ACTA IMEKO
ISSN: 2221-870X
March 2022, Volume 11, Number 1, 1 - 8

Macro X-ray fluorescence analysis of XVI-XVII century Italian paintings and preliminary test for developing a combined fluorescence apparatus with digital radiography

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ABSTRACT
Using portable instruments for the preservation of artworks in heritage science is more and more common. Among the techniques, Macro X-Ray Fluorescence (MA-XRF) and digital radiography (DR) play a key-role in the field, therefore a number of MA-XRF scanners and radiographic apparatuses have been developed for this scope. Recently, the INFN-CHNet group, the network of the INFN devoted to cultural heritage, has developed a MA-XRF scanner for in-situ analyses. The instrument is fully operative, and it has already been employed in museums, conservation centres and out-door fields. In the present paper, the MA-XRF analysis conducted with the instrument on four Italian artworks undertaking conservation treatments at the conservation centre CCR "La Venaria Reale" are presented. Results on the preliminary test to combine DR with MA-XRF in a single apparatus are also shown.

Section: RESEARCH PAPER

Keywords: MA-XRF; digital radiography; pigments identification; paintings

Citation: Leandro Sottili, Laura Guidorzi, Alessandro Lo Giudice, Anna Mazzinghi, Chiara Ruberto, Lisa Castelli, Caroline Czelusniak, Lorenzo Giuntini, Mirko Massi, Francesco Taccetti, Marco Nervo, Rodrigo Torres, Francesco Arneodo, Alessandro Re, Macro X-ray fluorescence analysis of XVI-XVII century Italian paintings and preliminary test for developing a combined fluorescence apparatus with digital radiography, Acta IMEKO, vol. 11, no. 1, article 6, March 2022, identifier: IMEKO-ACTA-11 (2022)-01-06

Section Editor: Fabio Santaniello, University of Trento, Italy

Received March 7, 2021; **In final form** December 13, 2021; **Published** March 2022

Funding: This project has received funding from: the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 754511 (PhD Technologies Driven Sciences: Technologies for Cultural Heritage – T4C); INFN-CHNet and Compagnia di San Paolo (NEXTO project, Progetti di Ateneo 2017).

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1. INTRODUCTION

Nowadays, the use of non-destructive non-invasive X-Ray based techniques is well established in heritage science for analysis and conservation of artworks [1]-[3]. X-Ray Fluorescence (XRF) technique plays a fundamental role since it provides information on the elemental composition of painted surfaces, contributing to identify the materials employed in artworks. Whenever XRF is combined with scanning capability on macroscopic surfaces, the technique is indicated as Macro X-Ray Fluorescence (MA-XRF) [4]. Conversely, due to the impossibility to transport most of the artworks inside a laboratory to undertake scientific analyses, e.g., for their preciousness or considerable weight, an important class of instruments is made up of portable and transportable scanners [5]. A number of MA-XRF scanners are nowadays in use in heritage science, both commercial [6] and built in-house [7]-[9]. Despite the high analytical capabilities of the MA-XRF technique, it is worth underlining the importance of a thorough multi-analytical approach for a better comprehension of the artworks.

Another well-established non-destructive non-invasive and transportable X-ray technique is the digital radiography (DR) whose potentialities are widely known [10] as a tool for conservators and art historians [11]. It is frequently used in combination with MA-XRF by means of a dedicated instrument for a more complete information of artworks, as in the case of painting on canvas and on wooden panels [12], [13]. However, the possibility to employ a single apparatus integrating XRF and DR is not yet well investigated [14]. The advantage would be to have a single X-ray tube for a straightforward combined analysis in the same area.

In this work, the MA-XRF scanner [15] developed in-house by the Cultural Heritage Network of the National Institute of Nuclear Physics (INFN-CHNet) was used to analyse XVI-XVII century paintings under conservation at the Centro Conservazione e Restauro (CCR) “La Venaria Reale” [16], located nearby Torino. To date, the INFN-CHNet network gathers 18 local divisions, 4 Italian partners among which the CCR “La Venaria Reale”, that is a second level node in the network, and international partners as the New York University of Abu Dhabi (UAE) [17].

