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The Importance of Preventive Analysis in Heritage Science: MA-XRF Supporting the Restoration of *Madonna with Child* by Mantegna

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Abstract: The *Madonna with Child* by Andrea Mantegna owned by the Museo Poldi Pezzoli in Milan is painted on canvas with an unusual distemper technique. During the period of 1863–1865, the painting was restored by Giuseppe Molteni. The identification of potential retouchings by Molteni, possibly covering part of the original layer, was the object of this work carried at the Opificio delle Pietre Dure. To evaluate the extent of both Molteni's intervention and Mantegna's original layer, the MA-XRF spectrometer developed by CHNet-INFN was used to discriminate between the two paint layers and identify the materials and the extension of both "artists". Indeed, the elemental maps showed that Molteni's work entirely covered the mantle of the Virgin, even changing the fold of the draperies and enriching the red robe with shell gold highlights, giving a different appearance to the painting. Moreover, MA-XRF also revealed that the original Mantegna was still mostly intact underneath Molteni's layer, thereby providing a decisive guide for conservation works. These results indeed formed the basis for the technical decision to remove the varnish and Molteni's version, unveiling the original Mantegna. A second MA-XRF campaign was then carried out to fully characterise the materials of this unusual painting technique.

Keywords: MA-XRF; heritage science; non-invasive analysis; portable equipment; pigment identification; Mantegna; distemper technique; retouching; INFN-CHNet

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1. Introduction

Analytical methods employed in heritage science for the analysis of materials and production techniques are a well-established research field, demanding high performance, non-invasive, non-destructive and portable instruments [1–7]. These qualities can be found in the X-Ray Fluorescence (XRF) technique, and for this reason it is one of the most employed analytical methods in heritage science, as indeed it allows relatively fast multi-elemental, non-invasive, non-destructive and in situ analyses [8–10]. Nowadays, modern instruments upgrade the considerable potentiality of this method by means of scanning equipment, yielding elemental distribution maps of a selected area. This technique is known as Macro X-Ray Fluorescence (MA-XRF) by the scientific community and is widely employed in the heritage science field [11–13]. It is typically exploited for the study of pigments in paintings [14–16] but also for archaeological finds [17,18], glasses [19,20] and many other applications.

The study presented here is a typical example of MA-XRF's capabilities as an analytical technique but also as a useful, and even decisive, tool for conservators as preventive analysis. The *Madonna with Child* by Andrea Mantegna, also named the *Madonna Poldi Pezzoli*, underwent conservation and restoration treatments at the Opificio delle Pietre Dure (OPD) in Florence, and one of the main goals of the study was the evaluation of the extent of likely wide retouchings by Molteni over Mantegna's original pictorial layer. These retouchings, painted during 1863–1865, were surely aimed at preserving and improving the aesthetic quality of the painting but unfortunately changed the pictorial aspect of the original distemper technique. OPD conservators faced then the choice of removing or not the large previous restoration intervention, and to do so, they needed to carefully and objectively evaluate the integrity of the original layer underneath.

To support this complex restoration intervention, MA-XRF analysis was carried out with the scanner developed by the Cultural Heritage Network of the Italian National Institute of Nuclear Physics (INFN-CHNet). MA-XRF analysis was carried out primarily with the aim of supporting the conservation treatment of the painting. The identification and determination of the extent of the interventions by Molteni was the primary goal of the study. It is needless to say that the object of the study was also the characterisation of the original painting materials and techniques employed by Andrea Mantegna. For this reason, the painting was entirely scanned before and after the restoration treatment to better characterise the original materials employed by the artist for such a peculiar painting technique. To our knowledge, only one scientific paper has been published exploiting MA-XRF on a painting by Mantegna, which was written by Laureti et al. [21].

It also has to be noted that performing MA-XRF analysis right after conservation treatment has been useful for OPD conservators to carefully evaluate the overall effectiveness of the thorough removal of Molteni's interventions.

It is worth underlying here the importance of the holistic approach of combining scientific analytical methods with history of art research, with the aim of supporting long-term preservation and understanding of artworks and tangible heritage in general.

2. Materials and Methods

2.1. The INFN-CHNet Collaboration

The Italian National Institute for Nuclear Physics (INFN), among its activities, conducts also technological research and instrument developments in the field of heritage science. In 2017, the INFN Network for Cultural Heritage (INFN-CHNet) was founded with the mission to harmonise and enhance the expertise of the institute in heritage science among its structures spread over the Italian territory. Several results have already been achieved in developing analytical methods for heritage science applications, as reported in [22–24], as well as devices such as the INFN-CHNet MA-XRF scanner employed in this study (see next Section 2.2). The LABEC laboratory [25], based in Florence, is the reference structure of the network. OPD also belongs to INFN-CHNet as a second-level node, sharing its expertise as one of the most important conservation centres in Italy and in Europe. The collaboration of institutes such as INFN and OPD is one of the main strengths of CHNet, as these share "common projects about research, education and technology transfer, thanks to specific conventions" [26].

