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Microchemical Journal

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Non-Destructive and portable analyses helping the study and conservation of a Saraceni copper plate painting in the São Paulo museum of art



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ARTICLE INFO

Keywords: Saraceni Copper Conservation Imaging XRF Cultural heritage

ABSTRACT

This study focuses on the results of the technical analyses performed in the copper painting "Venus with Mars and cupids", dated around 1606-1608, attributed to the Italian painter Carlo Saraceni. As this painting is the only example of this kind of refined technique at the museum and as it is one of the masterpieces of the collection, an interdisciplinary project of in-depth study was realized at MASP's conservation studio. On the one hand, the aim was to understand the features and the making of the artwork, bringing new insights and enhancing our knowledge of Saraceni's painting technique, since little technical information has been published about the painter's work. On the other hand, it was necessary to understand the condition of the painting by means of non-destructive analyses, as several damages were compromising the conservation of the painting in the future. Complete multispectral imaging, including infrared reflectography, and X-ray fluorescence spectrometry were made in order to characterize the original materials - as the painter's palette - and to understand the painting's creation process. Imaging and close examination allowed also to distinguish and map all the alterations presented in the painting, leading to appropriate diagnosis and treatment. This project introduced interdisciplinary approaches and decision-making into the Conservation's studio of the museum, as well as a systematic scientific examination when confronting technical and conservation issues. This paper shows also the gains of confronting different scientific examination with scientific literature in artworks study and conservation's methodologies.

1. Introduction

The São Paulo Museum of Art (MASP) is a renowned Brazilian museum, hosting the largest collection of European paintings in South America. The painting "Venus with Mars and cupids", $39.5 \times 52 \text{ cm}^2$ (Fig. 1) is an oil painting on copper representing one of the Ovid's Metamorphoses (IV, 167-189), which narrates the passion of the gods Mars and Venus. It is one of the masterpieces of the São Paulo Museum of Art (MASP).

The painting was presumably realized between 1606–1608 by the Venetian painter Carlo Saraceni (1579–1620). This attribution was made by the specialist Roberto Longui, because of the similarities between the MASP's painting and an ensemble of paintings conserved in the Galleria Nazionale of Naples in Milan [1]. This ensemble is composed of six oil paintings on copper representing mythological scenes of Ovid's Icarus myth. The first protectors of Saraceni, the Farnese family,

commissioned it around 1608. The ensemble presents indeed very similar stylistic features and dimensions to MASP's painting and it was attributed in the past to the German painter Adam Elseheimer, before being attributed to Saraceni, as MASP's painting [2]. The copper painting "Venus and Mars" of the Thyssen-Bornemisza Collection in Madrid, dated ca. 1600 (39.5 \times 55 cm²), can also be related to our painting. With similar dimensions, they both use analogous sources and workshop prototypes.

The use of copper plates as support was developed under the experiment context of the Renaissance during the 15th century, in Italy [3]. However, its diffusion was especially due to the development of metallic engraving and etching, and thanks to the German and Flemish painters who worked or studied in Italy during the 16th century and spread the technique in North Europe [4–6]. In the Americas, this technique was developed from the 17th to the 19th century in Peru, Colombia and especially in Mexico [7]. Yet, it is the only exemplar in

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Fig. 1. Photography with visible light from the front of the painting "Venus with Mars and cupids", attributed to Carlo Saraceni, before treatment. .

MASP's collection.

The painting needed an in-depth technical study in order to bring new information about the painter's technique and palette, and to determine a suitable diagnosis of the alterations presented. Indeed, we realized that little information was available about Saraceni's technique. Only few technical analyses were found [8], neither of them about his copper's production. A better understanding of the technical features, the material history and the conservation condition of the painting was therefore essential.

