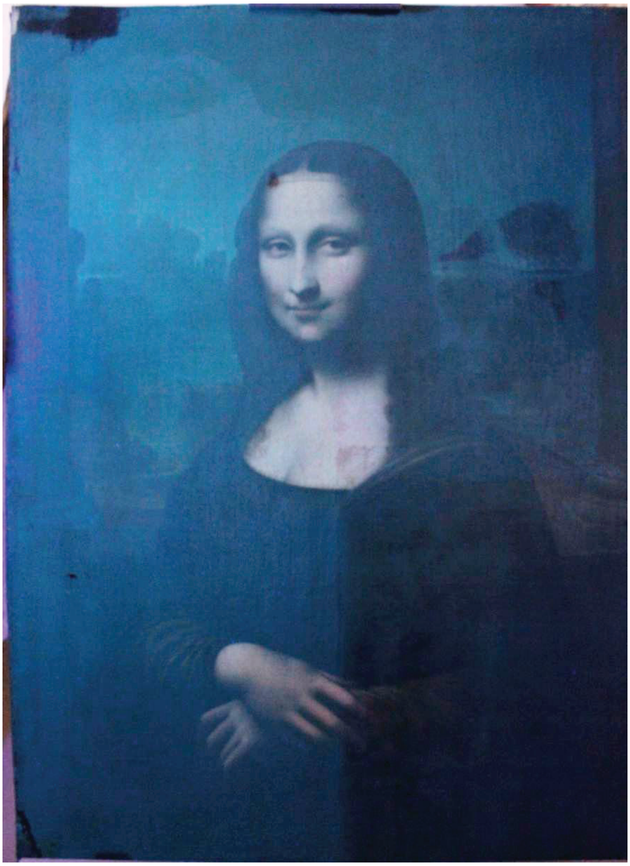


Figure 14. Detail of the figure in ultraviolet

Videomicroscopy, moreover, shows the pictorial surface of the flesh tone has very fine light vertical cracks (Figure 13).

Images produced using ultraviolet (Figure 14) show how the face and neckline have numerous tiny points that have been retouched. Both the face and neckline have also undergone cleaning which, however, did not include the hands. Retouching on the chest follows a direction which goes vertically and to the right and is also vaguely of a square form. The hair shows significant wear on the right side above the forehead, but the brown colour hides the degraded parts. Retouching can be seen along the hair that falls over the left shoulder of the figure.

The curls in the hair that stand out on the flesh color have been damaged by cleaning, and either badly and partially redone or retouched. The brown decoration of the bodice is perfectly painted using great precision. The lights and shadows of the mantle are not very clear, apart from the light part of the folds higher up, but which are not of very good quality. Highlights have been added on the sleeves of the dress.

4. Analyses

4.1. Textile support

• Sampling

Sampling of the original support and the subsequent removal of the thick layer of resin attributable to the lining has allowed the technical characteristics of the canvas to be highlighted.

As there were no repercussions, sampling was performed on a part of it, that is on the left side of the painting in correspondence with the left column.

• Diagnostic-analytical investigation and results

The diagnostic-analytical investigations were conducted using technology such as microscopy and scanning electron microscopy.

Below are the structural characteristicsof the canvas.

The *flax fiber* is constituted by a bundle of cells with a thick wall, frequently decomposed into single units. The characteristics, in particular, are:

Longitudinal appearance: straight fibers with x-shaped transversal dislocations along the fiber, called nodes (Figure 15).

Cross section: bundle of polygon-shaped cells with a small lumen and thick walls (Figure 16).

Torsion: Direction of the torsion: in the form of a "Z".

Frame: woven cloth with alternating weft threads over warp threads (1 weft, 1 warp).

Density: 14 threads per centimeter in the warp and 12 threads per centimeter in the weft.

Microscopic examination of the fiber shows it is constituted by long filaments formed of bundles of aggregated fibers each with a diameter of between 30 and 40 microns. These fibers appear gathered together with encrusting substances, wood residues, partially lignified membranes and various impurities. The individual fibers have a cylindrical shape with a thin central channel and ending in a sharp point. Observed longitudinally, the fibers have marked cross-striations that cross each other obliquely to form an x and have a slight swelling at almost regular intervals.

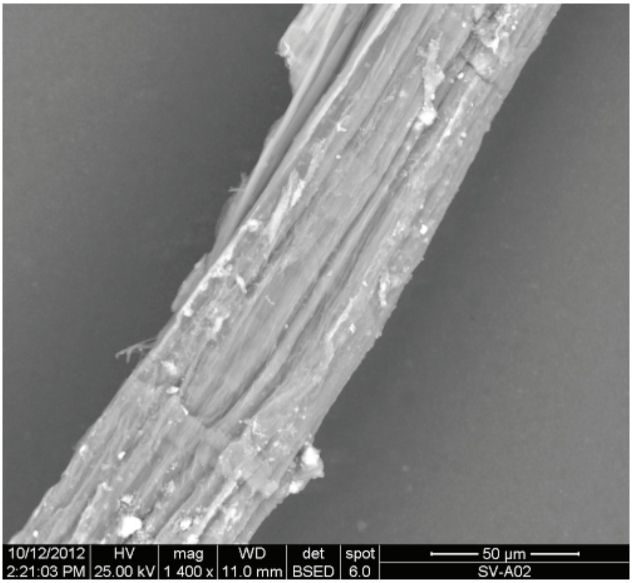


Figure 15. Flax fiber seen with SEM (1400x)

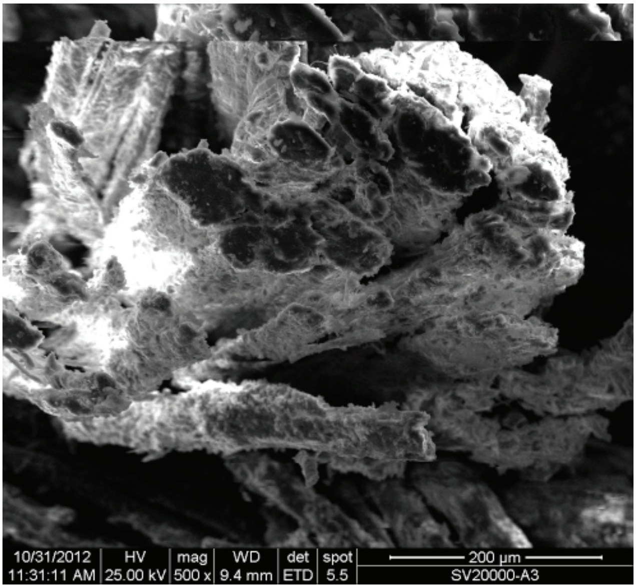


Figure 16. Transversal section of the flax fiber seen with SEM(500x)

The canvas is therefore realized in flax fiber and has a high average density (Figure 17) suited to the format of the painting. In fact, the choice of the woven clothdecided by the artists was based on format: closely woven for small sizes, loosely woven, but stronger for large canvases [7].