Following this trail, the INFN-CHNet group, in collaboration with the Conseil Européen pour la Recherce Nuclèaire (CERN) and the Opificio delle Pietre Dure, has started the construction of MACHINA [27], a transportable accelerator weighting about 600 kg with a reduced footprint of roughly 2.5 × 1.6 m^2 that will work with a power consumption of a few kW. It will be equipped with the so-called total-IBA approach, taking advantage of the IBA expertise of the INFN Florence division both in cultural heritage and also nuclear physics in general [28–31].

2.2. The INFN-CHNet MA-XRF Scanner

The INFN-CHNet instrument, thoroughly described in [32], is a lightweight (about 10 kg) and compact (60 × 50 × 50 cm^3) instrument completely designed and built for heritage science applications within the INFN-CHNet collaboration. It allows easy transport (two middle-sized boxes are enough for the instrument and other auxiliary elements, e.g., workstation and power supplies) but at the same time provides relatively wide mapping with good spatial resolution and statistics per pixel in reasonable acquisition times (e.g.,

30×15 cm^2 area, 1 mm spatial resolution and 75 min). Briefly, the main parts are the measuring head mounted on 3 linear motors (Physik Instrumente©, different length available, 200 mm travel range in the x and y directions for this version, plus a 50 mm stage along the z perpendicular direction) and a carbon-fibre case containing electronics controlling motion and acquisition, power supplies and other auxiliary elements. The measuring head is composed of an X-Ray tube (Moxtekc© MAGNUM, 40 kV maximum voltage, 0.1 mA maximum anode current, Mo anode—and other anodes also available) equipped with a collimator (several diameters available, ranging from 400 µm to 2 mm), a silicon drift detector (Amptek©c XR100 SDD, 50 mm^2 effective active surface, 140 eV FWHM at 5.9 keV) and a telemeter (Keyence, model IA-100); signals are collected with a multichannel analyser (model CAEN DT5780, also inside the carbon-fibre case). Furthermore, 3D-printing technology was employed to produce supports, holders and other mechanical aids, features which give wide flexibility to customise to a great degree the instrument for many different applications. The software controlling the motion, acquisition and data elaboration was developed within the collaboration and allows both online and offline analysis. It has been employed in several successful applications in the last few years [33–36].

The operating conditions of the X-ray tube for all measurements discussed here were: 35 kV anode voltage, 90 µA filament current and a Mo anode with an 800 µm diameter collimator. The scanning velocity was 10 mm/s and the equivalent-pixel size 1 mm. Several scans were performed for the full mapping of the painting.

2.3. The Madonna with Child of the Poldi Pezzoli Museum Collection

Andrea Mantegna (Isola di Carturo, 1431–Mantua, 1506) is one of the most important north Italian artists of the Renaissance times. The artist worked in Padua, Mantua and Ferrara, and one of the characteristics of his style is the passion for ancient classical art which can be found in most of his works of art [37].

The object of this study is the *Madonna with Child* by Andrea Mantegna (Figure 1a,b), painted around 1490–1499 and belonging to the collection of the Poldi Pezzoli Museum in Milan (Italy). It is a small-sized portrait, roughly 45 cm $\times$ 35 cm, on linen canvas of the Virgin with the Child and belongs to a group of small-format Madonnas produced for private devotion. Similar to this painting, there is the *Madonna with Child* of the Accademia Carrara in Bergamo (Italy), which underwent conservation processes in 2012 [38] at the OPD—as happened to the *Madonna Poldi Pezzoli* a few years later, in 2019 [39].

It was painted with an unusual and peculiar distemper technique, in which pigments are ground with animal glue or vegetable gum, instead of the more traditional egg tempera [40,41]. Paints were then applied directly on the thin canvas, which underwent just a simple priming treatment—thus not having the traditional preparation layer. Distemper paintings were meant to be left unvarnished, having thus a very matte appearance, resembling a wall painting exploiting the roughness of the canvas. This painting technique is close to the Netherlandish *tüchlein* [42], introduced during the XIII century, in which the pigments are ground with an aqueous binder and employed over a dense linen canvas.

