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Imaging and spectroscopic data combined to disclose the painting techniques and materials in the fifteenth century Leonardo atelier in Milan

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ABSTRACT

The project “Leonardesque Artists beyond the Visible” was planned on the 500th anniversary of the death of Leonardo da Vinci, with the occasion of an exhibition held in Milan in 2019, where more than twenty works made by Leonardesque masters have been put on display. Among them, five representative paintings made by his closest pupils were selected for a comprehensive and multidisciplinary project. Portable non-invasive imaging and spectroscopy techniques were applied to supply useful information to scholars but also to the wider public: description of the material composition of the pigments, of the preparation and of the binders, existence or absence of underdrawing, and identification of the painters’ technique and style. Particular attention was paid also to the image processing techniques, mostly for hyperspectral and radiographic data, to get the most from both innovative and traditional techniques.

Results highlighted for each author a peculiar painting technique showing hidden features such as *pentimenti* and the panel preparation methods, pigments, binders and varnishes.

1. Introduction

2019 marked 500 years since the death of Leonardo da Vinci and in Milan, where he worked for 17 years, major exhibitions were dedicated to his life. One of them was held at the Poldi Pezzoli Museum (7 Nov 2019–10 Feb 2020): “Leonardo e la Madonna Litta” (Leonardo and the Litta Madonna), an exhibition focused on the temporary comeback of one of the most famous masterpieces from the State Hermitage Museum to the city where it was painted. Together with this masterwork, a selected group of twenty paintings and drawings borrowed from both public and private collections all around the world was on display. They were all painted by Leonardo and his closest pupils in the last two decades of the 15th century when the *maestro* lived in Milan at the court of Ludovico il Moro. In fact, during these Milanese years, Leonardo da Vinci was the Master of a large workshop: in the final decade of the fifteenth century, the great amount of commissions determined the need of a fair number of assistants. The atelier became a well-established model for important artistic production, involving painters such as Marco d’Oggiono, Giovanni Antonio Boltraffio and Francesco Napoletano, three of the oldest pupils present in Leonardo workshop since about 1490, creators of significant works that helped disseminating Leonardo’s innovative style.

Leonardo and the la Madonna Litta appealing event took place as a part of the national celebrations promoted and supported by the Italian Ministry of Culture, thanks to the patronage of the Regional Government of Lombardy, the Municipality of Milan, and the Bracco Foundation, which also funded the diagnostic project “Leonardesque Artists beyond the Visible”, launched in this context. The project was planned in close

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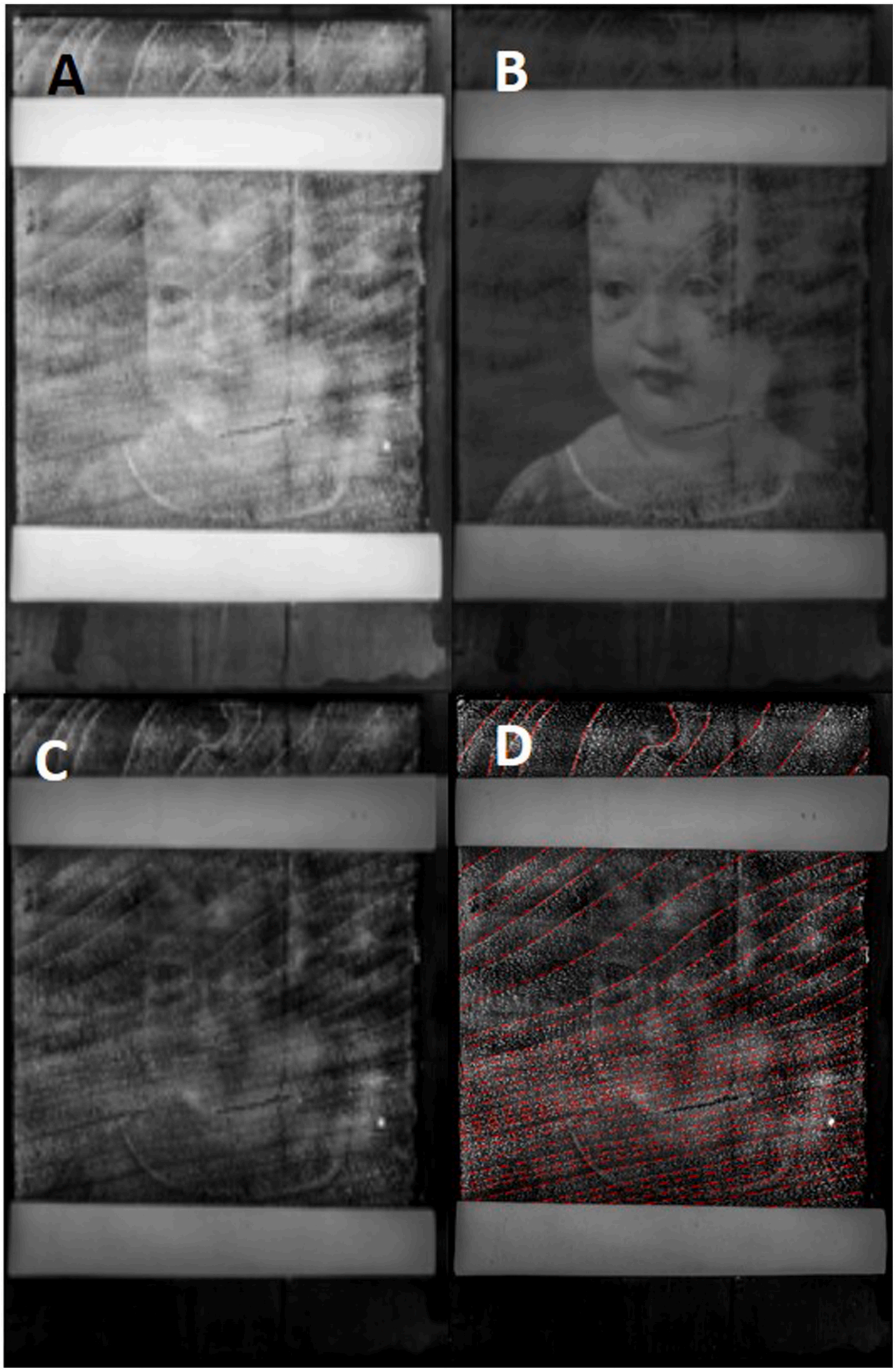

Fig. 1. A) RX image; B) RX elaborated image highlighting the radiopaque layer of imprimitura; C) RX elaborated image D) eye-guide for the original wood panel.

relation with the exhibition itself, promoting relations between science and art, and was centered on a selection of paintings by some of the earliest pupils of Leonardo. In collaboration with art historians, conservators and restorers, it was possible to define a specific protocol of measurements and data analysis in order to achieve as large as possible information.

A series of diagnostic analyses has been carried out under the coordination of the CNR Istituto di bioimmagini e Fisiologia Molecolare in cooperation with Università di Milano, Università di Milano-Bicocca, and the innovative spin off of Scuola Universitaria Superiore (IUSS) from Pavia –DeepTrace Technologies S.R.L. The Physics technologies applied to the study of paintings are widely regarded to give useful information to experts in the field, but also to the wider audience. Besides supplying the mere description of the pictorial material composition and the possible existence of preparatory drawing, if guided by specific questions, Physics technologies can help the identification of the painters' technique and style.

Although the consolidated use of limited materials, typical when dealing with Renaissance products of workshops, the rendering technique could vary greatly, from the wooden support to the preparation, *imprimitura* and pigment layers with different types of binding media and varnishes. Moreover, underdrawings and possible drawing transfer methods by means of cartoons can explain and reveal multiple information to cast light on the reconstruction of the story of a painting, especially in relation with the rest of the workshop production. Conveniently integrated with historical and documentary analysis, imaging and spectroscopic analyses have today the acknowledged – though not exclusive – role of favouring the understanding of processes and materials used for the execution of a pictorial work, by an interdisciplinary, non-destructive, non-invasive approach, and help the experts in responding to key questions, not only about the conservation and restoration of the work, but also about its interpretation. In spite of the growing interest around Leonardo, systematic studies through physical and chemical analyses are still not so many [1–13].

To this purpose, the project planned non-invasive scientific investigations, in accordance with a suitable protocol applied to all the paintings. The measurements and data analysis were chosen to be synergic and complementary and innovative data handling was applied, as detailed in the following sections. The experimental protocol was wider with respect to the previous ones applied in similar works, already quoted above, and allowed to completely characterize the works studied from a technical point of view. The art-historian experts were thus offered objective information, useful for establishing the best conservation practice and to support their evaluation and critical interpretation, as evident in the artwork records in the exhibition catalogue [14]. Nonetheless, the same analyses have been a perfect training for new technical and methodological developments in the Heritage Science, and a springboard for challenging developments. The research had also the benefit of being part of the exhibition itself, allowing visitors to discover the hidden features of the analysed paintings trough video contents expressly produced.