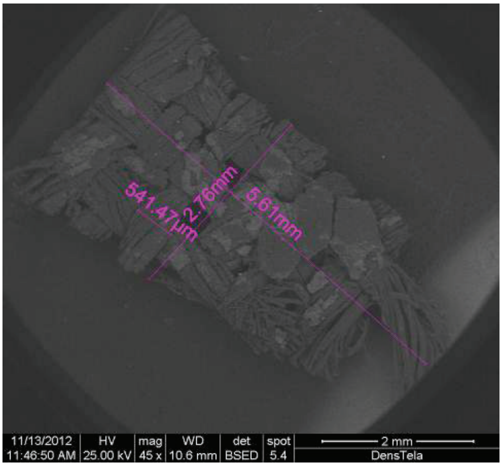


Figure 17. Cloth sample observed with SEM

The cloth has irregularities in the weaving due to the closeness of the warp and the slight variation in the section of the thread.

The fabric has undulations in the threads in the area of the long sides, deformations due to the tension of the painting on the frame.

The conservation state of the canvas is mediocre. As a result of its complex history of conservation, the canvas is extremely fragile and worn, with weakening of the fibers and points where it is deteriorated, attributable mainly to the products used in the lining process.

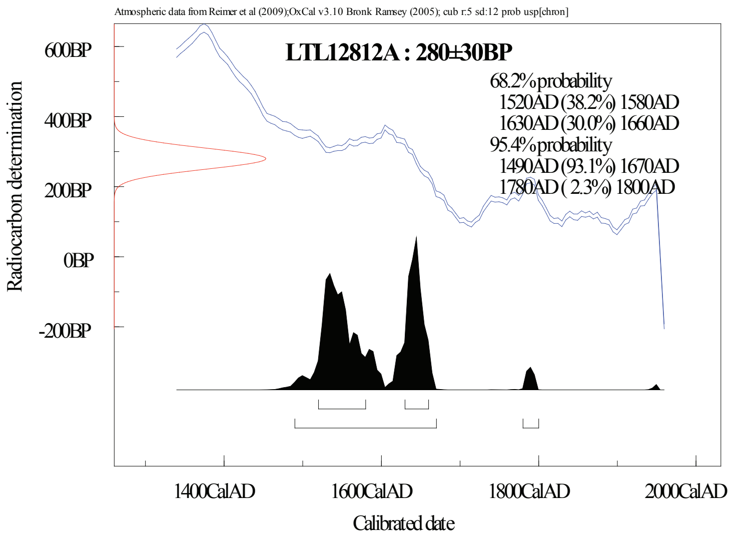


Figure 18. Radiocarbon dating

• Radiocarbon dating

The sample was subjected to radiocarbon dating, that is, the radiocarbon dating method using high resolution mass spectrometry (AMS).

The micropollutants in the sample were viewed using an optic microscope and mechanically removed.

Conventional radiocarbon dating was corrected for the effects of isotopic fractionationboth by measuring δ13C value made directly with the accelerator and the base of the measurement.

The concentration of radiocarbon was determined by comparing the measured values of the currents ^{12}C and ^{13}C and the counts of ^{14}C with the values obtained from standard samples of Saccarose C6 supplied by IAEA (Figure 18).

4.2.Ground layer

• Sampling

The sampling was done on a fragment which included the entire stratigraphy: from the support to the varnishes. The sampling was carried out on the lower left side of the painting in correspondence to the left-hand column.

The preparatory layer is a hidden layer to which little attention is given normally and for which texts describing painting techniques are vague. It is of great importance however, especially, for conservation of the work of art. In fact, it is the part of the painting which is more subject to mechanical stress due to the fact that it is interposed between two layers with completely different physical characteristics: the flexible layer of the cloth and the rigid layer of the oil and pigments.

Even specialist bibliography on the subject is vague and it is difficult to find anything specific other than the generic indications covering compositional typologies, except for a few rare specialist scientific investigations.

Additional information which is scarce, is in any case contrasting and consequently denotes only a limited accuracy about a subject which was probably jealously guarded in workshops external to the artist's studio itself.

• Diagnostic-analytical investigation and results

A description is given of the investigations carried out on cross-sections of samples embedded in resin (for analysis in scanning electron microscopy) and in potassium bromide (for analysis in infrared spectroscopy).

The elemental analyses carried out using scanning electron microscopy (Figure 19-20) identified the presence of the following elements: carbon (C), oxygen (O), aluminium (Al), silicon (Si), lead (Pb), calcium (Ca), iron (Fe).

The following inclusions were also found: sulphur (S), barium (Ba).

The simultaneous presence of sulphur and barium in the grains lead to assume the presence of barium sulphate. This is found in the form of disseminated inclusions in the preparation; the sizes ranging from a few micrometers to dozens of micrometers demonstrate that it is natural baryte rather than an artificial pigment. If this had been the case the grain would have had a more regular morphology.

Analysis in Fourier transform infrared spectroscopy revealed the presence of calcium carbonate, aluminosilicates and oil (Figure 21).

The binder in particular was found to be an aged oil since, by means of IR spectroscopy, the presence of free acid groups were detected (-COO-), whose formation is the result of hydrolysis of the ester bonds of the triglycerides contained in the drying oils.

Protein binders were not detected.

Before application of the preparatory layer on the canvas, to isolate the fibers and avoid direct contact with the preparation and to fill the dimensional difference between the threads, it was a customary procedure to treat the canvas with glue dissolved in water [8-10].