Moreover, a flat panel detector for DR coupled with a mini-X-ray tube that will be used in a modified version of the INFN-CHNet MA-XRF was tested on a painting on canvas. Information obtained by means of elemental mapping and radiography were combined for a better comprehension of the realisation of the artwork.

2. EXPERIMENTAL SET-UP

For the measurements presented in this paper two set-up were used: the MA-XRF scanner developed by the INFN-CHNet group for compositional information and a mini-X-Ray tube combined with a flat panel detector for DR, that will be added in a modified version of the MA-XRF scanner in the near future.

2.1. The INFN-CHNet MA-XRF scanner

The INFN-CHNet MA-XRF scanner (Figure 1) is a compact (60 × 50 × 50 cm³) and lightweight (around 10 kg) instrument. Its main parts are the measuring head, a three axes motor stage and a case containing all the electronics for acquisition and control.

The measuring head is composed by an X-Ray tube (Moxtek©, 40 kV maximum voltage, 0.1 mA maximum anode current, 4 W maximum power, Mo anode) with a brass collimator (typically 800 μm of diameter), a Silicon Drift Detector (Amptek© XR100 SDD, 50 mm² effective active surface, 12.5 μm thickness Be window) and a telemeter (Keyence IA-100). The motor stage (Physik Instrumente©, travel ranges 30 cm horizontally (x axis), 15 cm vertically (y axis) and 5 cm in z direction) holding the measuring head is screwed on the carbon-fibre case. Typical operating voltage is around 30 kV. Signals are collected with a multi-channel analyser (model CAEN DT5780) and the whole system is controlled by a laptop.

The control-acquisition-analysis software is developed within the INFN-CHNet network and allows both an on-line and an off-line analysis. The output of the acquisition process is a file containing the scanning coordinates and, for each position, the spectrum acquired. For each map, a single element can be selected and shown in the scanned area, or in a part of it. Using the raw data, for each element the relative intensities are shown

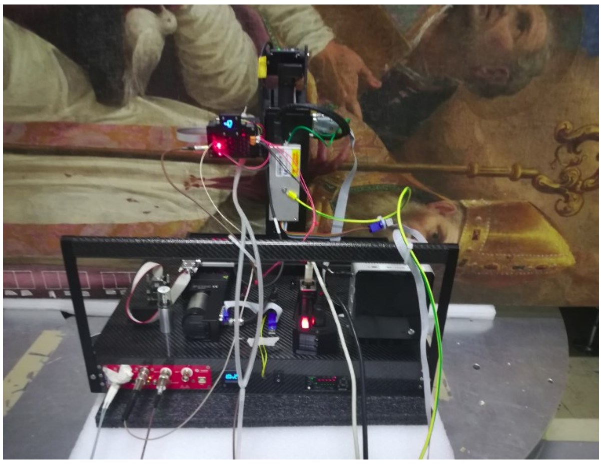

Figure 1. INFN-CHNet MA-XRF scanner placed in front of the panel painting *Madonna e i Santi* by Cristoforo Roncalli, known as il Pomarancio.

in grey scale, in which the maximum intensity is in white and the lower is in black. Scan is carried out on the x axis, and a step size of typically 1 mm is set on the y axis resulting in a pixel size of 1 mm². A complete review on the instrument can be found in [15]. The instrument has already been used for a number of different applications, i.e. paintings [18]-[21], illuminated manuscripts [22], coins [23], ceramics [24], and furniture [25].

2.2. The digital radiography set-up

Structural information of artworks can be obtained by a radiographic approach. Although a radiography could be carried out in principle using the same X-ray tube employed in the present INFN-CHNet MA-XRF apparatus, for future applications a modified version with a different source will be considered. Considering the higher distance from the object needed to obtain a radiography than XRF maps, and the thickness of artworks to be passed through, an X-ray tube with a slightly higher voltage and power was used. In particular, the measurements were made with a Moxtek©, 60 kV X-Ray tube (1 mA maximum anode current, 12 W maximum power, 0.4 mm diameter nominal focal spot size, Rh anode). If not collimated, it generates a 20 cm diameter beam at about 25 cm of distance. As the present MA-XRF apparatus only has a 5 cm z travel range, the future version will be capable of a translation in z up to 30 cm to avoid the handling of the artwork between XRF and DR measurements.