Gian Giacomo Poldi Pezzoli bought the painting in 1861, and two years later the painting was restored by Giuseppe Molteni, a famous painter–conservator of those times. The intervention by Molteni, surely aimed at preserving the painting but also at satisfying the taste of the client by improving the aesthetics of the pictorial layer, profoundly changed the characteristic aspect of the distemper technique. He surely, at the least, lined and varnished the painting, and most likely he also applied several retouchings to the painting.

(a) (b)

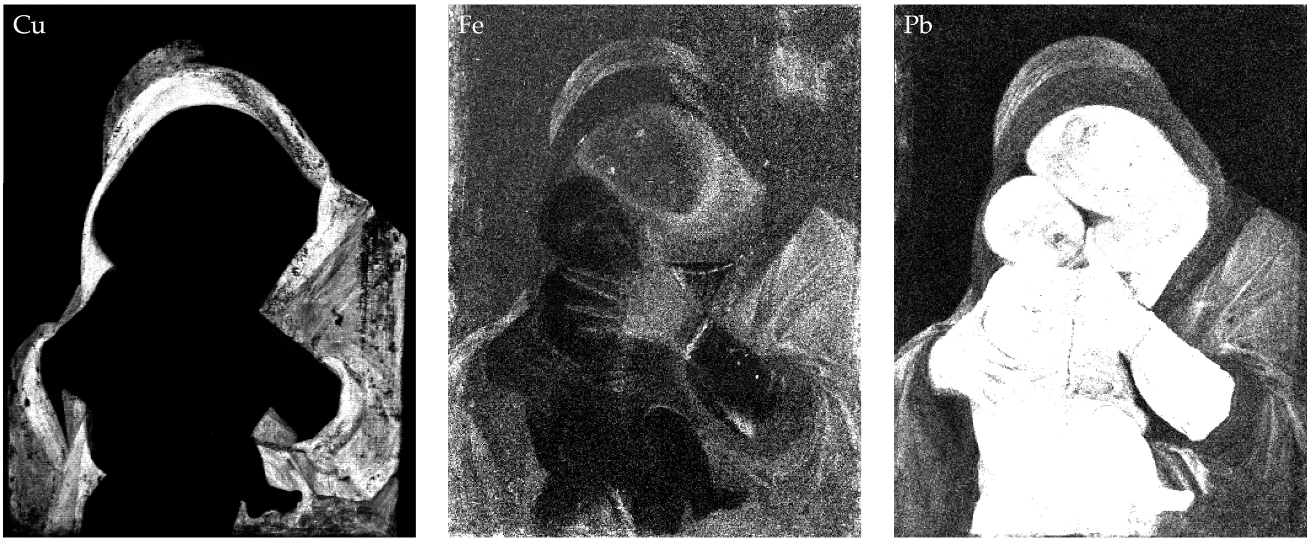
Figure 1. The *Madonna Poldi Pezzoli* (**a**) before and (**b**) after restoration (courtesy of the Poldi Pezzoli Museum).

3. Results and Discussion

3.1. MA-XRF Before Restoration: Evaluating the Extension and the Conditions of the Original Pictorial Layer

The presence of an extended intervention by Molteni was initially evident to conservators, and the comparison between the Cu and Fe maps strongly supported their hypothesis (Figure 2a,b). Two different modelling of the blue drapery are indeed visible, in particular on the Virgin's proper left shoulder and sleeve. Moreover, in the blue portion of the mantle over the head, Cu is present on only one side; on the contrary, Fe is present in the whole area. In addition, there is a difference also on the Virgin's proper left shoulder, which is slightly "higher" in the Fe map than in the Cu one. Moreover, few paint losses are visible in the Cu map, while the Fe map shows an intact painting layer. From these evaluations it is possible to hypothesise that Cu is most probably characteristic of the original pictorial layer composed of azurite [43] and thus painted by Mantegna, while Fe is possibly present as Prussian blue, introduced during the early XVIII century and thus available during Molteni's intervention [44]. The drapery visible in the painting (before restoration intervention) matches with the distribution of Fe, confirming that this element is present in the superficial layer. It is, however, true that Prussian blue cannot be absolutely determined with XRF alone and needs other analytical methods to be conclusively identified, such as FTIR [45].

Lead white, the presence of which is suggested by the distribution of Pb (Figure 2c), was most likely employed together with Prussian blue in Molteni's layer. Indeed, the modelling of the drapery visible in the Pb map matches with that of Fe. The mixture of Prussian blue, deep dark in colour, and lead white (or other white pigments) is common [46] and thus not surprising. However, it cannot be conclusively excluded that lead white is present (also) in the original pictorial layer. It has to be noted that the presence of Pb in principle may be due also to other lead-based compounds, such as massicot (yellow) or minium (orange) and cannot conclusively distinguished by XRF [47]. It is, however, true that the hypothesis of the use of lead white is the most probable.