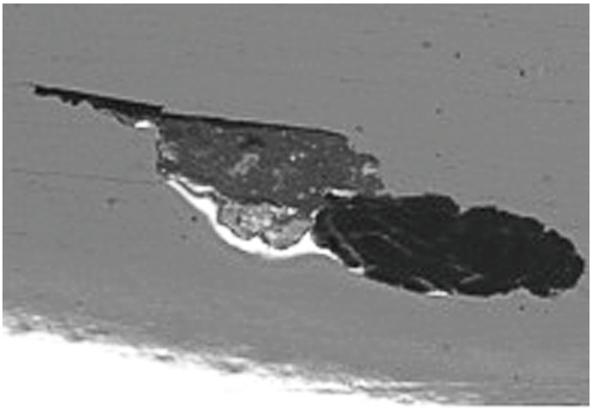


Figure 19. Photograph using electronic microscopy (250x)

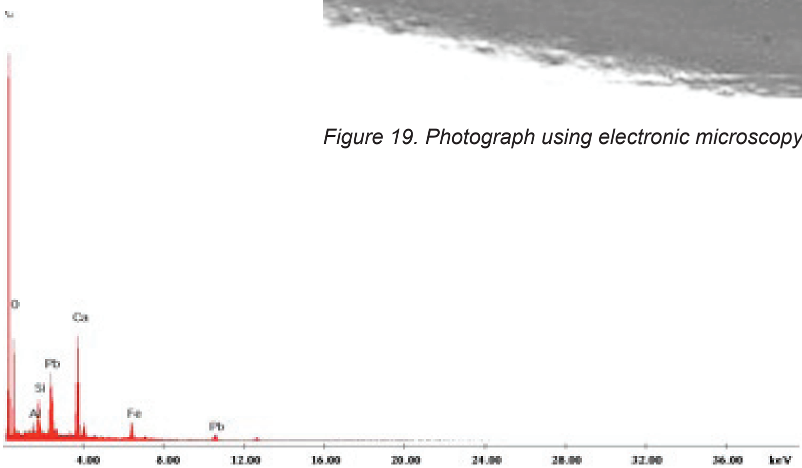


Figure 20. EDX spectrum of the preparatory red layer (Energy Dispersive X-ray spectroscopy)

In this case, as no trace of protein binders was found, application of the aforementioned technique was excluded.

The preparatory layer, therefore, is constituted by an organic binder composed of drying oil, a calcium carbonate-based white component of a white clay type or "*bianco di Spagna*" type, iron aluminosilicate hydrate-based red/brown component of "*terra bolare*" type and a lead-based component in the form of oxide (or minium Pb_3O_4 – red or litharge PbO yellow-orange), as the presence of ceruse ($PbCO_3$) or hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$). The presence of barium sulphate ($BaSO_4$) was also found in the form of inclusions.

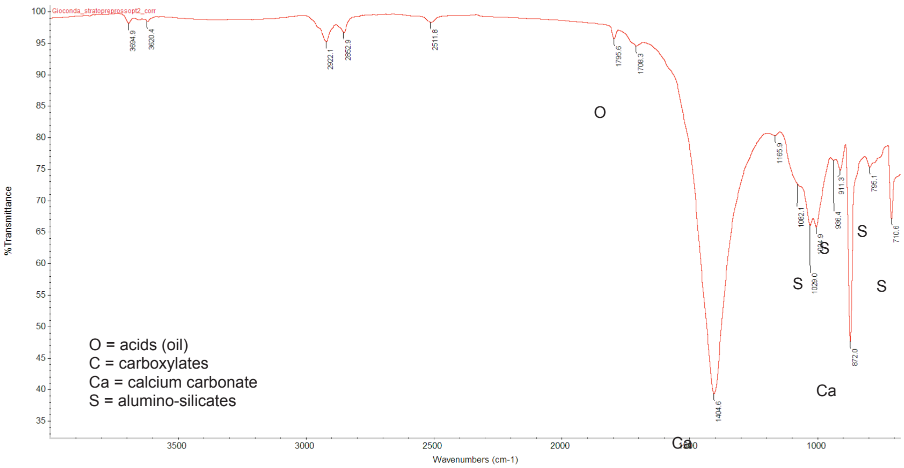


Figure 21. FTIR spectrum of the preparatory layer

4.3. Primer

• Diagnostic-analytical investigation and results

The primer is yellow-brown in color, containing black, white, red and colorless inclusions. It has a thickness of about 40 microns.

The analytical investigations on the preparatory layer were conducted using scanning electron microscopy and Fourier transform infrared spectroscopy. Below are described the investigations performed on the cross-sections of the samples embedded in the resin (for analysis in scanning electron microscopy) and potassium bromide (for analyses in infrared spectroscopy).

The results of the elemental analyses using scanning electron microscope with microanalysis identified the presence of the following elements (Figure 22): carbon (C), oxygen (O), iron (Fe), magnesium (Mg), aluminium (Al), silicon (Si), phosphorous (P), lead (Pb), potassium (K), calcium (Ca).

The analyses in Fourier transform infrared spectroscopy revealed the presence of calcium carbonate, aluminosilicate hydrates and oil (Figure 23).

The presence of the oily binder in particular, was detected thanks to identification of the ester component of the triglycerides contained in the drying oils.

In addition, the presence of carboxylates of lead which were formed by the reaction of a lead-based pigment (Pb_3O_4 or PbO) with the oily medium.

The priming therefore, is constituted by an organic binder consisting of drying oil, a calcium carbonate-based white component of a white clay type or "*bianco di Spagna*" type, an iron aluminosilicate hydrate-based brown component and black coal.

For the purpose of establishing the spatial-temporal collocation of the painting under examination, it is interesting to stop and consider the presence of lead in relation to the specific formulation of the drying oil used.

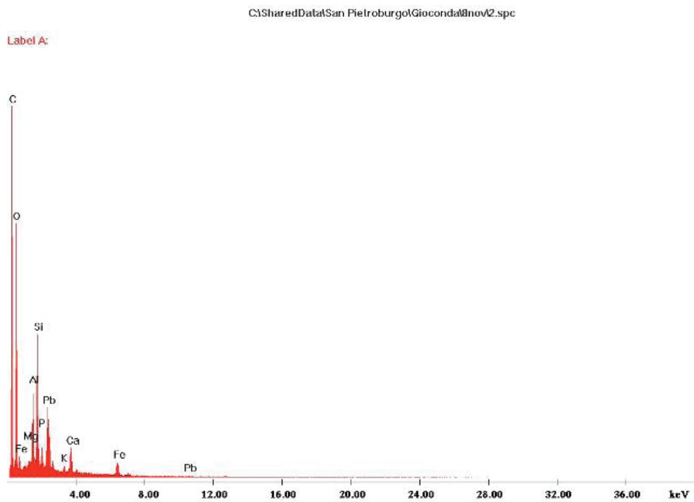


Figure 22. EDX spectrum of the primer

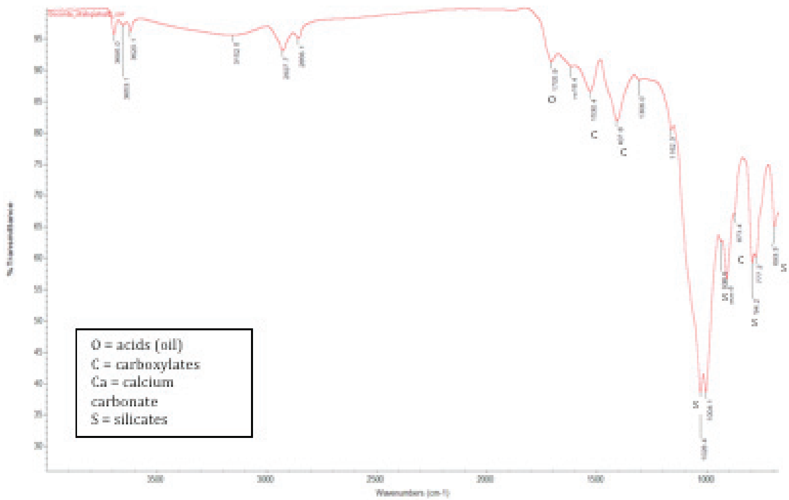


Figure 23. FTIR spectrum of the primer

As the color of the primer layer is yellow-brown, the application of the lead in the form of minium as a pigment (red - Pb_3O_4) can be excluded in favor of the hypothesis that it is litharge (yellow-orange – PbO) which is the drying agent in the oil.