About X-ray imaging, a Shad-o-Box HS detector by Teledyne, model 6K was selected. The detector contains a large active area (11,4 cm × 14,6 cm) that is fully covered by the X-ray beam at 25 cm of distance from the source; the pixel size is 49.5 μm and the maximum integration time 65 s. The video signal is digitised to 14 bits, reassembled within the camera’s FPGA, and then transferred to a computer via a high-speed Gigabit Ethernet interface. The CMOS sensor inside the detector contains a direct-contact CsI scintillator, that converts X-ray photons into visible light that is sensed by the CMOS photodiodes. A thin graphite cover protects the sensor from accidental damage as well as from ambient light. The Shad-o-Box HS camera also contains lead and steel shielding to protect its electronics from X-ray radiation. The cameras are sensitive to X-ray energies as low as 15 keV, and may be used with generators up to 225 kV_p. The detector, that has already been used for X-ray imaging with conventional tubes [26], is part of the NEXTO project that has the aim to integrate MA-XRF, DR and X-Ray Luminescence (XRL) [27] in a single portable instrument.

3. APPLICATIONS AT THE CCR "LA VENARIA REALE"

In this section different applications of the instrumentation on paintings are presented. The works of art represent case studies from Italian central regions of different periods (from the beginning of the 16th to the beginning of the 17th century). They were analysed during conservation processes carried out at the CCR "La Venaria Reale" [28]. For the MA-XRF measurements, a collimator of 800 μm diameter was used. The vertical step was set to 1 mm and a scanning speed of 3 mm/s. Furthermore, the Keyence IA-100 telemeter was switched on to maintain the sample distance during the scanning process.

3.1. *Madonna di San Rocco* by Francesco Sparapane

The first painting presented is the oil on panel *Madonna di San Rocco* depicting the Virgin with the Child, Saint Antonio from Padua and Saint Rocco by Francesco Sparapane (Preci, Umbria region, 1530 ca.). The importance of the work of art is related to the lack of documented paintings by the author, thereby its study represents a key-feature for understanding the painting technique of the artist [29].

The MA-XRF measurements were conducted on two areas as shown in Figure 2, from which a number of maps were created. The source voltage was set to 30 kV and its anode current to 20 μA.

The maps around Saint Rocco (Figure 3) show the use of lead white, most likely due to the imprimatur layer and as proper pigment in the flesh tones. From the map of copper, the green part of the hat was realised with copper-based compounds [30]. The presence of tin is also detected in this same region, although in moderate amounts, and might be due to the use of lead-tin yellow in mixture with the copper-based pigment. A more precise identification of the material cannot be made with XRF technique: for instance, it is not possible to distinguish between a mixture of tin-based yellow with malachite rather than with azurite [31].

Figure 2. Painting *Madonna con Bambino e S. Antonio e S. Rocco* by *Francesco Sparapane*. The scanned areas are indicated in the white boxes.

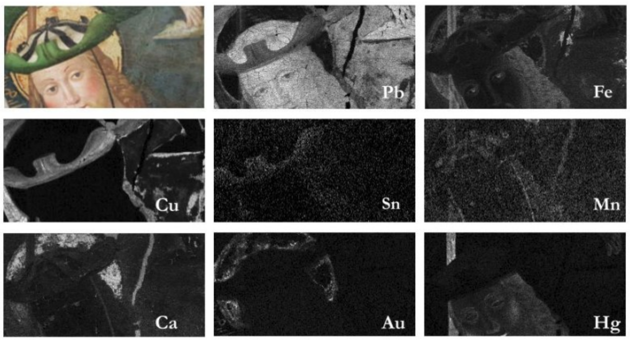

Figure 3. MA-XRF maps of area 1 of the *Madonna di San Rocco* by Francesco Sparapane (size 280 mm × 70 mm).