(**a**) (**b**) (**c**)

Figure 2. The *Madonna Poldi Pezzoli* before restoration, MA-XRF maps: (**a**) Cu Ka; (**b**) Fe Ka; (**c**) Pb Lα. White is associated with maximum counts and black with minimum. The grey scale in the Pb map is edited to enhance its distribution in the Virgin's robe.

The distribution of the Cu map has been of utmost importance for the restoration intervention. Indeed, the Cu map showed that the most likely original painting layer, with the exception of sporadic lacunas, was in a good conservation state and possibly rather intact. Together with X-ray radiography carried out by the OPD scientific laboratory [39], MA-XRF allowed researchers to determine that the percentage of lacunas overall in the supposed original layer was less than 3%. This information strongly supported the choice of removing Molteni's layer.

There are other elements detected which are most likely related to Molteni's intervention. For instance, the presence of Co traces in the mantle of the Virgin, particularly over the shoulder and in the border (close to the edge of the painting), may be due to the use of Cobalt blue by Molteni himself or to an earlier intervention with smalt (a blue Co-based glass pigment employed in painted works from the mid XV century [48]). Most probably, Molteni also added the "marbling" effect on the red garment of the Virgin, realised with shell gold and visible in the Au map (Figure 3a). Similarly, the red edge of the sleeve was retouched by Molteni with vermilion (see Hg map, Figure 3b). In these cases, the evaluation of Molteni's intervention is not directly possible with XRF, as shell gold and vermilion are materials which are coeval with Mantegna, and this evaluation was accomplished by visual and optical microscopy inspection by OPD conservators [39]. Similarly, the red sleeve cuff (visible in Hg map in Figure 3b) was considered a later addition by OPD conservators.