It can therefore be assumed that the drying oil was made such by the addition of litharge, a practice indicated in a wide range of recipes [11].

4.4. Pictorial layer

• Diagnostic-analytical investigation

Identification of the pigments used by the author to execute the pictorial layer was carried out by means of x-ray fluorescence spectroscopy.

X-ray fluorescence spectroscopy allows the elements constituting the artifact, present even in traces, to be identified [12].

As this technology is non-destructive, investigation of the artifact in various points, was carried out, without any risk of damaging the work of art: it is evident that as there are a number of pigments present in the painting, it is necessary to repeat the measurements in different zones to gather any significant data. It must be mentioned however that the methodology poses several problems owing to the superimposition of the spectral lines and the fact that the acquired signals refer to several pictorial layers starting from the surface. Identification of the pigments was carried out through the reading of the spectral lines that correspond to the main elements.

Figure 24 shows the points examined.

The spectra obtained show a series of peaks which correspond to each element present. This instrumental technique allows the elements of the periodic table from atomic number 14 up to 92 [12] to be examined. It is also necessary to "purify" the graphs from the peaks of the elements that are always present, in trace amounts, or that are caused by external interference [12].

This refers to Ar (argon), present in the air, and to W (tungsten or wolframium) which is consistently present: this is because part of it is constituted by the instrument itself, while it is absolutely extraneous to the painting, except in minute quantities. Furthermore, calcium (Ca), iron (Fe), and lead (Pb) are also always present, because they are fundamental components of the preparation and the primer of the canvas. It is also necessary to point out that in almost all the paints analyzed varying amounts of copper (Cu) were found: often small quantities of copper-based pigments (a class of pigments that give a color from blue to green) are found in the dark shades of almost all colors, demonstrating the use of these pigments to darken the shade of the color. In addition, with regard to the flesh colored tones, it is presumed that the addition of small quantities of copper-based pigments were used by the author to cool down the paint [13-15]. We believe it is appropriate and significant to show in Figure 25 the XRF spectrum related to point 5 (shaded part of neck).

• Results

The following is a description of the results relating to the various selected points of the painting.

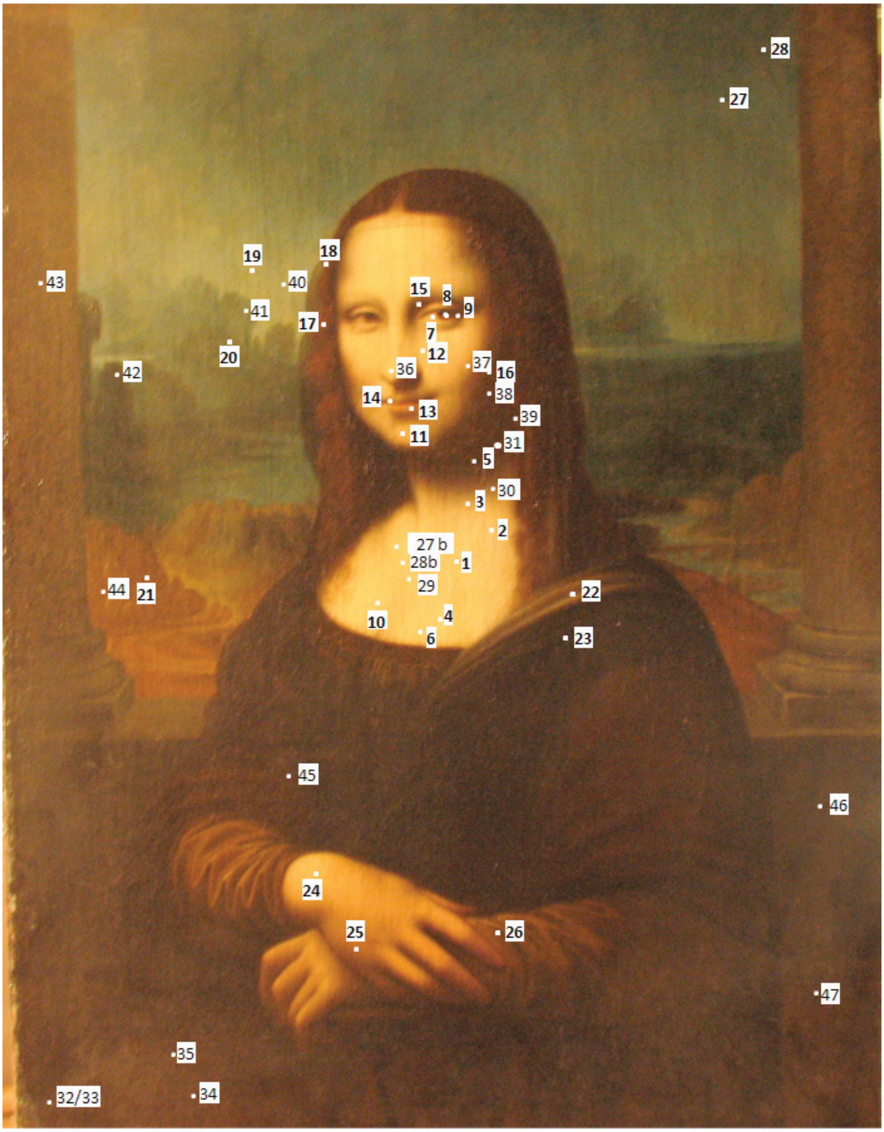


Figure 24. Points examined using x-ray fluorescence spectroscopy

► Light flesh tones

Two areas of the lighter flesh tones must be examined: that of the face and neckline. In fact a large part of the neckline has undergone major restoration work that has made it noticeably lighter than the flesh color of the face. In addition, the shadows in the center have disappeared to the point that the part that has been retouched lacks depth. The XRF analysis revealed, precisely in the part that has been extensively retouched the presence of chromium (Cr) and a consistent concentration of lead (Pb).