The shadows of the flesh tones were realised with ochre-earths, as can be inferred from the match between iron and manganese maps [32]. Corresponding to the red tone in the checks, a high signal of mercury is present, most likely due to the use of vermilion-cinnabar (HgS) [33]. Furthermore, calcium is present in the strings of the hat, the dark strips and in the eyes, that may indicate the use of bone black for darkening [34] as well as manganese in the same areas may indicate the use of manganese black [35].

The halo was made with gold (Figure 3), while the corresponding presence of calcium and iron is probably due to a calcium/iron-based preparation, as discussed in [36].

The second area around the upper part of the head of S. Antonio (Figure 4) presents similar results. However, a marked difference is related to the sky, that is made with a copper-based compound (most likely azurite [31]) with a glaze realised with smalt, a material rarely used as a pigment from the 15th century and which was widespread from the 17th c. onwards. Concisely, smalt is a blue potash glass (thus characterised also by presence of potassium and aluminium) where the chromophore is cobalt and it usually contains impurities, among others, of bismuth when produced after 1520 [37]. Its presence is thus hypothesised by the maps of the corresponding elements. A similar palette was probably used for the sky in the first area; however, due to the bad conservation condition, only traces of the characteristic elements are present in the maps of copper and cobalt.

3.2. Madonna con bambino e santi by Pomarancio

The oil on canvas *Madonna con bambino e santi* by Cristoforo Roncalli, known as il Pomarancio, was made in the first decade of the 17th century, and it is placed in the Santa Maria Argentea church in Norcia (Umbria region, Italy). The Virgin and the Child are depicted with the Saints Eutizio, Fiorenzo, Santolo, and Spes.

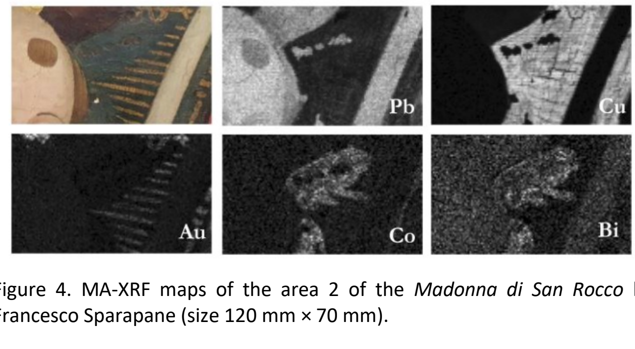

Figure 4. MA-XRF maps of the area 2 of the *Madonna di San Rocco* by Francesco Sparapane (size 120 mm × 70 mm).

Figure 5. Painting *Madonna con bambino e i Santi* by Il Pomarancio. The scanned areas are indicated in white boxes. The saints are, from left, S.Eutizio, S. Fiorenzo, S. Santolo, and S. Spes.

The focus of the analysis was the painting palette used in the flesh tones by the author [38], of which two representative areas were scanned, as shown in Figure 5.

The source voltage was set to 28 kV and its anode current to 20 μA.

The maps realised in the first area (Figure 6) show the use of lead white for the flesh tones and the book, while a high signal

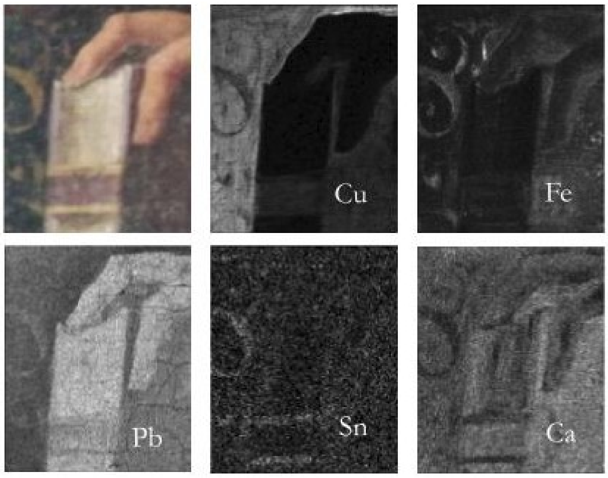

Figure 6. Maps of the area 1 of *Madonna con bambino e i Santi* by il Pomarancio (size 130 mm × 110 mm).