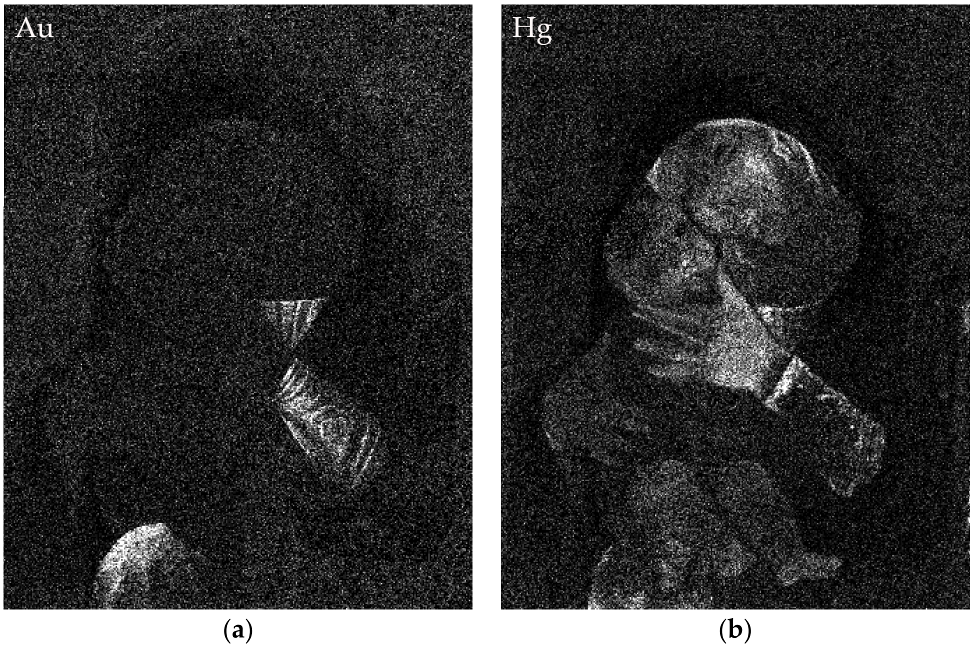


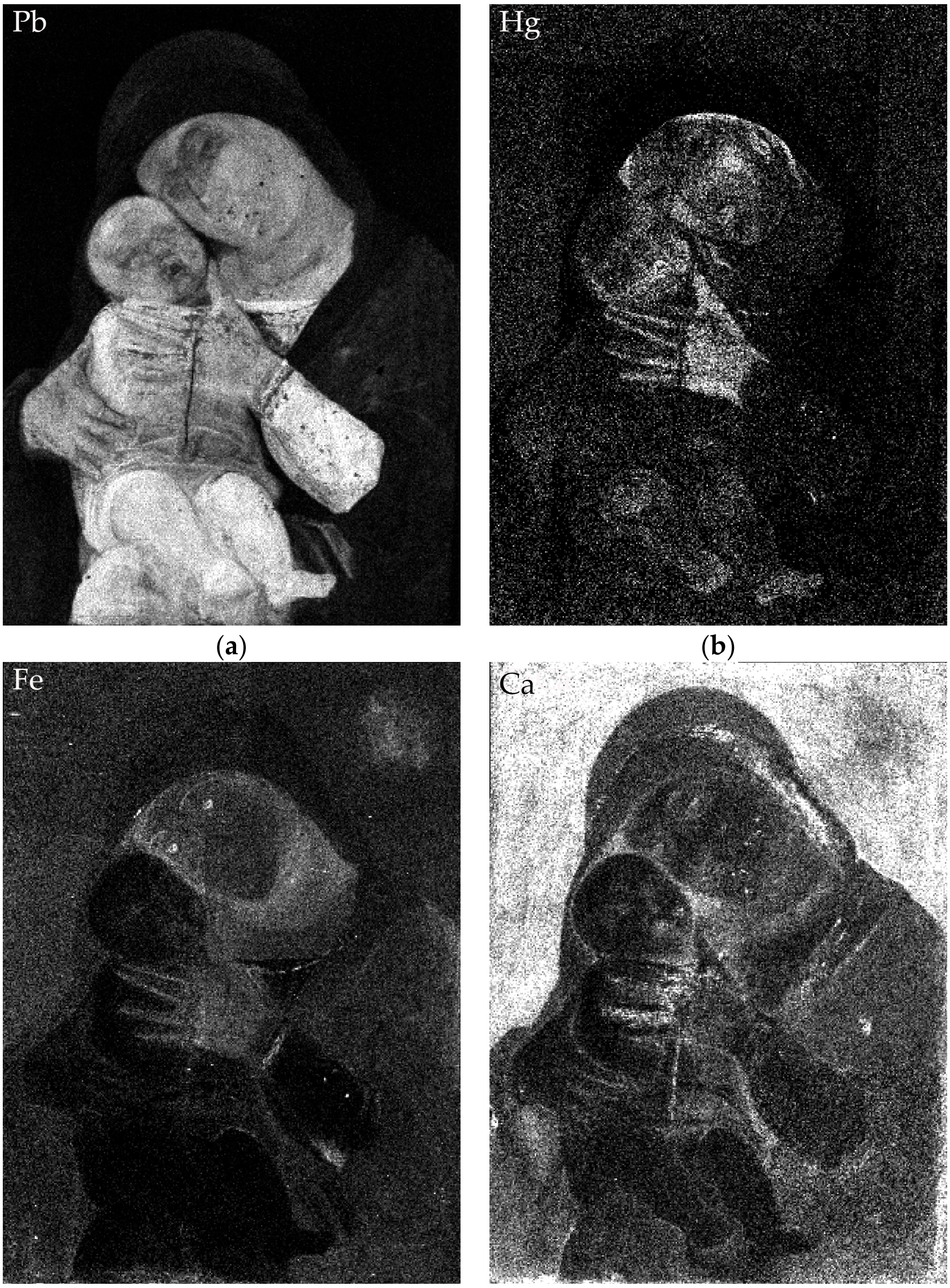
Figure 3. The *Madonna Poldi Pezzoli* before restoration, MA-XRF maps: (**a**) Au Lα; (**b**) Hg Lα. White is associated with maximum counts and black with minimum ones.

3.2. Mantegna's Painting Materials and Technique

The restoration treatment, which removed the large Molteni retouching mechanically with the use of scalpel and aided by stereomicroscopy [39], allowed a more complete characterisation of the painting materials and techniques of the original painting by Mantegna. The elements detected by MA-XRF and the deduced hypothesis regarding the materials employed by the artist, as discussed here, are broadly consistent with those expected during the late XV century.