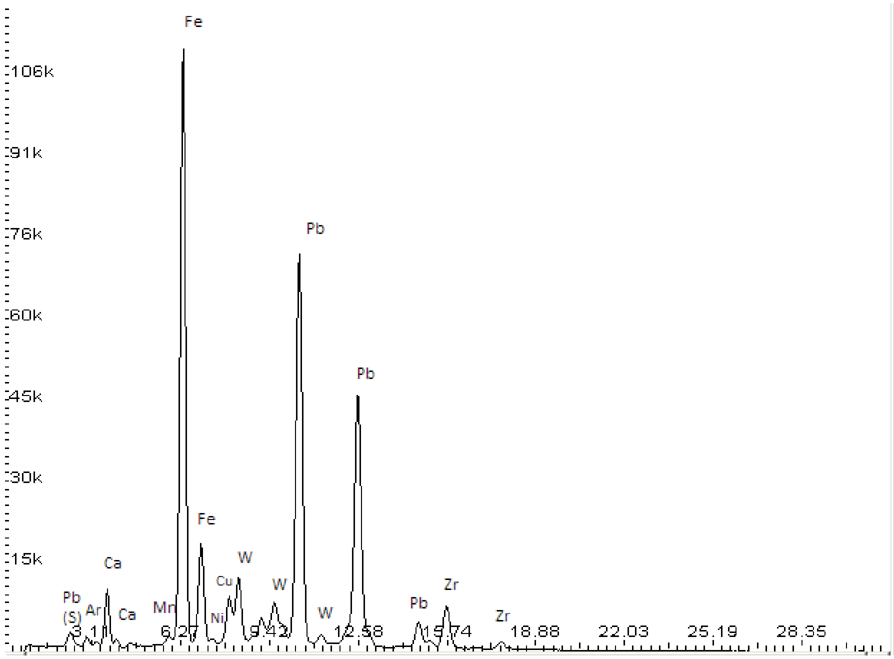


Figure 25. Sample no. 5 shaded part of neck (dark flesh tones)

The presence of chrome is undoubtedly related to the use of chrome yellow (lead chromate) in use since the beginning of the 1800s [12, 16-18].

The investigations carried out on the light flesh tones of the face are compatible with the results of the analysis conducted on the flesh tones of the neckline which have not been retouched: the color is the result of white and red. The white pigment is lead-based (Pb), while the red is definitely attributable to iron (Fe). It is deduced that the pigments used for the light flesh tones are constituted by red earth mixed with white lead ($2PbCO_3 \cdot Pb(OH)_2$).

► Dark flesh tones

According to the XRF analyses the dark flesh tones are obtained using an iron-based pigment (Fe) with percentages of manganese (Mn). Being unable to quantitatively estimate the amount of manganese (Mn), it can be assumed that burnt sienna or burnt umber mixed with white lead was used.

Traces of copper (Cu) were found in the composition of the flesh tones. The readings of the XRF analyses indicate that more copper (Cu) is found in the dark flesh tones. This suggests that copper (Cu) was used to create brown pigments also as a base for the light flesh tones and that to make the flesh tones darker the amount of copper (Cu) was increased.

► Lips

The red of the lips was obtained with an iron-based pigment (Fe) and presumably a red earth (ocher) mixed with white lead.

► Iris

The brown of the iris is obtained using an iron-based earth (Fe) with minimum percentages of manganese (Mn), diluted with white lead. Consequently, from the XRF analysis high quantities of iron (Fe), lead (Pb) and traces of manganese (Mn) are evident.

In this case too, a small amount of copper Cu was found, probably used for making the pigments darker.

► Pupil

The pupil above the iris was presumably executed using a carbon-based black which is not detectable using XRF technique.

► Sky

From the XRF analyses the presence of a copper-based pigment is evident in the color used for the sky. Based on the XRF data alone, it will be necessary to speak generically of copper-based green pigments, as this is the only heavy element in the context of the series of antique and modern green and blue pigments. From the analyses it emerged that the copper is not present below the column but on the contrary, in traces which are substantial at times in the portion represented by the mountains (reddish color obtained with Fe and traces of Mn) in the background. It may be assumed that the column and the sky were painted at different times, while the mountains were painted directly on the pictorial layer of the sky after it was completed.

The figure of the woman was also probably painted separately, at a different time to that of the sky and the columns.

► Hair

The color of the hair which to the naked eye appears of a reddish brown is obtained with an iron-based earth (Fe) with minimum amounts of manganese (Mn) diluted with white lead.

The XRF analyses therefore reveal a high quantity of of iron (Fe) and lead (Pb) and traces of manganese (Mn).

In this case too, a small amount of copper Cu was found which was probably used to make the pigments darker.

► Robe

The color of the robe was also obtained using an iron-based earth with small percentages of manganese (Mn) mixed with white lead. The XRF analysis therefore showed high quantities of iron (Fe) and lead (Pb) and traces of manganese (Mn).

In this case too, a small quantity of copper Cu was found which was probably used to make the pigments darker.

► Sleeve

The yellow color of the sleeve is obtained thanks to the use of an iron-based pigment (Fe), presumably ocher, diluted with white lead. It is believed that the appreciable amounts of calcium found, are attributable to the highlighting carried out using a white - *San Giovanni* - (calcium carbonate).

► Low wall and floor

In this case too, the browns were obtained using an iron-based earth (Fe) with minimum percentages of manganese (Mn) mixed with white lead. The results of the XRF analysis therefore show high quantities of iron (Fe) and lead (Pb) and traces of manganese (Mn). A small quantity of copper Cu was found which was probably used to make the pigments darker. In addition, it is evident how the pigment of the wall, darker than that of the floor, has a higher manganese (Mn) content than the brown used for the floor and the robe.

• Pictorial technique

For investigation of the painting technique, infrared reflectography was used, which enables the layer below that of the first pictorial layer to be observed and analyzed. For the areas of *sfumato* (shaded), spectrophotometric colorimetry was used to try to describe the pictorial technique employed by the artist to produce the chromatic effects [19-20].

The images in infrared reflectography, compared to those in the visible, obtained at different wavelengths (NIR1 – NIR2 – NIR3), did not reveal the presence of the preparatory drawing. From the images, however, the definition of a planned design is clear, which places the main forms into the figurative space (as in the case of the painting "La Gioconda"). It is evident how the author's need to define the individual figures and groups of figures in monochrome emerges, thinking primarily in terms of contour and tone, and then color.

Figure 26 below, shows a detail of the painting relative to the hands, using infrared reflectoscopy.