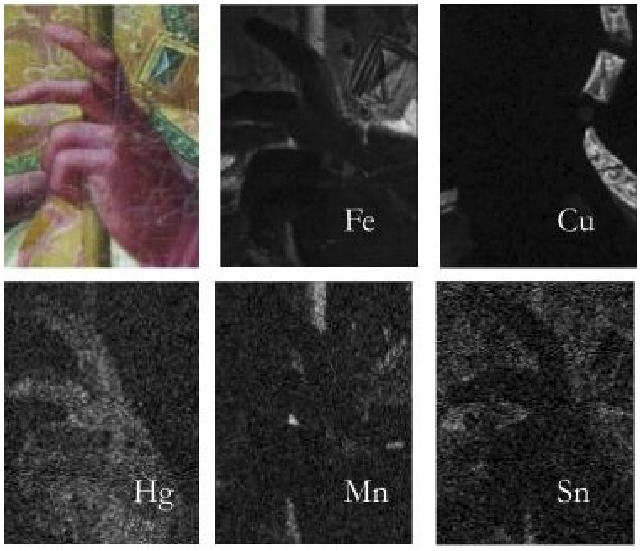

Figure 7. MA-XRF maps of area 2 of *Madonna con bambino e i Santi* by il Pomarancio (size 150 mm × 137 mm).

of iron is present corresponding to the shadows. The blue cope of Saint Fiorenzo shows an intense signal of copper, due to a copper-based compound, leading to the hypothesis of azurite [31].

The darkest colour is related to a high signal of calcium, that, by only means of the XRF technique, cannot lead to a precise hypothesis on the material used.

Furthermore, the presence of tin was detected in the squiggles as well as a higher intensity of lead, most likely due to the use of lead-tin yellow [32].

The second area (Figure 7) shows a different composition: the map of mercury matches with the hand, leading to the hypothesis of vermilion-cinnabar for the glove. As opposed to the previous area, the map of iron does not show an intense signal in the hand of Saint Spes. The main signal of iron comes from the stick and the cope in correspondence to the yellow colour. By comparing the maps of iron, manganese, mercury, and tin, it can be noted that all of them are present in the crosier, even if tin and mercury are in the highlights, whereas the manganese and iron are in the shadows. This result can be explained by the use of vermilion-cinnabar mixed with lead-tin yellow [32] in the highlights, and the use of ochre-earths [32] in the shading. Iron, manganese, and tin are also present in the yellow cope. Furthermore, iron and manganese are present in the green medallion, which present a strong signal from copper, related to copper-based pigments.

From the map of copper, it may be seen that all the green colours in the area are related to its presence. However, as in the hat of Saint Rocco seen in the previous section, it is not possible to hypothesise a conclusion on the material used.

3.3. Adorazione dei Magi by Sante Peranda

The oil on canvas *Adorazione dei Magi* by Sante Peranda (Figure 8) is dated around the first decade of the 17th century. In this case the interest was focused on the blue colours.

The measurements were conducted in three areas: one on the robe of the Virgin, one behind the Magus on the far left wearing the white dress, and the last one behind the kneeling Magus. The composition detected is different for each area. The source voltage was set to 28 kV and its anode current to 30 μA.

In the first area, the Virgin's robe (Figure 9), cobalt is present. As in the previous sections, this may suggest the use of smalt as

Figure 8. *Adorazione dei Magi* by Sante Peranda. The scanned areas are indicated in white boxes.

blue pigment [37]. The match between the cobalt and the silicon maps most likely indicates the use of such blue glass in this area. Furthermore, the localised lack of these two elements in the area is related with the presence of a conservation intervention with a titanium-based material [32].

In the second area, shown in Figure 10, the composition of the blue is similar to the previous, despite the presence of a significant iron signal, probably due to the use of ochre-earths for the shading [34]. However, with this technique alone a later retouch with Prussian blue cannot be excluded [39]. Beside the map of cobalt, the map of bismuth is also reported to confirm the hypothesis of smalt and, consequently, the dating of the painting [34]. Moreover, it can be seen that the Lα-line of lead (10.55 keV) is detected in the whole area, whereas the M-lines (2.34 keV) are present only in the robe. This is due to the different absorption for different X-Ray energies (the lower is the energy and the higher is the absorption), therefore the comparison of the two maps suggests that lead white was used for the imprimatur, as well as for the white robe of the Magus on the far left.