2. Materials

The analyses presented in this paper were performed on five easel paintings during the conservative works prior to the exhibition “Leonardo e la Madonna Litta”. The masterpieces selected for this project, all by Leonardo pupils, are part of Poldi Pezzoli Museum collection or were borrowed to the Museum on the occasion: *The Virgin and Child* (The Madonna of the Rose) by Giovanni Antonio Boltraffio (see Fig. S1a in supplementary materials), *The Virgin feeding the Child* by an unknown painter of the Lombard school (see Fig. S1b), and *The Christ Child* by Marco d’Oggiono are all held by the Poldi Pezzoli Museum in Milan (see Fig. S1c). *The Virgin and Child* (see Fig. S1d) by Francesco Galli, known as Francesco Napoletano, is held by the Brera Art Gallery in Milan, and *The Virgin and Child* (see Fig. S1e) by unknown painter of the Lombard school is property of a large private collection.

3. Methods

All the paintings were studied *in situ*, either at the owner institution or, in case of restoration still in progress, in the restorer working space. The goal of the research was to give art historians and restorers as much information as possible and to highlight the painting technique, in term of underdrawing, panel preparation and reconstruction of the pictorial techniques. With this aim, besides the pigments used, we also tried to propose a stratigraphy sequences of pictorial layers. We performed different analytical techniques, namely imaging investigations [15–17] and pointwise spectroscopic analyses for both material and stylistic characterization. We thus inferred the kind of materials (pigments and binders) and how the painters used them in the studied masterworks. Moreover, although microscopic cross-section analyses were strictly avoided in the current project, the possible stratigraphy was deduced from the applied techniques, exploiting different wavelengths and having different penetration depth [18–21]. Indeed, ED-XRF (Energy Dispersive X-Ray Fluorescence), FORS (Fiber Optics Reflectance Spectroscopy), Raman and Fourier Transform Infrared (FTIR) punctual analyses have already proved to be more effective when applied in synergy [22]. The association of these four techniques makes it possible to overcome the limit of each one and to detect all class of pigments (organic, inorganic, dyes …) and to recognize pigments having the same characterizing elements, but different chemical formula. The different penetration depths of the primary sources allow to infer, in the simplest cases, the stratigraphy without any sampling [18,23,24]. In fact, X-rays penetrate deeply into the matter, usually crossing the complete pictorial stratigraphy; outgoing characteristic X-ray fluorescence of medium-heavy elements can still pass the whole thickness, while relatively light element X-rays (such as Ca and K) have a higher probability to be absorbed, giving an incomplete information about the lowest layers, often made by gypsum. Besides, FORS is a powerful technique for surface pigment characterization, but it undergoes difficulty in spectra interpretation arising from possibly altered surface (presence of dust, yellowing or old varnishes) or complex mixtures and dark shades [18, 25]. Micro-Raman spectroscopy is a technique of choice for painting analysis [26] because it allows a rapid, unambiguous and *in situ* non-invasive approach for the examined objects. Since Raman spectroscopy probes molecular and crystal lattice vibrations, it is sensitive to the composition, bonding, chemical environment, phase and crystalline structure of the examined material and therefore it is able to unambiguously identify the majority of the pigments; furthermore its spatial resolution allows discrimination among different chemical components in pigment mixtures and the measurements are free from interferences, except for the fluorescence due to binding media and/or varnishes [27]. Although the vibrational information obtainable by Raman spectroscopy is similar to that obtained by infrared spectroscopy (IR), they are not identical but rather complementary due to the different selection rules governing vibrational Raman scattering and IR absorption [28]. When applied in the laboratory, Fourier-transform infrared (FTIR) spectroscopy offers a fast analysis of micro-samples and is able to provide information on the nature of the organic and inorganic materials used by an artist. Its application in a non-invasive manner requires measurements to be performed in the reflection mode and, even if several examples of such application are reported in the literature, it still deserves further exploitation. Of particular interest is the different penetration depth that can be achieved in the medium-IR (MIR) and in the near-IR (NIR) regions. Indeed, NIR can penetrate more than MIR due to its higher energy, thus enabling a greater depth to be reached then in MIR, where only a few micrometers are possible. Thus, in principle, by acquiring IR spectra from MIR to the longer-wavelength portion of NIR it is possible to probe a layered structure from the surface to underlying layers. In addition, thanks to the smaller absorption coefficients, good quality reflection spectra on undiluted materials can also be obtained. Finally, it is well known from the literature that NIR spectra are particular suitable for identifying organic binders in paintings [29]. On the imaging analyses side, UV induced fluorescence investigates the very superficial pictorial layer while IR radiation can reach deeper layers up to the preparation or *imprimitura*. Furthermore, the use of a multispectral IR reflectography approach allows to differentiate the pigment transparency and highlights specific features related to the drawing technique [30]. X-ray radiography, given the nature of X-rays to penetrate deeply into the matter, provides information about the spatial distribution of heavy materials in every layer of the painting and the support. However, the information is presented in a single 2D image, making it difficult to separate the information related to each layer. In order to extrapolate the contribution of each layer, statistical calculations based on iterative subtractive method were applied through comparisons between the images of the pictorial layer (obtained in the visible spectrum) and the corresponding radiographic images. These statistical algorithms allowed to separate the radiopaque image of the pictorial layer from those belonging to lower layers (materials of preparation plus support).

Data analysis method applied to the hyperspectral $H(x,y,\lambda)$ results allowed to take into account the similarity of each hyper spectrum with the other ones by means of supervised classification procedures, such as Spectral Angle Mapper (SAM) [31–33]. The « end-members » have been chosen by referring to spectroscopic data; the result is a stack of images, I(x,y,α), where the value of each pixel represents the angle, α, between the spectrum identified by (x, y) and the end member.

3.1. Experimental setups

3.1.1. High resolution multispectral imaging

The photographic system consisted of digital back Phase One IQ3, with 'Trichromatic' (100 MP) detector, able to detect radiation from 350 to 1000 nm. For all the acquisitions a Schneider Kreuznach 120 mm LS f/4.0 Macro lens was used in combination with different filters and light sources to select the appropriate wavelength range for the investigation.

3.1.2. Visible-reflected (Vis) image

For the acquisition of this images, a UV-IR cut filter was used mounted on the lens of the device described above. For the lighting were used 2 halogen lamps, maximum power 150 W with a condenser lens to optimize direct lighting of paintings and to reduce surface heating.

3.1.3. Ultraviolet-induced (UVF) fluorescence

Together with the UV-IR cut filter, a 418 nm long-pass filter was applied to the same device. For the lighting two 3 W 365 nm LED light were used in a completely darkened room.

3.1.4. Near infrared (NIR) reflectography (850–1000 nm)

Two 150 W incandescent lights with an 850 nm long pass filter mounted on the lens of the device were used.

3.1.5. Infrared False Color (IRFC) imaging

Vis and NIR image were combined using the green and red channel of the Vis image, shifted respectively to the blue and green channel of the IRFC image, and the NIR image was used shown in the red channel.

3.1.6. ShortWave infrared (SWIR) reflectography (1000–1700 nm)

This technique has been performed with a new portable scanning system prototype based on a spherical scanning system [34] successfully used in previous important scientific campaign [35]: an InGaAs camera (Xenics Xeva- 1.7-640, 640 × 512 elements, spectral sensitivity: 1000–1700 nm) was mounted on a motorized head that allowed precise and small movements (0.01° resolution for the rotations and 0.1 mm for the linear stage). For all the multispectral acquired images the resolution was of 20 pixel/mm.

3.1.7. Images in visible light with optical microscope

A digital optical microscope AM4013MZ with polarizing filter (5 MP, 220×, magnification) was used to obtain magnified images in the visible range.

3.1.8. Hyperspectral imaging in the range 400–1000 nm

Hyperspectral imaging was performed using a Specim IQ spectral camera. It employs the push broom method [36] measurements of a scene made by scanning line-by-line across a spectral range of 400–1000 nm, thereby capturing the spectral information for each line of the scene across that spectral range. Across that spectral range, there are 204 binnable bands, partially overlapping, at 7 nm resolution. It is able to produce a square image of 512 × 512 pixels, each 17.58 μm × 17.58 μm in size.

For the lighting, a system of 2 halogen lamps, with maximum power 150 W, condenser lens to optimize direct lighting of paintings and to reduce surface heating, was used.

3.1.9. X-ray radiography data processing

To get the most from X-Ray radiography, images already acquired were elaborated to improve the signal to noise ratio; techniques to augment contrast through the application of filters, segmentation of region of interests, and extraction of characteristics useful for comparisons were applied.