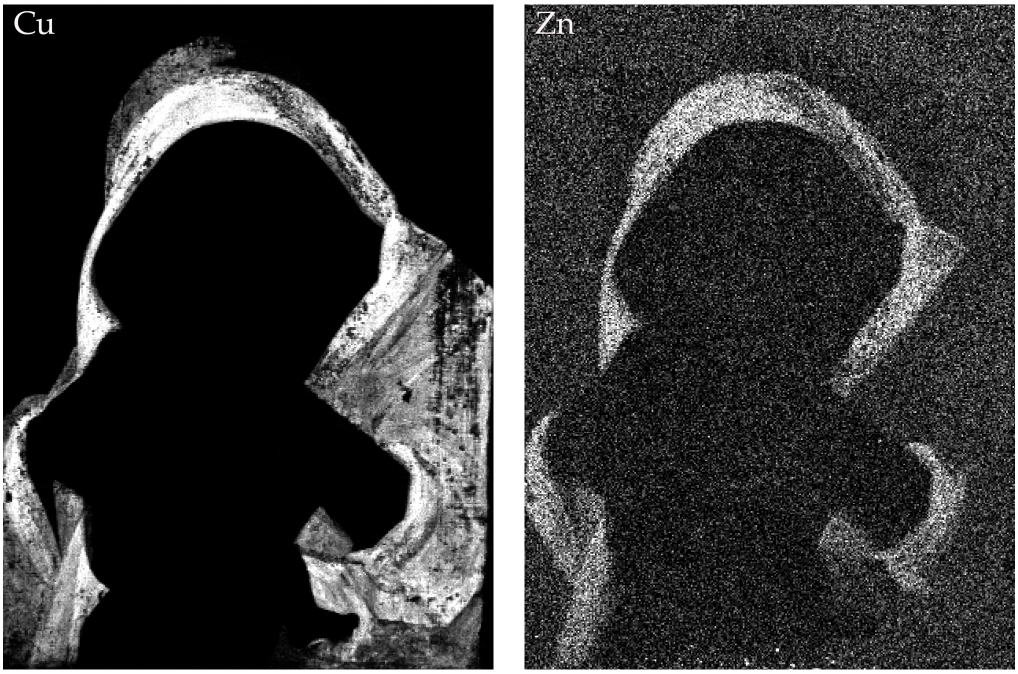
Lead white, the use of which is most likely attested by the presence of Pb (Figure 4a), is employed in flesh tones (where it is most likely present as background as seen by optical microscopy [39]), in the red Virgin's garment and in the white Child's robe. Pb traces are also detected in the Virgin's blue mantle, even though those might be related to residues of Molteni's retouching. Instead, no Pb is found in the background as consistent with the absence of a preparation/imprimatura layer, as expected in the distemper painting technique.

Flesh tones, in addition to Pb, are characterised by the presence of Hg (Figure 4b) used in cheeks, lips and highlights in general, both in the Virgin and in the Child, attesting the use of vermilion/cinnabar. The Virgin's hair also contains Hg. Volumes in the Virgin's flesh tone are built with the use of Fe-based materials, such as earth and ochres, employed mostly in shadows (Figure 4c). On the contrary, the Child's flesh tone does not contain a significant amount of Fe-based materials (with the exception of the shading of the eyes, nose and cheeks); visually, the two flesh tones are indeed different. The Virgin's eyes also contain Fe-based materials.



(a) (b) (c) (d)

Figure 4. *Cont.*



(**e**) (**f**)

Figure 4. The *Madonna Poldi Pezzoli* after restoration, MA-XRF maps: (**a**) Pb Lα; (**b**) Hg Lα; (**c**) Fe; (**d**) Ca; (**e**) Cu; (**f**) Zn. White is associated with maximum counts and black with minimum ones.

The red robe of the Virgin is characterised by the presence of Pb, which similarly to flesh tones is present as a white base [39]. Elements typical of red mineral pigments, such as Hg or Fe for vermilion and red earth, were not detected in this area, leading to the likely hypothesis of the use of a red organic dye. Original shell gold decorations are also present over the red robe (less extended than in Molteni's retouching). The white puff of the Virgin's proper left sleeve is painted with lead white with the addition of a Ca-based compound. Possibly, Ca is present as a component of Bianco di San Giovanni, maybe to give transparency effects [39].

The blue mantle is painted with a Cu-based compound (Figure 4e), most likely azurite. The green border contains Cu as well and an evident amount of Zn traces (Figure 4f), which is consistent with rosasite impurities in malachite [49].

The dark background is characterised by the presence of Ca, possibly related to the use of bone black (P is hardly detected, as no He was employed during measurements), and Fe, indicating the presence of earth/ochres likely used to warm the black tone. In the Ca map, a long vertical lacuna, visible also in the Pb map, is evident on the Virgin's proper left hand. In the upper-right corner of the painting, there is an area presenting higher counts of Fe and less Ca. This area corresponds to a region of the painting where the conservator found gold particles (so tiny that they could not be detected by XRF). These particles form the words "Nigra sum sed formosa", the first sentence of the *Canticle of Canticles*, words that are no longer visible and were most likely concealed/covered at some point [39] with Fe-based materials.