A different composition is detected in the last blue area (Figure 11). In this case a strong signal of copper is present,

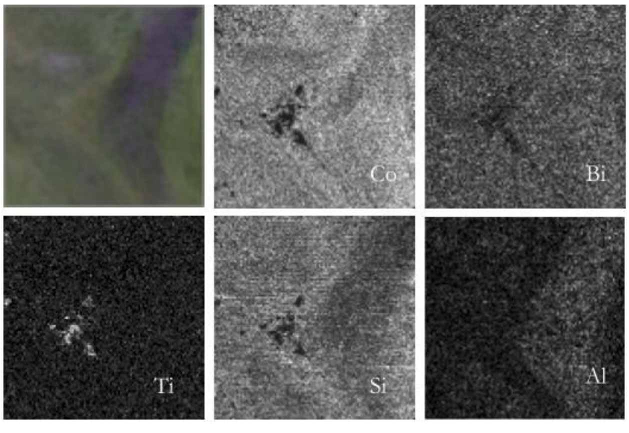

Figure 9. Maps of area 1 in the robe of the Virgin in Figure 8 (size 100 mm × 100 mm).

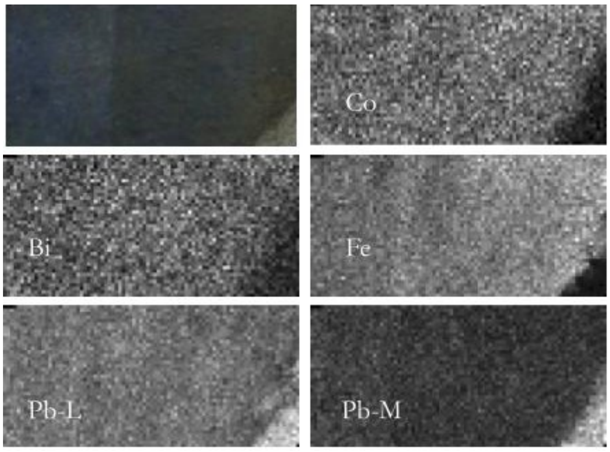

Figure 10. Maps of area 2 in the robe of the Magus wearing the white dress in Figure 8 (size 85 mm × 40 mm).

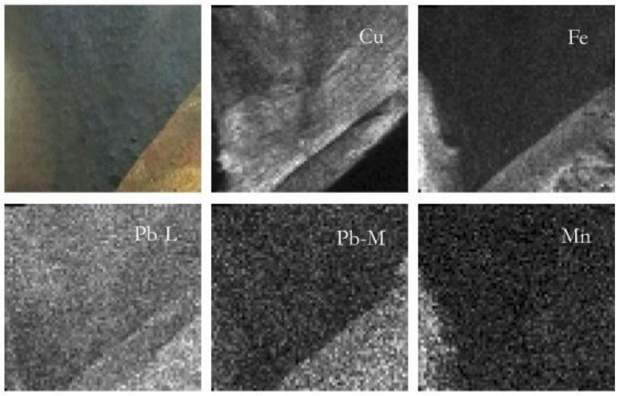

Figure 11. Maps of area 3 in the blue robe behind the kneeling Magus in Figure 8 (size 70 mm × 65 mm).

whereas no presence of cobalt was detected. For this reason, conversely to the previous cases, the use of azurite can be hypothesised for the blue tone in the area. It is also clearly visible from the map of copper its presence beneath the yellow robe, probably due to a pentimento in the back of the kneeling Magus. The last hypothesis can be also supported by the maps of lead, in which its use up on the copper can be hypothesised by the detection of the M-line only in the region of the robe, whereas the rest of the area shows only the L-lines of lead.

The yellow robe shows the presence of iron and lead, which may suggest a combined use of white lead and yellow ochre-earths [31].

The hair of the servant present in the area shows a signal of iron and manganese, probably due to the employment of ochre-earths.