3.1.10. X-ray fluorescence spectroscopy (XRF)

Assing LITHOS 3000 portable spectrometer was used, with quasi monochromatic excitation at 17.4 keV, obtained with a transmission Zr filter (100 μm thick) mounted on a Mo target X-ray tube, giving a 4 mm radius of analysis on the samples. The transmission filter allows to minimize the background at low energies, avoiding the scattering of incident radiation from the elements of the substrate. In fact, Compton scattering could be quite important also at relative low energies for light matrix materials. The system was equipped with a Peltier-cooled Si-PIN detector, area of circular measurement (d = 5 mm). X-tube typical working conditions were 25 kV and 300 μA and the measuring time was about 30–60 s. The efficiency of the handheld spectrometer is low for elements with $Z < 17$. For each studied painting, please refer to the Supplementary Materials Section for the location of analysed points. (Fig. S1a, S1b, S1c, S1d and S1e).

3.1.11. Fibre optic reflectance spectrophotometry (FORS)

A portable Vis-NIR spectrophotometer (HR4000, Ocean Optics Dunedin, FL, USA) was used for FORS analysis, with a linear array, 360–1100 nm, 2.7 nm spectral resolution with a 45°/45° geometry of measurement and a detection area of about 2 mm^2. The spectrophotometer was connected to a tungsten halogen light source (D65, HL2000, Ocean Optics): light is transmitted through a quartz fiber optics bundle 1.5-m-long (Ocean Opticts), composed by six fibers (400 μm each), to collect reflected light around the single central illuminating fiber (400 μm). 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. For each studied painting, please refer to the Supplementary Materials Section for the location of analysed points. (Fig. S1a, S1b, S1c, S1d and S1e).

3.1.12. Raman spectroscopy

Micro-Raman analyses have been performed by a compact portable Raman spectrometer I-Raman Plus BW Tec, with fibre optic configuration. The probe has a flexible fibre coupling encased in a protective jacketing material that performs Rayleigh scatter rejection as high as 10 photons per billion.

It was fixed to a xyz stage for micrometric positioning and the latter placed on a tripod. A diode laser emitting at 785 nm was used; the power at the sample was about 5 mW, the spectral range of our measurements was 200–3000 cm^{-1}, while the spectra resolution was about 3–5 cm^{-1}.

The TE Cooled Linear Array detector (2048 pixel; pixel size 14 μmx200 μm) was cooled by means of a Peltier device.

All spectra were obtained as a sum of 20 accumulations with an exposure time of 4 s for each accumulation. Raman spectra were analysed as obtained and the identification of compounds was performed comparing the spectra recorded on the painting with the ones belonging to our personal database of Raman spectra or to libraries available in the literature [37,38]. The database was created recording the Raman spectra on pure pigments and on reference paint samples prepared ad hoc. For each studied painting, please refer to the Supplementary Materials Section for the location of analysed points. (Fig. S1a, S1b, S1c, S1d and S1e).

3.1.13. Fourier-transform infrared spectroscopy (FTIR)

A portable FTIR spectrometer Alpha Bruker equipped with an accessory for reflection measurements was used to acquire spectra from 7000 to 400 cm^{-1}. Each spectrum was recorded as sum of 200 scans, with 4 cm^{-1} resolution. The diameter of the measurement spot was 6 mm.

First-derivatives of the NIR spectra were calculated by using Grams AI (Thermo Fisher) software. The Savitsky-Golay algorithm was used, with polynomial degree 2 and number of points from 16 to 33, according to the noise level of the spectra.

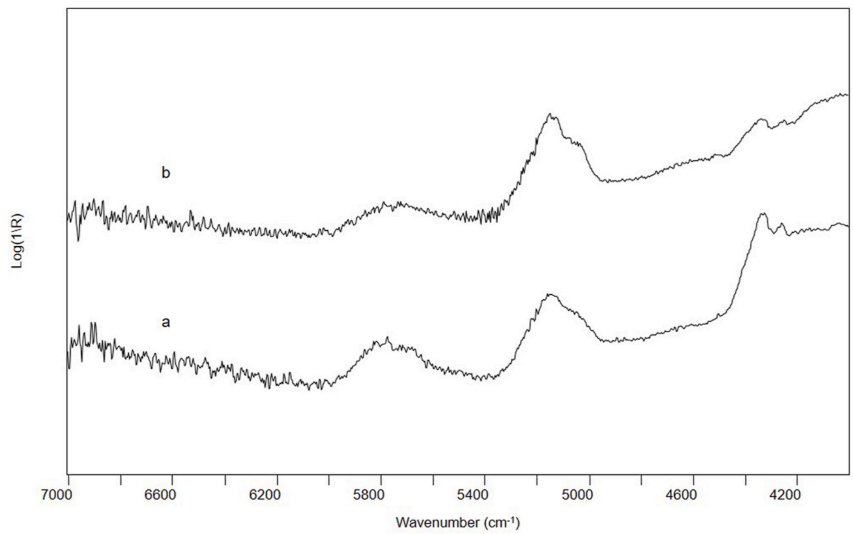

Fig. 2. FT-NIR reflection spectra of (a) area 2 and (b) area 3 of the painting "Virgin and Child" by G. Boltraffio.

3.1.14. Fluorescence spectroscopy

Just on some red details of one of the paintings, namely the Virgin and Child by Francesco Galli, fluorescence spectra were acquired with visible excitation at 435 nm. The proper excitation wavelength was obtained from the emission of a halogen source (maximum power 150 W) by an interference filter. The radiation was focused on the measurement area by a 20× microscope objective and the emitted radiation was collected through the same objective. A dichroic filter, with 458–680 nm transmission range, was used to eliminate the reflected incident radiation. The spectrum was acquired by a Lot Oriel MS125 spectrometer equipped with a Peltier-cooled Andor CCD detector. Both the source and the spectrometer were connected to the microprobe by fibre optics.

For each studied painting, please refer to the Supplementary Materials Section for the location of analysed points. (Fig. S1a, S1b, S1c, S1d and S1e).

4. Results and discussion

The various issues discussed in the following represent a detailed catalogue of the techniques and materials used for the paintings, including a comprehensive discussion of the panel, preparatory layers, pigments and binding media, obtained not only from the non-invasive analyses but also from the application of image-processing algorithms. The summary below is intended to draw out some particular points and comparisons, as well as more general observations on the group of paintings considered here; although we studied panels of the same workshop, we found typical and different methods of realizing the artworks, from the panel to the upper paint layers.

4.1. Wood panel

All the paintings in this study are on panels and, in one case, it was possible to identify the wood species starting from radiography. It is important to highlight that, in many cases, the radiographic images are not clear due to thickness of the preparation or *imprimitura* and the wood thickness with respect to the pigment layer where the X-ray absorption is far less. To overcome this issue, all radiographic images were elaborated to extract important features from distinct layers that would not otherwise be visible through traditional methods. For *The Christ Child* panel, by Marco d'Oggiono, the radiographic image (Fig. 1A) was elaborated with iterative calculations of statistical probability using the comparison between the visible image and the radiographic image, in order to separate the radiopaque image belonging to the Christ Child (Fig. 1B) from the one belonging to the wooden support (Fig. 1C–D). As a first step of the procedure, mathematical processes - such as gaussian filtering, aimed to reduce image noises, and co-registration - were applied for a correct overlap of the radiographic image and the visible image, a necessary step for making local comparisons between the information provided by the two images. Secondly, statistical algorithms based on Bayesian filters were applied to separate radiopaque signals belonging to the different layers of the painting. The algorithms implemented were specially developed for the elaboration of this peculiar panel's images by the start up DeepTrace Technologies. In Fig. 1A, we can note the use of two different kinds of wood for the upper-median portion and the lower portion of the panel. The wood of the upper-median portion, better extracted by the radiography elaborations (Fig. 1C–D), shows parallel fibres differently from the wood structure visible in the lower part, which is to be attributed to an intervention made before 1836 [14], that added about 3 cm to the original project designed by the author.

From the literature, it is also possible to deduce information about *The Virgin and Child* (*The Madonna of the Rose*) by Giovanni Antonio Boltraffio. During the restoration carried out ten years ago [39], it was found to be painted on a single panel of walnut, 8 mm thick. It seems to have been a typical choice of painting support in Milan in the 1480s and 90s, when this wood was also widely used for furniture.

For the other three paintings, it was not possible to identify the type of wood used and the character of the grain as seen by eye on the reverse suggests that it might be oak for both the Virgin and Child paintings attributed to the Lombard school.

Even if Leonardo, in his Codex A of 1492, does not mention oak, nor poplar, as species used for paintings (but instead lists cypress, walnut, whitebeam and pear wood) oak is known to be the support he used for his French paintings while poplar was the most common wood used for panels during this period, generally speaking of Italian painters [4].

4.2. Ground preparation and priming

The panel support of *The Virgin and Child* by Boltraffio has been prepared with a layer of gesso mixed with a siccative oil. This preparation has been deduced from the comparison of XRF and FTIR experimental data. XRF detected in all the analysed points (Fig. S1a) the presence of calcium among the minor elements; this is probably due to its presence in a deep layer, which leads to the absorption of its k_α and k_β lines (respectively at 3.691 keV and 4.013 keV). Moreover, in the NIR range (7500-4000 cm^{-1}) for all the analysed areas (Fig. S1a) it was possible to observe at 5140 and 6920 cm^{-1} the bands of gypsum $CaSO_4 \cdot 2H_2O$ [40], hypothetically associated with the preparation layer

Fig. 3. Panel a, on the left, UV image of the Virgin and Child by Boltraffio; panel b, on the right, RX of the Virgin and Child by Boltraffio.