Figure 26. detail of the hands NIR4

As regards colorimetry, various points were considered as follows:1,2,3,4,5, where 1 is the flesh tone in full light, 2,3,and 4, are the *sfumato* flesh tones and 5 is the shaded flesh tone (Figure 27).

The luminosity L of these points was evaluated, the value along the a+axis (red), the value along the b+axis (yellow) and saturation C (Figure 28). The color of the *sfumato*, which originates from white, is made using a mixture of red and green colored pigments. The luminosity decreases proportionately from the lightest parts to the darkest parts through the use of continuous and numerous veils of pigments which provide poor coverage, a technique that produces a *sfumato* effect.

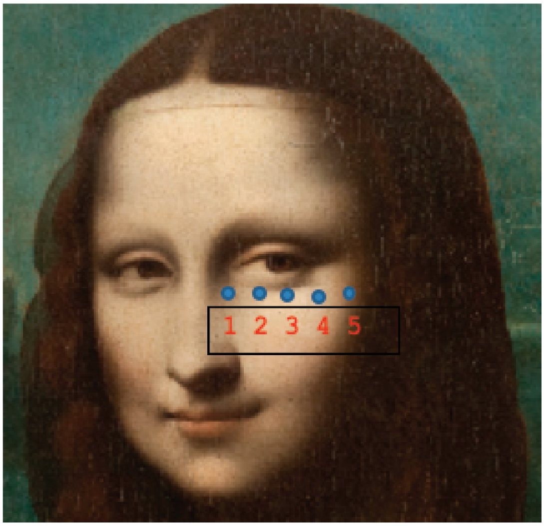


Figure 27. Points analyzed in spectrophotometric colorimetry

	L	a^x	b
1	54,3	7,96	22,11
2	53,15	7,60	21,17
3	50,44	7,63	17,58
4	45,77	7,02	16,8
5	30,80	3,16	7,06

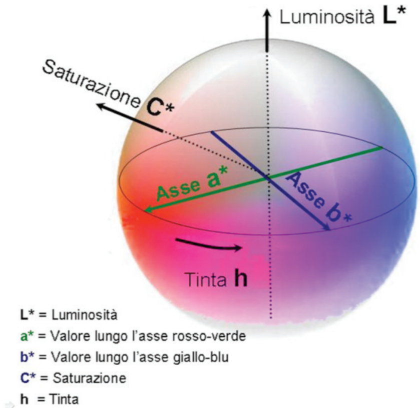


Figure 28. Colorimetric values of the flesh tones and colorimetric chart CIE-LAB

5. Conclusion

Based on the results of the diagnostic and analytical investigations carried out: textile support, preparatory layer, primer, paint layer/film, siccative oil and radiocarbon dating of the support, the following is a summary of the findings and considerations with regard to the different historical periods:

1) For the textile support, in the present case:

a) Linen cloth, the weave of which is coarse and irregular.

b) The size of the support is compatible with “standard” ones which were in common use from the first half of the 1600s in the Flanders area [21-22].

Moreover, in referring to historical sources relating to weaving over the centuries, it is to be noted that weaving was done producing linen cloth that was tightly woven, smooth and neat, using a light, fine yarn, throughout Europe from 1450. Towards the mid-1500s, the use of diagonal and herring-bone patterned weaving became widespread. In the 1600s the need for a rougher surface which was more suited to a faster denser paint, determined the appearance of cheaper and less accurately worked canvases, characterized by a coarse grained textured and looser weaving [22-23].

Consequently, if it is true that canvas was already used in 1450 [7, 17] throughout Europe, it is just as certain that during Leonardo’s life – from 1452 to 1519 [19]– it was not very widespread in Italy. This non-compatibility of historical periods is even more evident when considering the type of weaving which, in this case, due to its coarseness, leads us to consider a later period going from the mid-1500s on [19].

However, to this can be added further historical sources which unanimously state that Leonardo used wood as a painting support [24].

2) The technique using oil, found in our painting was little used during Leonardo’s lifetime, whereas the technique using tempera was more frequent.

3) The use of calcium carbonate in the preparatory layer is rarely found in Italy up to 1520-1530 and used very little even in subsequent periods, while it was commonly used in Northern Europe from the second half of the 1400s [25-26].

4) The use of the colored preparatory layer found in the work was first used from the 1500s [25-26].

5) According to a study carried out by Alain Duval on 155 coloured preparations of seventeenth and eighteenth century French schools, baryte is not considered an impurity associated with a compound, but it is hypothesized that it was instead added to pigments voluntarily. Baryte is often found together with pigments based on iron oxides. Thus it is believed that this product was introduced by a supplier of pigments. As the drying oil and the barium sulfate have a similar index of refraction, this latter has less covering capacity and is almost invisible. Consequently, Duval infers that a Paris supplier developed a product designed specifically for the preparations. The addition of barytes allowed merchants to reduce the expensive part of the pigment maintaining the desired quantity and color for the realization of the preparations. According to Duval’s study, in the period between 1620 and 1680 about 50% of the preparations taken into consideration contain barytes, while after this period its use is less frequent [17, 21].

6) The colored primer on top of the bole preparation was used from the second half of the 1500s [27].

7) The presence of litharge in siccative oil spread across Northern Europe from the end of the 1500s and later in Italy [28].

8) Radiocarbon dating of the textile support dated the work to between 1490 and 1670 with a probability of 93.1%: this dating includes the period of Leonardo's life and work, while the reading for the dating between 1520 and 1660 with a probability of 68.2%, excludes, instead, the period of Leonardo's life and work.

This information is illustrated in Figure 29, comparing the resulting time spans with the period of Leonardo's life.

It can therefore be demonstrated that this period does not essentially and significantly coincide with the previously mentioned time spans also because Leonardo, on the death of his patron Giuliano de' Medici in 1516 left Italy for good. In fact, in May of 1517 he was the guest of the French king, Frances I, in the castle of Clos-Luc, near Amboise. He was given the title of *premier peintre, architecte, et méchanicien du roi,* and received a pension of 5,000 scudos: this, therefore excludes, his activity in Italy [19, 29].

It is also a fact that he produced very little artwork in France, weakened as he was by old age and a possible cerebral thrombosis which paralyzed his right hand, whereas he was able to continue his studies and scientific research with passion and dedication [19].

In addition to the above considerations regarding the technique used in executing the work under examination, the following annotations are given related to several aesthetic-stylistic aspects:

- the face lacks the graphic elements of Leonardo's painting and early works in Leonardo's style [30-31];
- the painting is much too "soft" to belong to the period prior to 1500 [32];
- even though hazy and misty, the drawing of the landscape in the background is modest [33];
- the brush strokes are not very full-bodied and lack the thickness of color, often obtained by spreading the paint with the fingertips, which characterize Leonardo's landscapes.