3.4. Madonna con Bambino ed i Santi Crescentino e Donnino by Timoteo Viti

The last painting presented is the *Madonna con Bambino ed i Santi Crescentino e Donnino* by Timoteo Viti (Figure 12), dated between 1500 and 1510. The work is a tempera on canvas, its size is 168 cm × 165 cm. The painting presented bad conservation conditions on the areas around the faces of the Virgin and the Child. The painting technique is *tempera magra* [40], in which the binder tends to be absorbed by the preparatory layer. Moreover, the application of a protective varnish was not envisaged, leaving the paint in direct contact with the external environment.

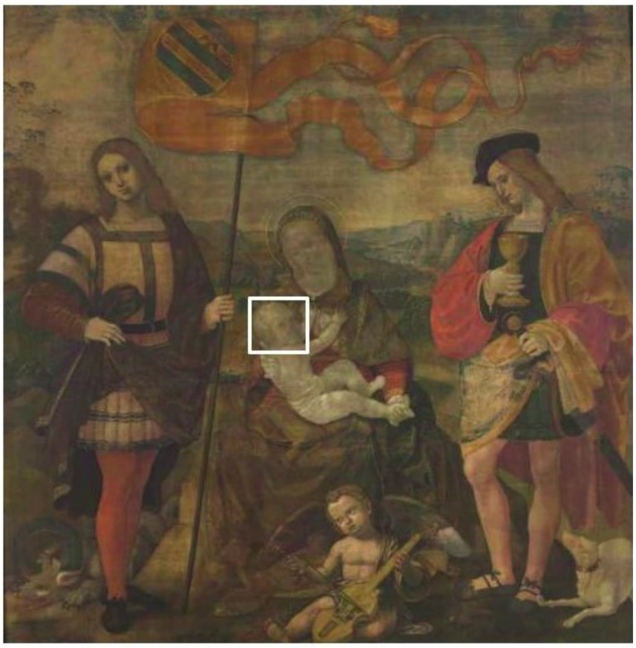

Figure 12. Madonna con Bambino e i santi Crescentino e Donnino by Timoteo Viti. The results presented are from the area in the white box.

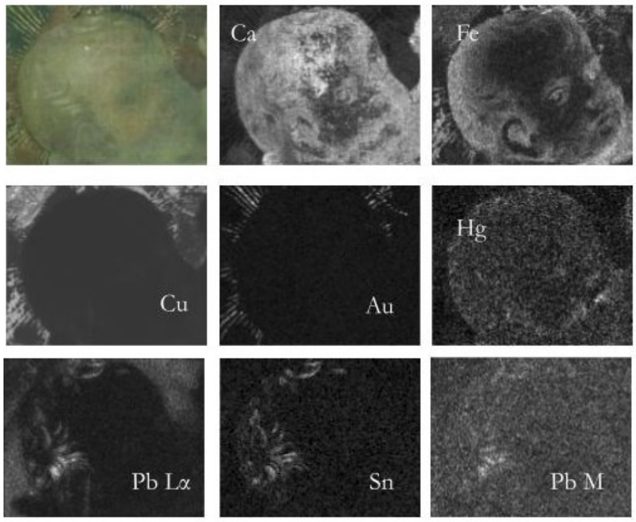

Figure 14. MA-XRF maps of the area around the face of Jesus Christ in *Madonna ed i Santi Crescentini e Donnino* painting (size 140 mm × 110 mm).

Figure 15. Radiography of the area around Jesus Christ's face.

The source voltage was set to 28 kV and the anode current to 30 μA. The maps of the area around the Child's head are presented in Figure 14.

As can be seen from Figure 13, the flesh tones are characterised by a strong signal of calcium, whereas no evidence of the use of lead was detected. Moreover, the shading was made most likely with ochre-earths, according to the map of iron. In addition, the highlights of the mouth and the cheeks show a signal of mercury, most likely due to the use of cinnabar-vermilion. The high presence of calcium can be explained with the use of white of San Giovanni (white lime) pigment or other calcium-based compounds [41].