Fig. 4. RX of the Virgin feeding the Child by an unknown painter of the Lombard school.

of the panel (Fig. 2). It is interesting to note that in area 3 (Fig. S1a), which on the basis of UV analysis appeared to have been restored (Fig. 3), the gypsum signals are significantly stronger than those of the binder.

A priming consisting largely of lead based pigment has been applied: the presence of white lead can be surely inferred, but former invasive analyses also detected the presence of small amounts of red lead and lead-tin yellow [39].

As already observed by restorer Carlotta Beccaria in her paper [39], this priming layer appears to have been applied with the painter's hands, mostly by the palm hands, to spread it onto the surface. In the x-ray image are in fact evident areas in which there is a non-uniform accumulation of priming layer (see Fig. 3b).

The preparation of the panel with gesso and the presence of a priming layer with the addition of earths/ochre have been also observed in the two *Virgin and Child,* both in the one by Napoletano and in the other by the unknown painter of the Lombard school.

Different are the cases of the Christ Child by d'Oggiono and the Virgin feeding the Child by an unknown painter of the Lombard school. For the latter panel, no evidence of preparation was found: neither XRF detects calcium, neither Raman nor FT-NIR spectroscopies individuate the typical bands of gypsum. Moreover, the priming seems to be layered with the same technique used by Boltraffio in *Virgin of Rose*: the X-ray image (Fig. 4) shows areas with different density distributed as leopard spots.

Also in the case of *The Christ Child* by d'Oggiono, no gypsum preparation was observed, except in the lower part of the painting that was in fact added later, as already pointed out, probably in the 19th century, to enlarge its size.

4.3. Underdrawing

The heterogeneous procedures for realizing the considered artworks is confirmed by the study of underdrawings. Through the high-resolution reflectographic investigation, carried out using the InGaAs scanning system described above, it was in fact possible to detect the presence of underdrawings in all the investigated panels owing to the good penetration into the paint layers. In Fig. 5, an overview of the five panels and their representative underdrawings is shown. As a basis for comparison, the drawing of the hand was selected, except for *The Christ Child* panel where a detail of the Child face is shown (Fig. 5c). A fluid carbon based medium applied with brush was found for *The Virgin feeding the Child* (Fig. 5a) and in *The Madonna of the Rose* (Fig. 5d) and Napoletano's painting (Fig. 5e) where the drawing is particularly bold

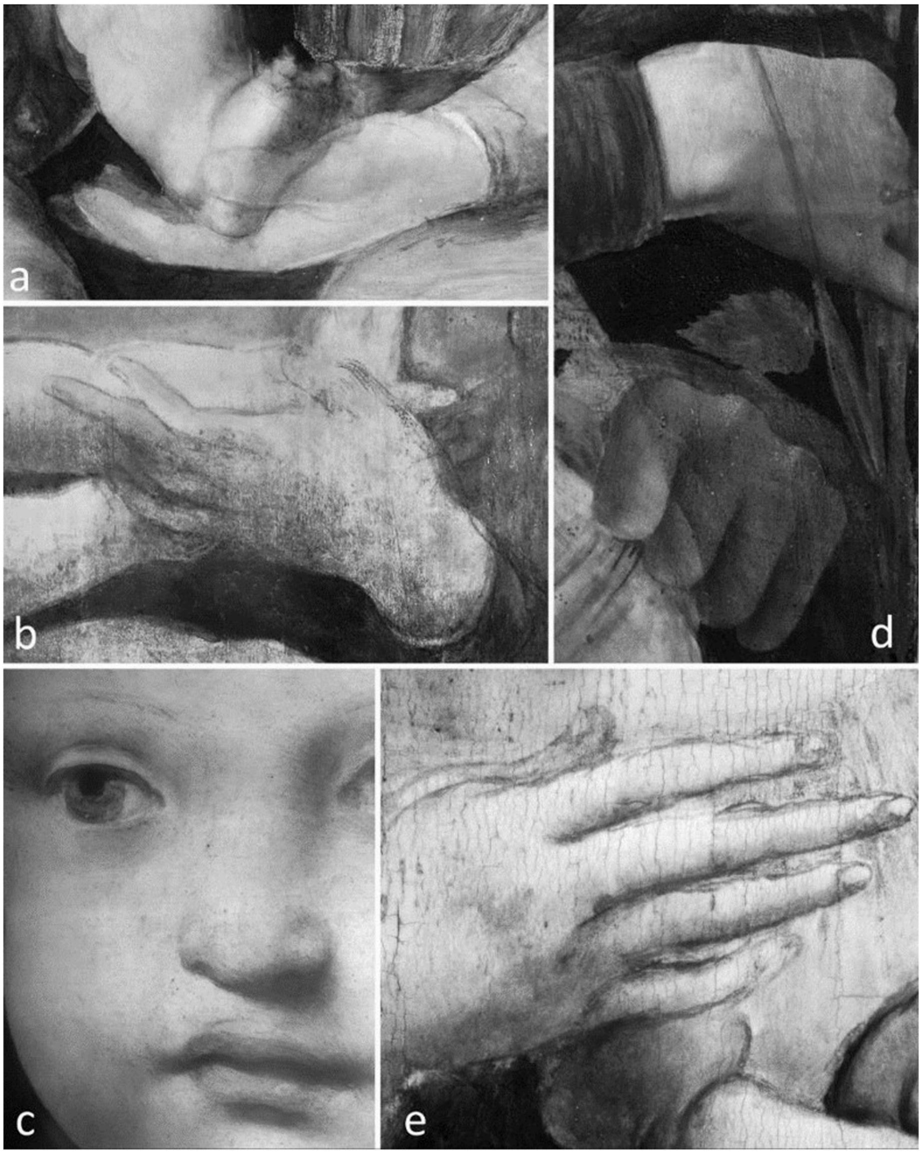

Fig. 5. Representation of the different types of underdrawing found in the five panels under investigation. a) A fluid carbon based medium applied with brush was found for the Virgin and child d) in the Madonna of the Rose and e) for the Napoletano's painting where the drawing is particularly bold and free. For the c) Christ Child by Marco d'Oggiono a thin dry material trace was used to define the face elements, with the presence of a fine and detailed hatching for the shadows. In the Virgin and Child of the Lombard school b) a dry material was also used for the underdrawing.

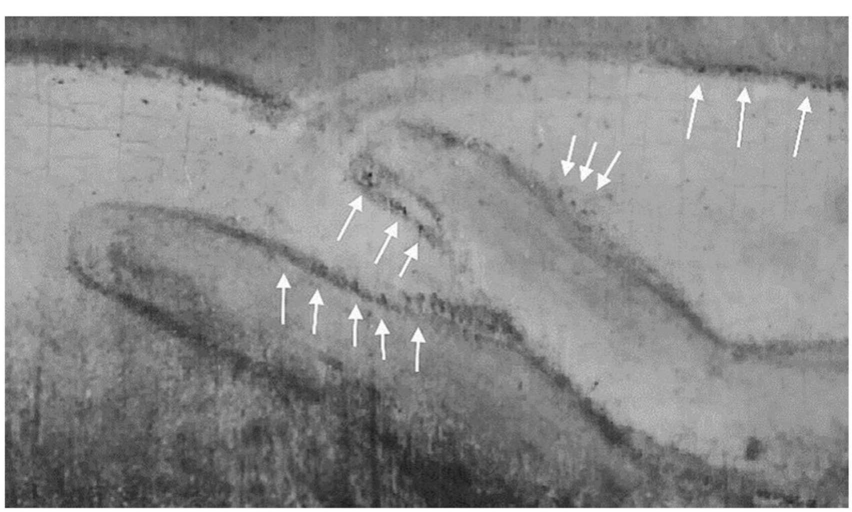

Fig. 6. Detail of the reflectogram for the Christ Child by Marco d'Oggiono: possible and limited traces of pouncing were found in correspondence of the fingers of the Virgin (white arrows).