As regards the execution of the landscape in particular, the comparison between our painting and that of the Mona Lisa in the Louvre is highly significant [34].

In the first the background is unclear and lacks depth, with a *chiaroscuro* that does not vibrate with luminous reflections and therefore devoid of the play of light and shadows, of that suffused brightness – dim light, enveloping atmosphere, almost dream-like from which the figures seem to emerge – typical of many masterpieces by Leonardo [29].

In the second however, the fluidity of the colors with the changeability of the shadows and the soft and shady *chiaroscuro* disperses the line, producing with the crumbling of the outlines, the atmosphere itself: that bluish darkness of the water and the sky, each relief vanishes, swallowed by the shadows [35].

Similarly in the work under examination, the flesh tones are less rich than those subtle vibrations of light and color, that merging imperceptibly, give depth to the shadows and the *sfumato* endowing it with the maximum expressiveness and the evocative power of Leonardo's painting [36].

In conclusion, on the basis of what the research findings have objectively demonstrated from a historical-artistic, technical-material and diagnostic-analytical point of view, it is possible to say that the oil painting "Gioconda with columns" is a copy of the "Mona Lisa (Gioconda)" by Leonardo, attributable to a period between 1590 and 1660.

Nevertheless, to complete the picture, the good workmanship, the readability and expressiveness emanating from the work must be taken into consideration, the execution of which is of Nordic derivation, in particular German-Flemish and is influenced by the French school [20, 37-41], due to the presence of barytes as an additive in the preparation [17].

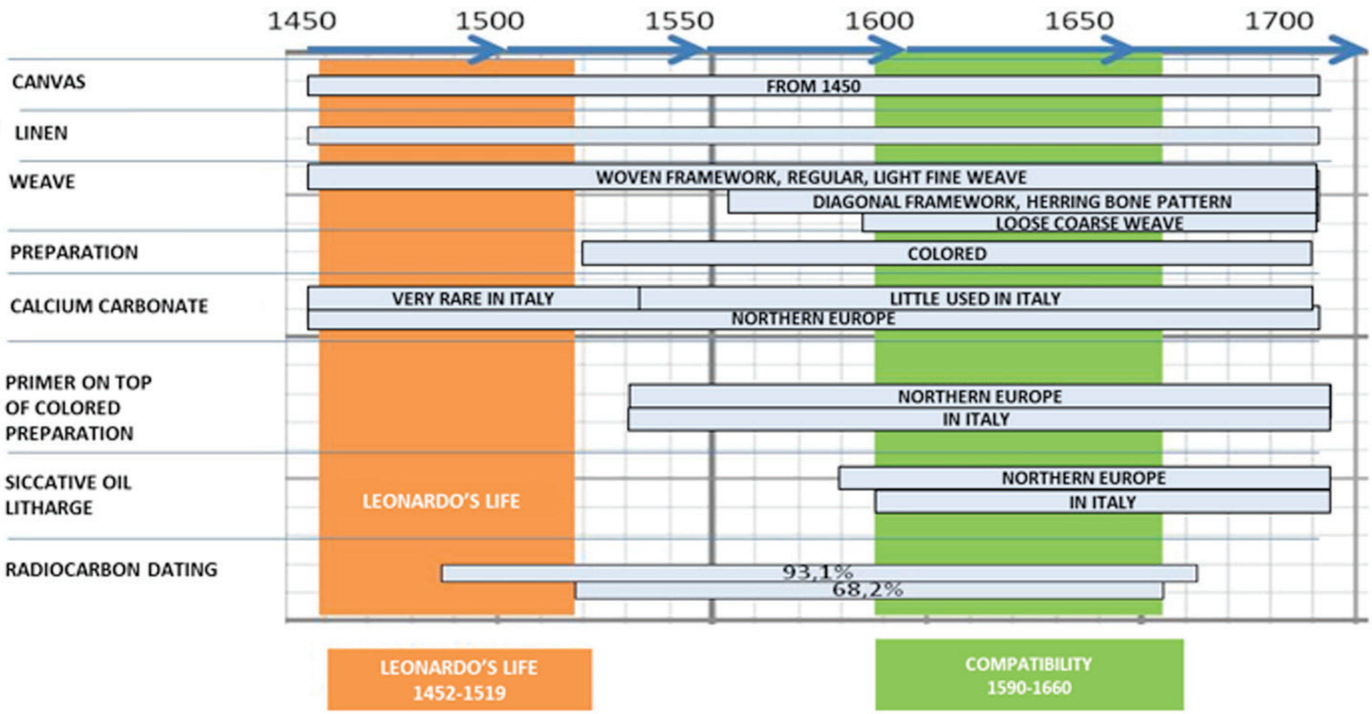


Figure 29. Temporal collocation of the work in relation to the period of Leonardo's life (in red) and possible compatibility with the temporal findings related to the analyses performed (in green).

Acknowledgements

We would like to thank Lucio Calcagnile, CEDAD (Centro di Datazione e Diagnostica), Dipartimento di Ingegneria dell'Innovazione, Università del Salento; Gianluigi Colalucci, Conservazione e Restauro, Torrimpietra (Roma), and Irene Bonacini, M2ADL (Microchemistry and Microscopy Art Diagnostic Laboratory), Università di Bologna, Ravenna campus.

References

[1] CONTI A., 1988, *Storia del restauro e della conservazione delle opere d'arte,* Milano

[2] PIVA G., 2007, *L'Arte del Restauro. Il restauro nei dipinti nel sistema antico e moderno,* Hoepli, Milano.

[3] FIORI, C., LORUSSO S., PENTRELLA L., 2003, *Restauro, manutenzione, conservazione dei beni culturali: materiali, prodotti e tecnologie,* Pitagora Editrice, Bologna

[4] BALDINI U., DAL POGGETTO P., 1972, *Firenze restaurata,* Firenze

[5] LORUSSO S., GALLOTTI L., 2007, *Caratterizzazione, tecnologia e conservazione dei manufatti tessili*, Pitagora Editrice, Bologna

[6] LORUSSO S., SCHIPPA B., 2001, *Le metodologie scientifiche per lo studio dei beni culturali*, Pitagora Editrice, Bologna

[7] VILLERS C., 1995, *Painting on canvas in fourteenth century Italy,* Zeitschrift fur kunstgeschighte, 58, III, pp. 338-358

[8] VILLERS C., 1981, *Artists' canvases*, Proceedings of the ICOM committee for conservation, vol. 2, pp. 1-12. Ottawa

[9] CENNINI C., 1971, *Il libro d'arte*, a cura di Brunello F., Vicenza

[10] ARMENINI G. B., 1979, *De' veri precetti della pittura*, Scritti d'arte del cinquecento, Torino,