Furthermore, by creating a spectrum in the area of the face, and comparing it with a spectrum obtained outside (Figure13), it can be noted a higher intensity of the 2.0 keV line compared with the Kα of calcium, that can be explained with the presence of phosphorus in the flesh tone. This may be explained with the presence of bone black, a pigment used for shading [34].

The signal of lead is present in the hair of the Child. Furthermore, the match of the spatial distribution of tin with lead may indicate the use of lead-tin yellow for it.

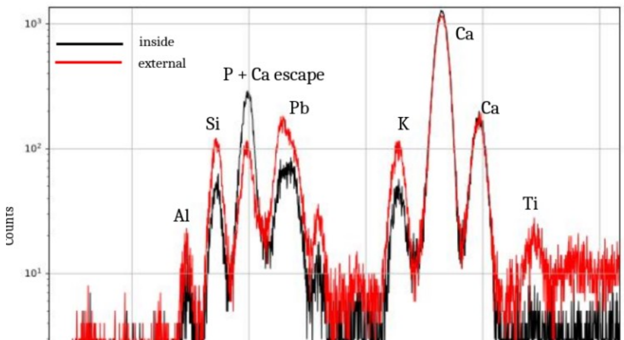

Figure 13. Comparison between two spectra, one obtained selecting an area inside the face (black) and outside (red).

The landscape of the background was realised with copper-based compounds mixed with ochre-earths, while the halo was realised with gold.

In addition to the MA-XRF measurements, a radiographic investigation was carried out in the same area using the set-up described in section 2.2. The voltage was set to 20 kV, the anode current to 0.6 mA and the integration time to 2 seconds. As shown in Figure 15, for example in Jesus Christ's hair, the image is more detailed than the MA-XRF map: this allows the visualization of warp and weft threads of the canvas. Moreover, it can be observed to match with the MA-XRF map distributions of the heavy metals (Pb, Sn, Au, Cu), and only partially with the distribution of calcium. This result is due to the very thin thickness of the painting layer, typical of the *tempera magra* painting technique.

4. CONCLUSIONS

The INFN-CHNet MA-XRF scanner was applied on four Italian paintings at the CCR "La Venaria Reale". For each application, different queries were advanced during the conservation processes and the described analysis achieved important information on the painting layers.

In the *Madonna di San Rocco* by Francesco Sparapane, the composition of the flesh tones of S. Antonio and S. Rocco were identified, even though a definite composition cannot be measured, due to the limitation of the XRF technique to detect elements lighter than sodium. A similar conclusion has been made for other parts of the painting (the sky and S. Rocco's clothes).

In the *Madonna con bambino e i santi* by il Pomarancio, the wide painting palette (lead white, lead-tin yellow, cinnabar-vermilion, copper-based compounds) was measured, confirming the skills of the author.

For the *Adorazione dei Magi* by Sante Peranda, the blue colours in the areas under study have shown different compositions. It is worth noting that a more precise identification of the materials employed in the painting layers is not possible with only XRF technique, but a further investigation with other techniques such as Fiber Optics Reflectance Spectroscopy (FORS) or Raman spectroscopy is needed.

In the last painting, the presence of calcium-based white in the face of the Child was detected. However, no signal of lead is present in that area, whereas it is present in the background. In addition, DR was conducted in the same area using a new set-up that was proven to be suitable to be combined with XRF in a single instrument. The test carried out at the CCR "La Venaria Reale" is the first step for the development of this multi-technique device.

The complete realisation will rely on the expertise of the INFN-CHNet group, which has already allowed to achieve several important technological results in heritage science applications [42]-[46].

Acknowledgement

This project has received funding from Compagnia di San Paolo (NEXTO project, progetto di Ateneo 2017) and the INFN-CHnet project.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 754511 (PhD Technologies Driven Sciences: Technologies for Cultural Heritage – T4C).

The authors wish to warmly thank Marco Manetti of the INFN-Fi for his invaluable technical support, the students Giulia Corrada, Francesca Erbetta, Daniele Dutto, Giulia Dilecce and their supervisors, Prof.ssa Gianna Ferraris di Celle, Prof. Alessandro Gatti, Prof. Bernadette Ventura, Prof. Antonio Iaccarino Idelson and the staff of the CCR "La Venaria Reale" for its support.

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