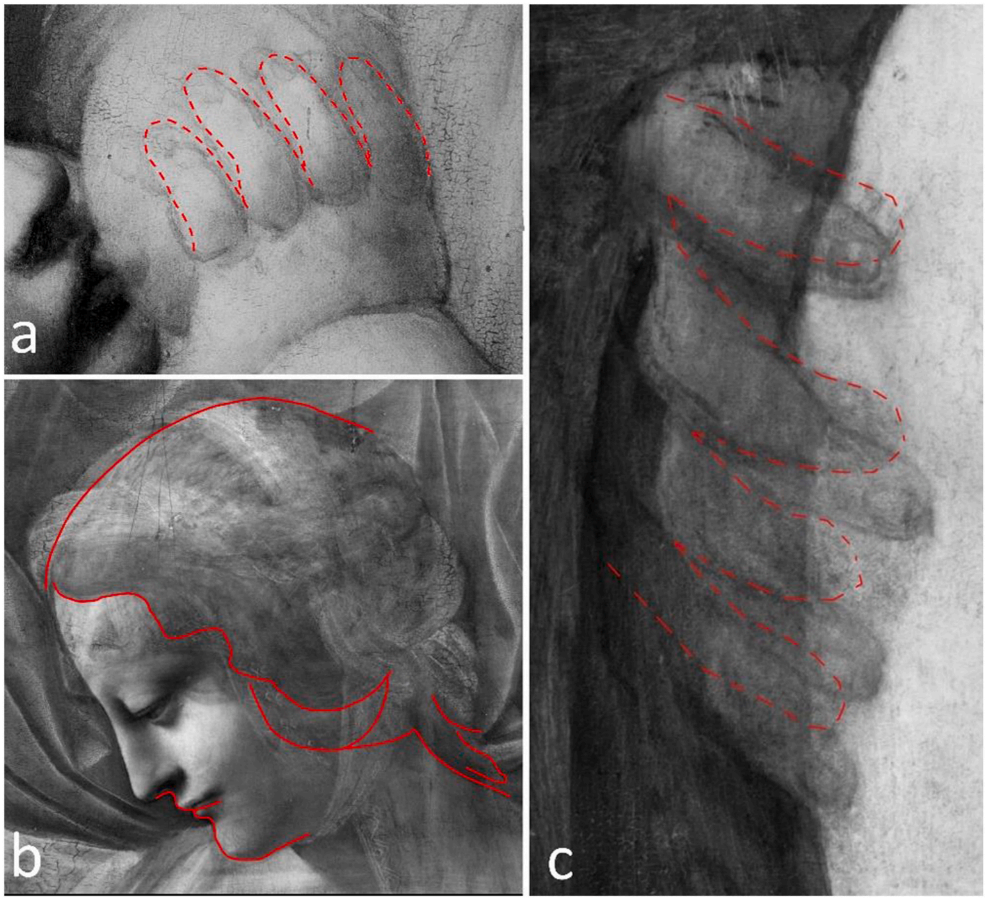

Fig. 7. Set of reflectographic details of the Virgin and Child of Lombard school. In these reflectograms it is possible to note modifications in the underdrawing (a, c) with a repositioning of the fingers of the hands and b) a detailed drawing for the face and hair of the Virgin after having them covered with the application of the veil.

Fig. 8. Virgin and Child of Lombard school, in the IR reflectogram is clearly showed that originally the background were realized as a vertical and rock-like landscaping, visible also beneath the curtain, with a building on the left that almost entirely covered the portion of the background.

and sketched. For *The Christ Child* by Marco d'Oggiono (Fig. 5c) a thin dry material trace was used to define the face elements, with the presence of a fine and detailed hatching for the shadows such as under the eyebrows and between the lips and the nose. In *The Virgin and Child* of the Lombard school (Fig. 5b) a dry material was also used for the underdrawings. In all the paintings, the drawing appears to be made freehand: there are in fact slight modifications at this stage.

No evident traces of drawing transfer from possible cartoons were found except for *The Virgin and Child* of the Lombard school where limited and possible signs of pouncing were found in correspondence of the fingers (Fig. 6). Modification of the sketch are particularly interesting for two paintings: the Lombard school and the Napoletano panels.

For *The Virgin feeding the Child* panel, several changes to the last version were made (see Fig. S2 in supplementary materials): for the Child, a shift of the fingers of the hand on the breast is present (Fig. 7-a), for the Virgin, a different position of one of her hands (Fig. 7-c). Comparing these two details acquired in the 1000–1700 nm range, it is noteworthy the evidence of two types of drawing materials, a fluid diluted ink applied with brush for the hand of the Child and a dry trace for the hand of the Virgin. It is interesting to note a detailed drawing of the head of the Virgin even under the veil that finally covers it (Fig. 7-b). The most important and radical modifications were however carried out on the background, which originally were realized as a vertical and rock-like landscaping, visible also beneath the curtain, with a building that

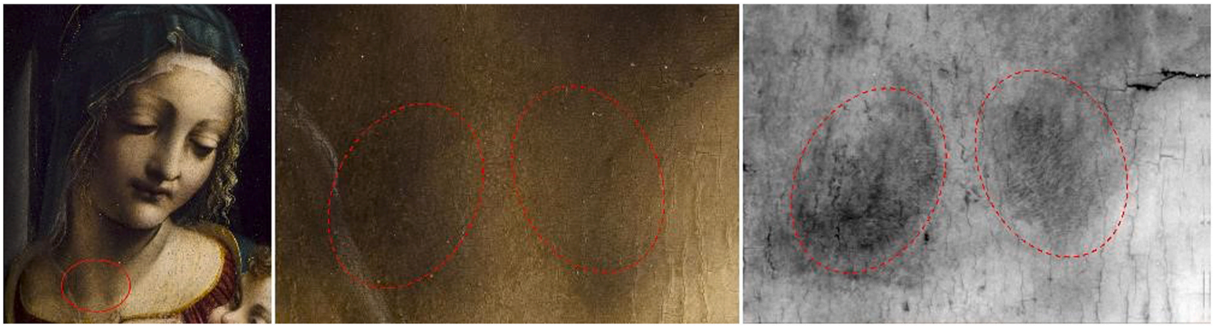

Fig. 9. IR reflectography of the neck of the Virigin: two distinct fingerprints have been firmly placed to add a dark background to the slope of the neckline painted subsequently.

almost entirely covered the portion of the background on the left (Fig. 8). This finding explains the results already obtained in 1988 for a stratigraphic sampling in the curtain area, when a layering of vermillion over azurite was detected [41].

For *The Virgin and Child* by Napoletano, beside the presence of a fluid freehand drawing with small changes in the paintings in many anatomical parts of the two figures, the most interesting finding is related to the presence of black fingerprints in various areas of the white background. In Fig. 9 is shown the IR reflectography of the neck of the Virgin where two distinct fingerprints have been firmly placed to add a dark background to the slope of the neckline painted subsequently. Other fingerprints were found also in other parts of the painting, again to darken, blend or connect some anatomical features.

4.4. Paint layers

The synergy between the imaging techniques and the spot spectroscopies gave us the possibility to infer the palette used by the five authors in the studied paintings with a complete non-invasive protocol. By studying the result of the UVF and microscope images, with the help of restorers, the areas to be analysed by spot techniques have been chosen. Regarding the painting materials, it is well known that in the Leonardo's workshop, exchange of drawings and ideas often occurred between pupils [4], so it is not surprising that the pigments used in all the five studied paintings are recurring. The chromatic effects were obtained with vermillion, lakes, earth in different shades (yellow, brown, red and golden), azurite and natural ultramarine, the blue from lapis lazuli stones, and lead based yellow. This section presents an overview of the detected pigments along with the speculated stratigraphic sequence of the pictorial layers for the most interesting cases; a complete summary of the results is reported in Table 1.

Starting from these results, taking advantage of the hyperspectral imaging (HYS) on the whole surface, the materials locally individuated by the comparison of data acquired by XRF, FORS, Raman and FTIR analyses have been detected and mapped in the paintings, with adequate data-processing methods.

It is well known that the HYS systems capture images at a large number of spectral bands and can identify materials with unique spectral features [16,17], which is a significant advantage compared with spectroscopic spot analyses. However, the spectral resolution of spectroscopic techniques is still much higher than that of HYS system (in our case: 2.7 nm spectral resolution for the FORS system versus 7 nm for the HSY instrument): for this reason, in the present work, the former have been used to support the processing and interpretation of HSY results.

In the following, for each painting, some peculiar aspects will be discussed, starting from *The Virgin and Child* by Boltraffio. In the last years, this panel has been submitted to different restoration works; during the 2011 intervention conducted by Carlotta Beccaria, it has been decided to remove some old instances of restoration that obscured the definition of the drapery of Virgin's cloak, making it less legible and flattening its form [39]. Therefore, it has been interesting to study the original materials resurfaced: the blue drapery was originally painted applying a light under-layer containing white lead and azurite, covered by a layer of natural ultramarine. In fact, the blue areas investigated (points 6, and 15) show, based on the FORS spectra (Fig. 10a), the use of ultramarine. The presence of azurite, possibly mixed with white lead, is identifiable as an underlying stratum because of the high quantity of copper detected by XRF; the Raman spectroscopy performed on the areas 15 and 18 (see Fig. S1a) shows the band at 1314 cm^{-1} assigned to a two-magnon scattering which arise from the interaction of two magnons created on antiparallel close spin sites in α-Fe_2O3 (Hematite), see Fig. 10b. Hematite perhaps belongs to a lower stratum, since the superficial layer is very much thinned, as the image at digital microscope acquired in the area 15 shows (Fig. 10c): there is a very thin-layered sequence in which the presence of a superficial layer of ultramarine and the presence of few red/brown grains are evident.