[11] PERIERD'IETEREN C., 1985, *Colyn de Coter. Technique picturale des peintres flamands du XVe au debut du XVIesiecle*. Bruxelles, Lefebvre &Gillet

[12] SECCARONI C., MOIOLI P., 2002, *Fluorescenza X. Prontuario per l'analisi XRF portatile applicata a superfici policrome,* Nardini Editore, Firenze

[11] ROY A., 1999, *Painting in Antwerp and London. The National Gallery Van Dycks: Technique and development*, National Gallery Technical Bulletin, vol. 20

[13] VOLPATO G. B., 1967, *Modo de tener nel dipingere*, Original treatises, dating from the XIIlth to XVIIIth cent. on the art painting, vol. II. New York

[14] DUNKERTON J., ROY A., 1998, *Uccello's 'Saint George and the dragon' : technical evidence revaluated*, National Gallery Technical Bulletin, vol. 19

[15] RINALDI S., QUARTULLO G., et al., 1995, *La fabbrica dei colori. Pigmenti e coloranti nella pittura e nella tintoria,* Bagatto libri, Roma

[16] LORUSSO S., 2002, *La diagnostica per il controllo del sistema manufatto-ambiente,* Pitagora Editrice, Bologna

[17] RUDEL J., 1962, *Le probléme du support dans l'historie de la peinture,* L'information de l'historie de l'art, 7

[18] VASARI G., 1962-1966, *Le vite*, a cura di Della Pergola P., Grassi L., Previtali G., Milano

[19] LORUSSO S., NATALI A., MATTEUCCI C., 2007, *Colorimetry Applied to the Field of Cultural Heritage: Examples of Study Cases*, Conservation Science in Cultural Heritage, **7**, pp. 187-220

[20] LAZZARINI L., 1983, *Il colore nei pittori veneziani tra il 1480 e il 1580*, Studi veneziani. Ricerche d'archivio e di laboratorio 'Bollettino d'Arte', Roma
[21] MARTIN G., 1970, *Flemish school, 1600-1900*, National Gallery Catalogues, London
[22] DE MAYERNE T.T., 1995, *Pittura scultura e delle arti minori. 1620-1646*, a cura di Simona Rinaldi, De Rubeis, Anzio
[23] HENDRIKS E., GROEN K., 1994, *Double grounds of this type for* [1] *portraits on canvas continued in use in England until at least the late 1640s,* Hamilton Kerr Institute Bulletin, 2
[24] PAPA R., 2011, *Leonardo. La tecnica pittorica,* Art e Dossier n. 281, Giunti, Milano
[25] PEDRETTI C., 2005, *Leonardo. La pittura,* Art e Dossier n. 215, Giunti, Milano
[26] PLESTERS J., 1968, *Photomicrographs of cross-sections of paint and ground samples*, Museum, XXI, n. 4
[27] PLESTERS J., 1980, *Tintoretto's paintings in the National Gallery*, National Gallery Technical Bulletin, n.4
[28] FAILLANT DUMAS L., 1980, *Restauration des peintures,* Catalogo a cura di Bergeon S., Paris
[29] WOLFTHAL D., 1989, *The beginnings of nederlandish canvas paintings: 1400-1530,* Cambridge, 1989
[30] MARANI P. C., 2000, *Leonardo da Vinci. The complete paintings,* Harry N. Abrams, New York
[31] PEDRETTI C., LAURENZA D., SALVI P., 2005, *Leonardo. L'anatomia,* Art e Dossier n. 207, Milano
[32] LARRY K., ROY A., MORRISON R., SCHADE P., 2011, *Leonardo da Vinci's Virgin of the Rocks: Treatment, Technique and Display,* National Gallery Technical Bulletin, n.32
[33] DUNKERTON J., 2011, *Leonardo in Verrocchio's workshop: Re-examining the tecnica evidence,* National Gallery Technical Bulletin, n. 32, London
[34] PEDRETTI C., 1992, *Leonardo. Il disegno,* Art e Dossier n. 67, Giunti, Milano
[35] MOHEN J.-P., (a cura di), 2005, *Aucoeur de La Joconde. Léonard de Vinci décodé,* Centre de Recherche et de Restauration des Musées de France, Gallimard, Musée du Louvre éditions
[36] HENDY P., LUCAS A. S., 1968, *The ground in picture*, Museum, XXI, 4,
[37] ZÖLLNER F., 2007, *Leonardo da Vinci. Tutti i dipinti e i disegni,* Taschen, Köln
[38] SLATKES L. J., 1965, *Dirck van Baburen. A Dutch painter in Utrecht and Rome,* Utrecht
[39] COREMANS P., THISSEN J., 1961, *Het calvarie, drieluiktoegeschreven van Justus van Gent en de bijbehorendepredella. Samenstelling en structuur van der verflaag*, Bulletin, IRPA, IV
[40] PLAHTER L. E., PLAHTER U. S., 1983, *The Young Christ among the Doctors by Teodoer van Baburen*, Actaadarchaeologiam et artiumhistoriampertinentia, III

Biographical notes

Salvatore Lorusso is full professor in "Chemistry of the Environment and Cultural Heritage" at the Scuola di Lettere e Beni Culturali of the University of Bologna, Italy. He is Director of the Master in "Planning and promotion of artistic and cultural events", of the two book series' "I beni culturali e l'ambiente", and "La formazione e la ricerca nel settore dei beni culturali e ambientali" and the historical-technical Journal "Conservation Science in Cultural Heritage". He is the author of more than 370 publications in national and international journals and of 22 volumes covering various subjects and sectors, such as commodities, technology and environment, focusing in particular on the field of cultural and environmental heritage.

Chiara Matteucci has a degree and is a specialized technician-diagnostician at the Department of Cultural Heritage of the Alma Mater Studiorum University of Bologna. She works extensively in the field of analytical-diagnostic investigations involving artifacts from different areas of interest: artistic-historical, archaeological, archival-library and music. Her work is carried out in the Diagnostic Laboratory for Cultural Heritage in the Department of Cultural Heritage of Bologna University, Italy.

Andrea Natali is professor at the Scuola di Lettere e Beni Culturali and a Research Fellow at the Department of Cultural Heritage of the Alma Mater Studiorum University of Bologna, Italy. His teaching and scientific work are carried out in the field of conservation and valorization of cultural and environmental heritage, authentication of works of art, art diagnostics and monitoring of the conservation environment.

Salvatore Andrea Apicella has a degree in "Diagnostics and restoration". He works in the Department of Cultural Heritage of the Alma Mater Studiorum University of Bologna, Italy.

Flavia Fiorillo has a Master degree in "Science and technology for conservation and restoration".