MA-XRF maps acquired before and after conservation are interesting to compare, as is visible in Figure 5. The most significant difference is visible in the Fe and Pb maps (Figure 5a,b and c,d respectively) in the blue mantle. Vermilion (Figure 5e,f) was present in the red robe of the Virgin, but after conservation it is found only in flesh tones. It is worth noting, as well, the Cu maps before and after conservation, in which no difference is evident. The comparison of the elemental maps before and after the conservation treatments has also been useful for evaluating the effectiveness of the process.

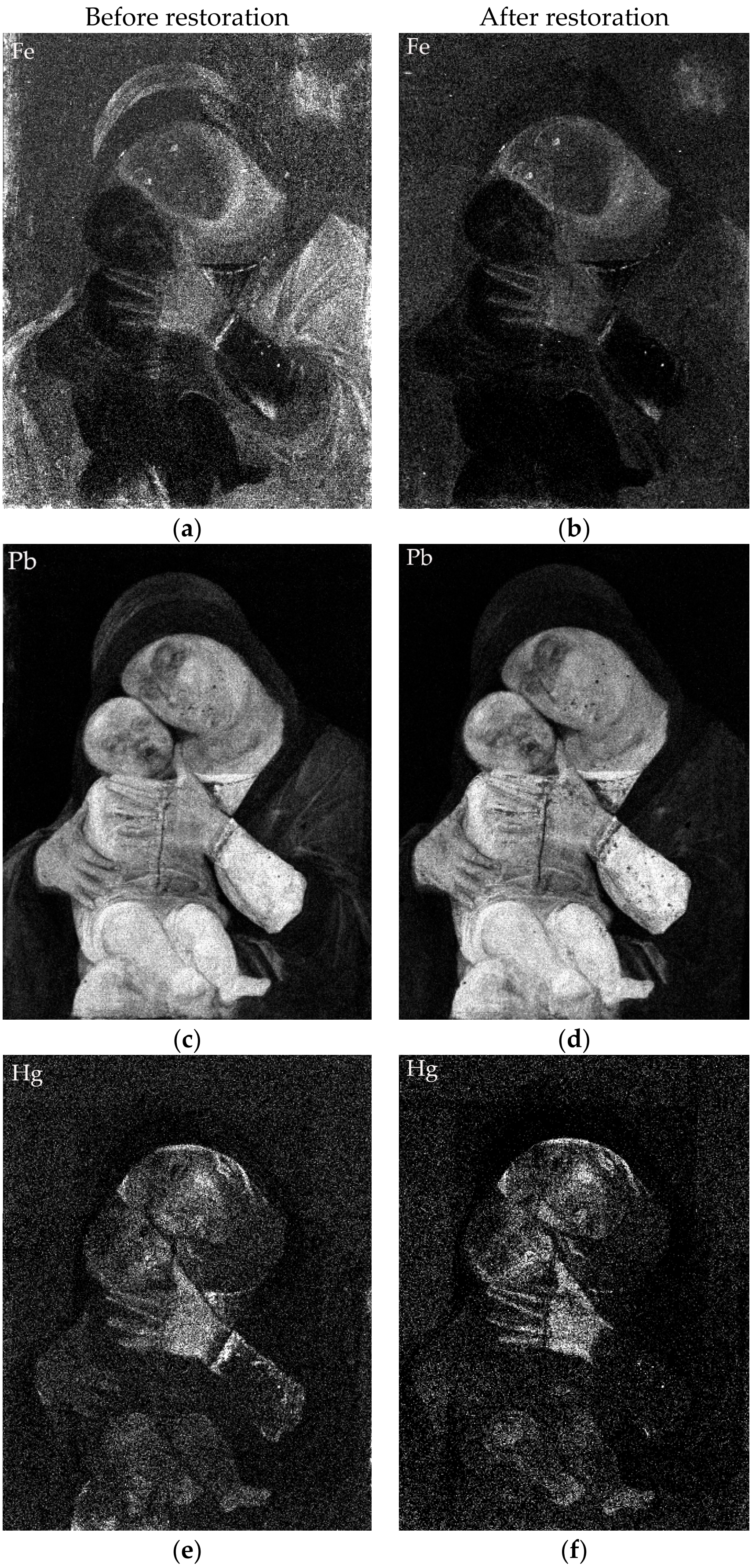


Figure 5. *Cont.*

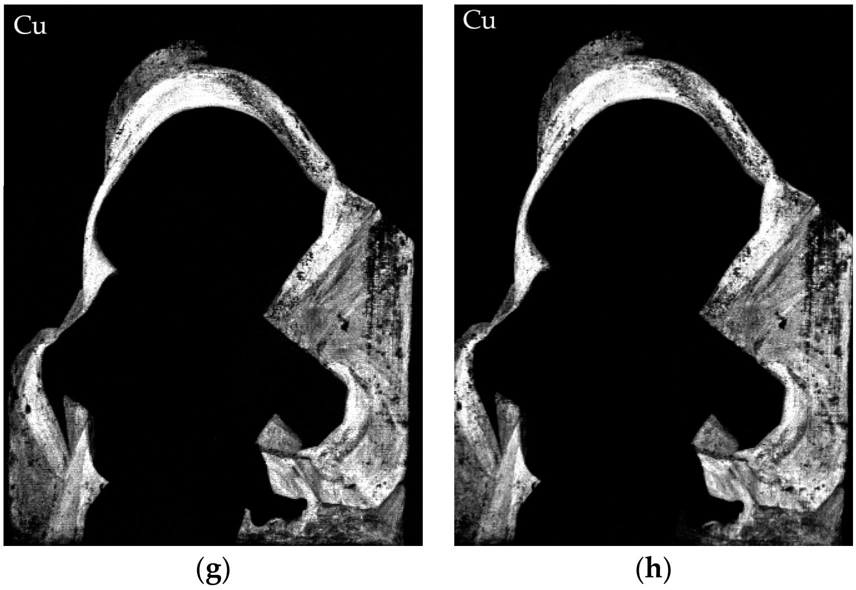


Figure 5. The *Madonna Poldi Pezzoli* before and after restoration: (**a**,**b**) Fe Kα; (**c**,**d**), Pb Lα; (**e**,**f**) Hg Lα; (**g**,**h**) Cu Kα. White is associated with maximum counts and black with minimum ones.

A brief summary of the results, i.e., the hypothesised original materials employed by Mantegna as evaluated by MA-XRF, is reported in Table 1.

Table 1. Summary of the results. Elements reported in brackets are intended as traces.

Colour	Elements Detected	Hypothesised Pigments/Colourants
White	Pb	Lead white
Blue	Cu Fe	Azurite Prussian blue (Molteni's)
Green	Cu, [Zn]	Malachite [1]
Red	Pb	Lead white (+organic dye?)
Flesh tone	Pb, Fe, Hg	Lead white Fe-based material (earth/ochres) Vermilion/cinnabar
Background	Ca, Fe	Bone black? Fe-based material (earth/ochres)

[1] Zn traces are common in malachite minerals.

4. Conclusions

MA-XRF analysis carried out on the *Poldi Pezzoli Madonna* by Andrea Mategna has proved to be of utmost importance for the conservation interventions carried out at the Opificio delle Pietre Dure in Florence. Indeed, it allowed the evaluation of the integrity of Mantegna's original pictorial layer, identifying the original azurite layer below the extended retouching painted with Prussian blue