It is precisely the presence of a precious pigment such as natural ultramarine, also spread in the landscape on the background and in the sky, that induce scholars to rethink the commission of *The Virgin feeding the Child* panel by the anonymous painter. Surprising is the use of this pigment for details negligible in the construction of the painting, such as the cushion's buttons (Fig. 11a); in fact, the Raman spectrum acquired on the 2_bis point (Fig. 11b), shows the (S_3^-) symmetric stretching mode at 549 cm^{-1} ascribable to lapis lazuli [42].

Moreover, the bands at 1314 cm^{-1} and 1355 cm^{-1} are present; they are two fluorescence emission bands resulting from an electronic mechanism activated by exposure of one of the associated minerals in this lapis lazuli sample to 785 nm radiation.

The band at 1050 cm^{-1} is due to the presence of white lead (hydrocerussite (lead(II) carbonate/lead(II) hydroxide)).

The IRFC image helps in correctly mapping some of the pigments found on this painting with the above mentioned technique. The most interesting results are the characteristic purple color of the ultramarine and the yellow false color of vermilion used for the rose (Fig. S3 in supplementary materials).

Also in his panel, Francesco Galli used precious materials; in particular, gold has been observed in many areas (see Table 1). In the halo (point 7, Fig. S1d), the veil on the hair (point 8 Fig. S1d), the dress (point 13 Fig. S1d) and the golden fringe of the Virgin's veil (point 17 Fig. S1d) it was detected together with copper, iron and lead by XRF. By comparing these data with those acquired with FORS and Raman spectroscopy, the presence of yellow ochre can be deduced. Moreover, in points 7 (Fig. 12a), 8 (Fig. 12b) and 17 gold was used (Fig. 12c), while at point 13 there was lead-tin yellow.

These results are interesting because confirm the hypothesis given by the restorer of Brera Art Gallery, Paola Borghese [43], about the presence of a veil with golden fringes placed on the head of the Virgin, the veil the Child is playing with.

For this panel, it was also possible to identify the red lake used for glazing with *velatura* technique the Virgin's dress. Red lakes were

Table 1
Overview of the pigments recognised in the considered paintings (for the collocation of measure points see Fig. S1a, S1b, S1c, S1d and S1e).

Points	Colour	Description	Pigment from the synergy of spectroscopic techniques
a	**Boltraffio, The Madonna of the Rose, Poldi Pezzoli Museum**		
1, 2, 5, 10, 13	Skin tones	Virgin/Child	Yellow Ochre, Vermillion, White Lead
3	Black	Background	Ochres in organic black
4, 16	Red	Flower	Vermillion
6	Light blue	Virgin dress	Azurite, Ultramarine
15		Virgin dress	Azurite, Ultramarine, Red Ochre (Hematite)
7, 14	Dark red	Child belt/Virgin dress	Vermillion (organic pigments cannot be excluded)*
8, 9	Brown	Virgin and Child hair	Yellow Ochre, Red Ochre
11, 12	Yellow	Virgin dress	Yellow Ochre, Red Ochre
17	Green	Leaf	Ochres
b	**Lombard School, The Virgin feeding the Child , Poldi Pezzoli Museum**		
1, 6	Skin tones	Child	Yellow Ochre, Vermillion, White Lead
2	Dark red	Cushion	Vermillion, Red Ochre with gold details
10, 20		Tenda	Vermillion, Red Ochre
2 bis	Ligh blue	Cushion detail	Azurite, Ultramarine
4, 5, 11, 14		Virgin dress and veil	Azurite, Ultramarine (gold traces)
8, 16, 17		Sky	Azurite, Ultramarine
15		Mountains	Azurite, Ultramarine
3	Ochre	Windowsill	Yellow Ochre
7		Child hair	Yellow Ochre
13, 13 bis		Virgin dress edge	Yellow Ochre
9, 19	Light red	Tenda	Vermillion, Red Ochre
12	Green	Virgin veil	Azurite, Green Earth
18	Not considered		
c	**Marco D'Oggiono, The Christ Child, Poldi Pezzoli Museum**		
1, 3	Skin tones	Face	Lead-tin yellow Type I ,Yellow Ochre, Vermillion, White Lead
6		Neck	Yellow Ochre, Vermillion, White Lead
7		Shoulder (restoration)	Lead-tin yellow Type I ,Yellow Ochre, Vermillion, White Lead
2	Red	Lips	Vermillion, Red Ochre
4	Brown	Hair	Lead-tin yellow Type I ,Yellow Ochre, gold
5		Hair (restoration)	Yellow Ochre
8, 13, 14	Blue	Dress (restoration)	Azurite
9		Dress	Azurite
10, 15	Dark brown	Background (restoration)	Azurite with organic pigments
11		Background	Azurite with organic pigments
12	White	Eye	White Lead
d	**Francesco Galli (Napoletano), The Virgin and Child, Brera Museum**		
1, 5, 6, 18	Brown	Background	Ochres
2, 3, 10, 16	Skin tones	Virgin/ Child	Yellow Ochre, Vermillion, White Lead
7, 8, 17	Yellow	Virgin halo, hair and veil fringe	Ochres (with gold details)
13		Virgin dress inside	Lead-tin yellow Type I, Ochres, gold details
9	Light blue	Sky	Azurite
12, 15		Virgin	Azurite with gold details
11	Red	Virgin dress	Lake (animal red dye, kermes?), Vermillion
14		Virgin dress	Vermillion
e	**Lombard School, The Virgin and Child, Palazzo Borromeo, Isola Bella**		
1	Skin tones	Child leg	Lead-tin yellow Type I , Vermillion, White Lead
5		Child lips	Lead-tin yellow Type I ,Yellow Ochre, Vermillion, White Lead
2, 10, 12		Virgin	Lead yellow, Vermillion, White Lead
3, 11	Blue	Virgin dress	Azurite
4	Brown	Virgin dress	Yellow Ochre, Azurite
6	Ochre	Child halo	Yellow Ochre (Azurite from the sky behind)
7	Ochre	Child hair	Yellow Ochre
8	Light Blue	Mountains	Azurite
9		Sky	Azurite

prepared from dyes both of vegetal (safflower, madder, and sappanwood) and animal (cochineal, kermes, and lac dye) origin, belonging to different molecular classes but especially to that of anthraquinones. In an extensive study about the painting materials used by the Milanese school at the end of the 15th century [4], the use of both madder and kermes lakes was demonstrated by chromatographic analyses. In the present work, by measuring visible-excited optical fluorescence, the red lake in the painting by Francesco Galli could be recognised as deriving

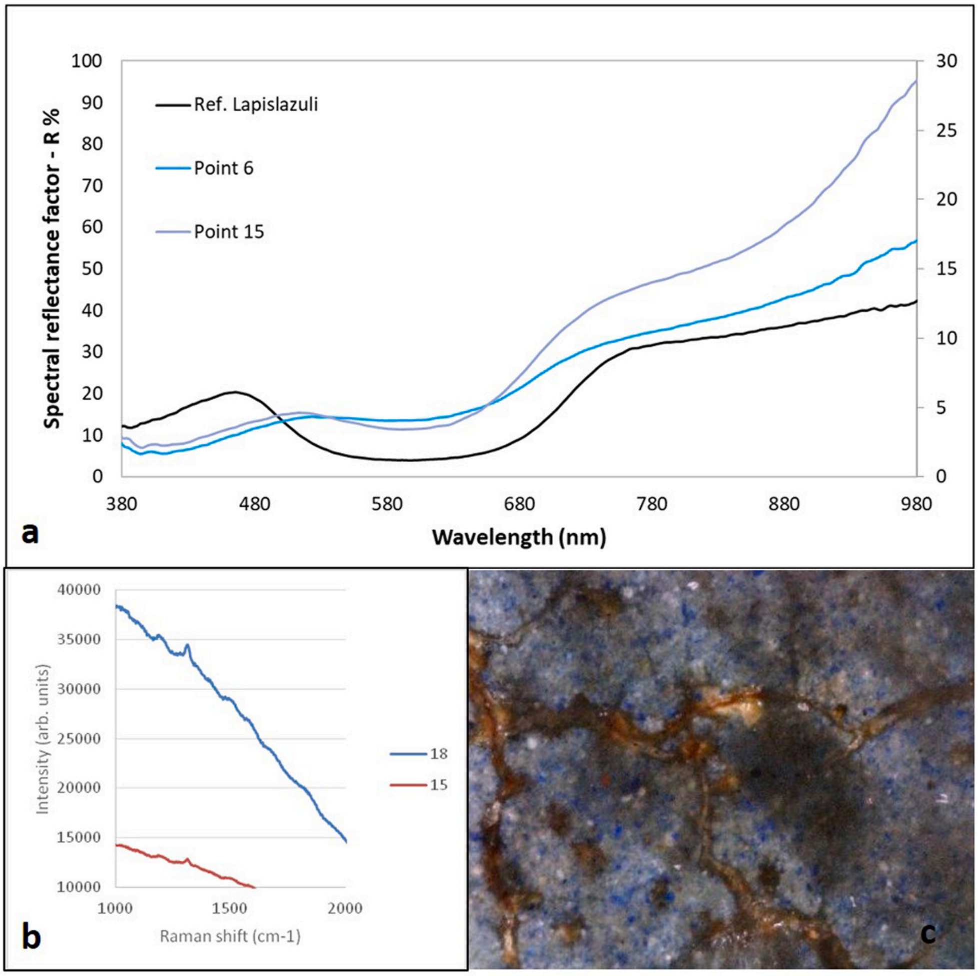

Fig. 10. FORS (a) and Raman (b) spectra for the investigated blue areas on Boltraffio's Virgin and Child; corresponding digital microscope image is reported in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

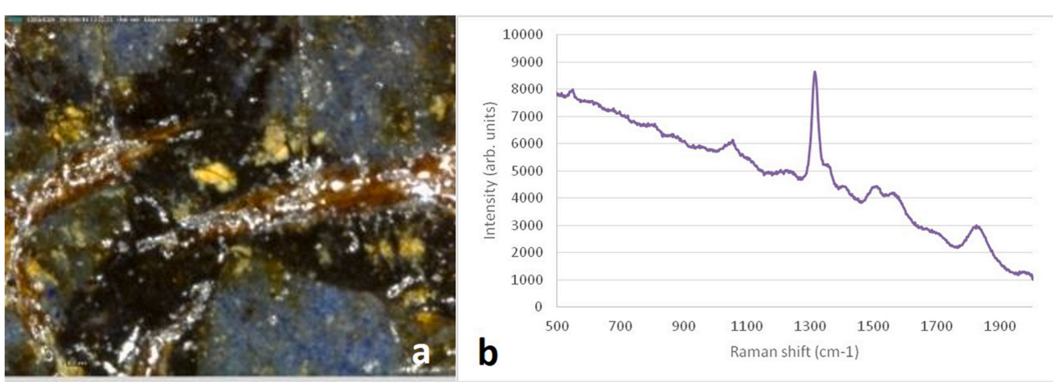

Fig. 11. Blue detail for the button in the Virgin feeding the Child panel: digital microscope image (a) and Raman spectrum (b). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

from a dye of animal origin, most probably kermes (Fig. S4 in supplementary materials). Also UVF images showed the presence of a red lake with its typical reddish-orangey fluorescence while in the IRFC image the azurite dress was highlighted (Fig. S5 in supplementary materials).

The unknown master who painted *The Virgin and Child* used an unusual mixture of azurite and yellow ochre to paint the Virgin's dress, reaching a very peculiar chromatic effect. This mixture can be mapped by chosen as end-member the reflectance curve acquired on the dress (point 4 in Fig. S1e); as a result of the mapping procedure, performed on the basis of the SAM algorithm, we obtain the image shown in Fig. 13a-c.

One similarity map, I(x, y, 4), has been created by considering as reference the spectrum measured in point 4 (Fig. S1e). The reflectance curve shows a behaviour ascribable to yellow ochre (see the two band at 580 nm and 780 nm in Fig. 14) with the contribution of an additional pigment that, considering the specific reflectance rise in the wavelength range above 880 nm, could be azurite.

Moreover, analysing the results obtained in the same area by the comparison between XRF, Raman and FT-NIR data, we can deduce the

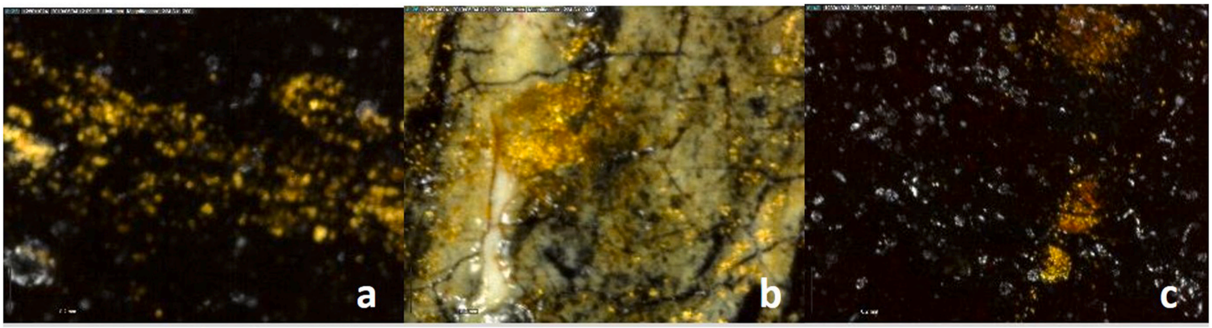

Fig. 12. Details of Francesco Galli panel, showing gold traces: a) point 7, the Virgin halo, b) point 8, the Virgin veil, c) point 17, the Virgin dress. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

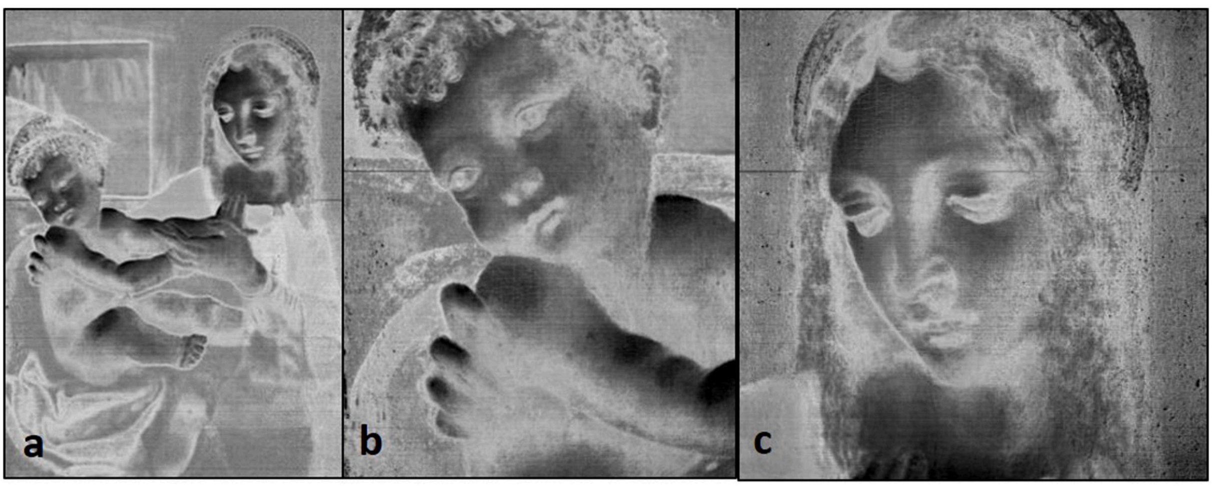

Fig. 13. Result of the mapping procedure for azurite and yellow ochre mixture in the unknown master panel, obtained on the bases of the SAM algorithm (a, the whole panel, b, The Child detail, c) the virgin face). Lighter parts show a higher similarity, darker ones a higher difference.

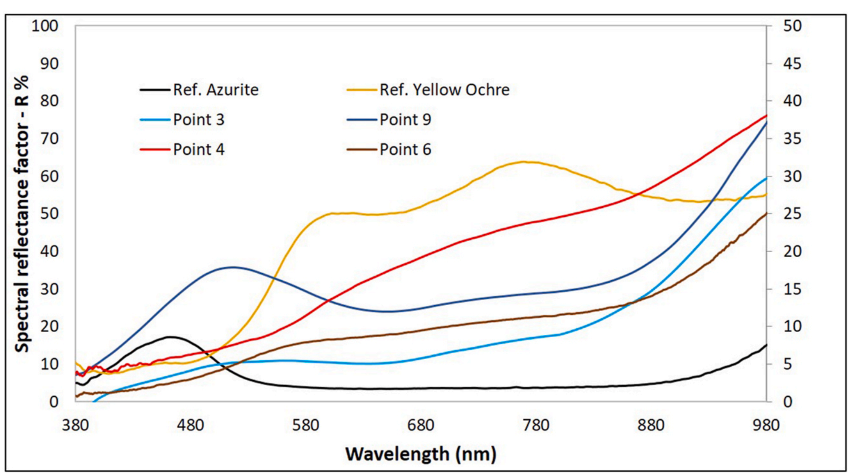

Fig. 14. Reflectance spectra for the Virgin and Child pane by an unknown painter (for the point location, see Fig. 1S).

presence of both azurite and yellow ochre. The presence of these two pigments is evident in the similarity map: in fact, the area of the Virgin's dress can be classified into two sub-regions with different spectral features: there are areas with a blue background with superimposed a yellow-brown painted layer. Moreover, there are other areas in which the mean reflectance spectrum of the blue background reveals spectral features similar to those of the blue pigment (identified as azurite) of Virgin's cloak and of mountain in the right part of the panel. The superimposed brown-yellowish layer reveals common features to yellow ochre that characterises the pigments mixture applied by the Master for the lips and the eyes of the Child (see Fig. 13b) and for the features and the shadows of Virgin's face (see Fig. 13c). UVF image (Fig. S6 in supplementary materials) shows a damaged painting layers with many conservation interventions applied on the entire painting surface while the IRFC image helps in showing the distribution of azurite in the dress.