and lead white. These results have thus proved to be a fundamental element for proceeding with the removal of this extended intervention by the painter/restorer Giuseppe Molteni. Carrying out MA-XRF analysis also after the conservation intervention was also useful for OPD conservators to evaluate the effectiveness of the process itself. Indeed, one of the greatest advantages of MA-XRF lies in the fact that it yields images rather than just X-ray spectra, which need expertise to be correctly analysed and interpreted. An image instead is just immediate to read and can give strong information even to those professionals who have not undergone specific professional training for scientific data analysis. It is also important to note that the removal of such an extended retouching, as was performed in this case, is of course of considerable interest for art historians: indeed, unveiling the original pictorial layers allows the correct and thorough visualisation of the artist's characteristic painting technique and thus the correct evaluation of his style, and even the possibility to conduct a more precise dating of the work of art.

After conservation treatments, MA-XRF was carried out also to investigate the original materials and techniques employed by Andrea Mantegna. In this painting, the artist made use of an uncommon painting technique, called distemper, in which the painting layer, making the use of animal glue or vegetable gum, is applied directly onto the canvas with no preparation layer. No varnish was employed with this kind of technique, with the specific aim being to create a matte appearance for the painted surface. The original pigments hypothesised by MA-XRF are consistent with those expected in a painting completed during the late XV century: lead white, azurite, malachite, vermilion, earth/ochres and possibly red organic dye were most likely employed in this painting.

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