It is particular how Marco d'Oggiono constructed the background in

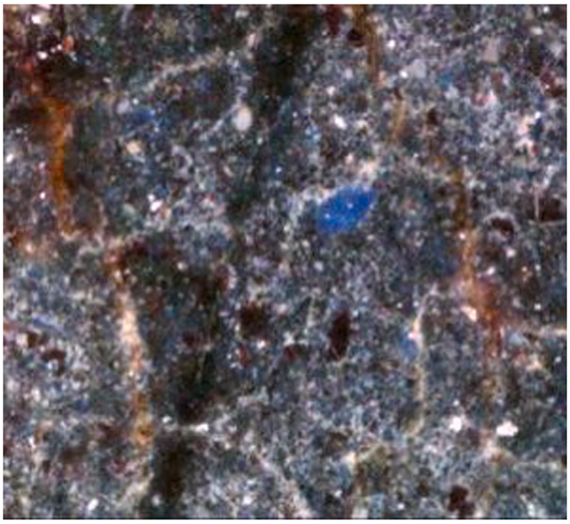

Fig. 15. Digital microscope image for the dark background of the painting by Marco d'Oggiono.

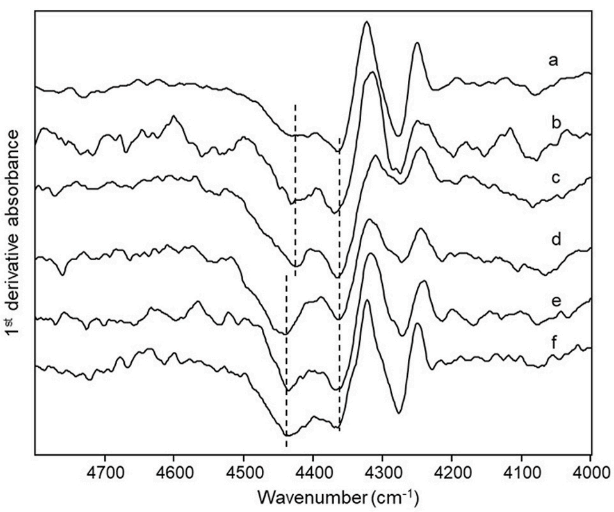

Fig. 16. First derivative of FT-NIR reflection spectra of: (a) linseed oil on a glass slide after 1-year ageing; (b) area 15 of the Virgin and Child by Boltraffio; (c) area 10 of the Christ Child by D'Oggiono (after cleaning); (d) area 3 of the Christ Child by D'Oggiono (before cleaning); (e) area 5 of the Virgin and Child by Galli; (f) walnut oil on a glass slide after heating at 100 °C for 72 h. Dashed lines indicate the peaks whose positions and relative intensities were used to distinguish the two oils.

The Christ Child panel: in the visible range, the background appears very dark, but both FORS and XRF analyses confirm the presence of azurite, probably in addition to some organic brown/black pigments, as evident from the OM image (see Fig. 15) which highlights a blue hue diffuse with few inclusions of a brilliant light blue.

UVF analysis carried out during the conservation interventions, showed several integration areas positioned mainly in correspondence of the Child face and in the lower part of the panel. In this part there is in fact a junction that extends the height of the panel. IRFC showed the use of vermilion for the lips and highlights many retouching areas on the mantle of the Virgin.

Analyzing the painting under UV light, we mapped limited conservation interventions that appears as non-fluorescent areas. IRFC, as in the previous cases, highlights the Vermilion areas such as for the curtain and for the lapel and the purple false color areas corresponding to the lapis lazuli used for the mantle of the Virgin, the background and the sky.

4.5. Binders

For all the examined areas of the five paintings of Leonardesque school, overtone and combination bands characteristic of siccative oils could be detected in the FT-NIR spectra at 4264, 4336, 5690 and 5784 cm^{-1} [29]. Just in a detail of the hair of the Virgin in *The Virgin and Child* of unknown painter, the presence of gum arabic besides oil could be hypothesized, based on bands at 4020, 4750 and 5175 cm^{-1} [44].

The identification of the specific siccative oil used by the painters is more challenging. To this aim, first-derivative of the spectra were calculated [29] and compared with those recorded for reference materials. In the already cited study about the painting practice of the Milanese Leonardo's pupils [4], analyses by gas chromatography-mass spectrometry confirmed that those artists usually employed an oil binder, supposed to be in most cases walnut oil. In the present study, reference samples were prepared by spreading fresh walnut and linseed oils on microscope glasses and then letting them dry, both naturally and by mild heating in an oven at 100 °C for 72 h. The linseed oil sample was also submitted to light-induced ageing by a 6.5 h-exposition to an Osram Powerstar lamp, with 150 W nominal power and emission between 390 and 600 nm. In all cases, the two oils showed different first-derivative spectral patterns, especially regarding the component around 4400 cm^{-1}, with slight shifts and changes in the relative intensities of the peaks (Fig. 16a and f). On these bases, it was tentatively supposed that the binder was indeed walnut oil, possibly heated (M. Spring et al., 2011), in the examined areas of *The Virgin and Child* by Galli (Fig. 16e) and of *The Virgin feeding the Child* by unknown author. More variable results were obtained for the details considered in *The Virgin and Child* painted by Boltraffio. In fact, the first-derivative of the spectrum recorded on a detail from the black background resembled more closely that of linseed oil (Fig. 16b), while for other areas the compresence of different oils, possibly also in superimposed layers, could not be ruled out. Interestingly, similar results were obtained by chromatographic analyses reported in the literature for samples from the same and also another painting by Boltraffio [4,39]. Again, the use of walnut oil, but without completely excluding the presence of linseed oil, was suggested by the first-derivative NIR spectra also for *The Virgin and Child* of the Lombard school. A peculiar situation was encountered for *The Christ Child* by D'Oggiono, that could be analysed both before and after restoration. It should be recalled that the painting had been enlarged by a later addition of a wooden support, painted in imitation of the original work, and thus it had been probably glazed to make it homogeneous. Before removal of the later glaze, NIR spectra resembling that of walnut oil were obtained (Fig. 16d), while, after cleaning, a greater similarity with linseed oil was observed (Fig. 16c). Therefore, it can be supposed that linseed oil was the original binder for the *Christ Child*, while walnut oil was employed in the 19th-century restoration.

5. Conclusions

The project "Leonardeschi oltre il visibile" (Leonardesque Artists beyond the Visible), funded by Fondazione Bracco and whose main results are given in the present paper, is a good example of the synergy of scientific, conservation and humanistic studies since its planning. Working strictly in contact with art historians, restorers and curators of an important exhibition has enhanced the possibilities of technical analyses, giving focuses on the interesting puzzling themes. This is reflected also in the exhibition catalogue where the artwork records are linked to the results of scientific investigations, in the spirit of the studied Renaissance.

This same research also proved to be a good training for new technical and methodological developments, resulting in the possibility of a more complete, non-invasive, survey of both organic and inorganic materials. Also data analyses have been strengthening and developed to allow an easier and more effective handling of large sets of data from imaging techniques: in particular SAM (Spectral Angle Mapper) analyses applied to hyperspectral images and appropriate mathematical processes on Radiographic images opened a new way to the elaboration of data from Cultural Heritage artefacts.

The possible attribution of masterpieces is beyond the aims of the present research, but surely systematic studies through physical and chemical analyses can cast new light on the work of art historians.

CRediT authorship contribution statement

Anna Galli: performed Raman analysis and elaborations; she planned the experimental timesheet and coordinated the merge process of analyses output and discussion. **Marco Gargano:** dealt with high resolution multispectral imaging measurements (UV, IR, visible) and FORS analyses, their data handling, elaboration and discussion. **Letizia Bonizzoni:** dealt with XRF analyses, data elaboration and discussion, she coordinated authors for the draft of the text. **Silvia Bruni:** dealt with FTIR and fluorescence spectroscopy, their data acquisition, analysis and data discussion. **Matteo Interlenghi:** performed X ray images elaborations and multispectral data acquisition and elaboration. **Margherita Longoni:** worked on FTIR and fluorescence spectroscopy data acquisition and elaboration. **Arianna Passaretti:** worked on FTIR and fluorescence spectroscopy data acquisition and elaboration, the graphical abstract. **Michele Caccia:** performed SAM elaborations and worked for planning. **Christian Salvatore:** performed X ray images elaborations and multispectral data acquisition and elaboration. **Isabella Castiglioni:** coordinated the project, provided the necessary funds and reviewed the final work. **Marco Martini:** coordinated the project, provided the necessary funds and reviewed the final work.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.109112.

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