The need for more in-depth analysis has increased parallel to the development of the conservation's field and the application of inter-disciplinary approaches has become essential to museums' conservation methodologies. Indeed, the information of many techniques can be carefully combined to build a clearer understanding of the structure, evolution and condition of a painting [9]. Thanks to external scientific teams like the Physics Institute of the University of Sao Paulo (IFUSP) and the Physics Department of the Londrina State University (UEL), it is now possible to perform several technical analyses, like multi-spectral photography – including Infrared Reflectography (IRR) – and X-Ray Fluorescence Spectrometry (XRF), allowing the study and conservation of more complex cases at the museum's studio. Both teams performed all the technical analyses in situ, in the conservation's studio, offering an interdisciplinary discussion environment.

2. Methods

Complete imaging of the painting was performed by IFUSP [10,11]. The entire photographic recording was done with a Canon 5D Mark III camera and Canon EF 24–105 mm f/4 L IS USM lens. All the visible light imagery was realized using a set of two 1000 W halogen lamps. For raking light photography was used a homemade led arrangement with twenty-four LED lamps (3 W per lamp). For ultraviolet fluorescence photography were used two sets of four Phillips UV fluorescent lamps (40 W per lamp). A ColorChecker® chart was employed to correct the white balance and camera color profile.

Visible and raking light photographs are important to register the painting before treatment and allow to understand some technical painting features that the human eye are not able to detect directly. Raking light examination brings valuable information about the

topography of the painting and the support, for example, thicker paint zones (containing more paint layers) or impastos, and support deformations. In addition, it allows detecting paint alterations, as liftings, and some old interventions, as the structure of old restoration inpainting and fillers often differs from the original paint structure [9].

In UV visible fluorescence, UV rays react with the materials on the surface of the painting responding differently, exhibiting different colors and intensities of fluorescence - while some others do not fluoresce at all - providing valuable information about the surface condition of a work of art [9]. This examination is extremely useful to detect restoration coatings as adhesives and varnishes. For example, old varnishes, as natural terpene resins, emit a particular green and slightly opaque fluorescence, which intensifies as they age and yellows, because the oxidation process of these resins results in increased absorption of the longer wavelengths of UV and of the shorter wavelengths of visible light. UV fluorescence also allows distinguishing in painting, which appears as dark patches scattered over the surface, especially if they are recent or if they were made on top of an old varnish layer. This is because the restorations were carried out in different materials that usually fluoresce much less than the aged varnish or the original oil paint. UV analysis can finally provide important information about the materials, pigments and media that have been used in a given artwork [9].

For infrared reflectography (IRR) an Osiris camera (Opus Instruments) was used, coupled with an InGaAs array sensor with 900-1700 nm operation range. The same arrangement of halogen lamps was used for the illumination. IRR is a non-invasive method based on wideband imaging in the near-infrared range, exploiting mainly the IR-A (780-1400 nm) band. It allows looking beneath the visible layers of paint, since many paints can become transparent in the longer-wavelength infrared portion of the spectrum. IRR passes through paint stratigraphy until it reaches something that absorbs it or it is reflected back to the camera. Preparatory drawings that lie beneath the finished surfaces of paintings - called underdrawings - are frequently made of carbon-rich material such as graphite, charcoal, or bone black, which is very absorbent of infrared radiation, appearing darker in the IRR. The 'reflect' element of reflectography refers to the reflection of a light source from the ground beneath a painting. It is particularly effective when a painting is made of a white or light-colored ground layer, which

is often the case in 15th to 17th century paintings [12].

The identification of the inorganic pigments composing the paint layer was realized with portable XRF equipment, after imaging was performed. Indeed, is important to have detected all the inpainting and altered areas, by means of close examination and imaging, especially with UV fluorescence and IRR, in order to carefully select the points to analyze. Otherwise, spectra can give erroneous or confusing results that difficult the identification of the original paint layer. The analyzed point could contain the original pigment, but also non-original pigments or other materials added after the creation of the painting, during past restoration campaigns. These non-original elements could be distinguishable with XRF if they are inorganic and if they are different from the elements used at the period when the painting was painted. Nevertheless, these non-original materials may contain the same elements present at Saraceni's period, as several pigments of the period were still used until the 19th century; some of them are still used today.

XRF measurements were carried out by means of a portable system developed by the Applied Nuclear Physics Laboratory (LFNA) at UEL [13], which consists of a mini X-ray tube from Moxtek Inc. (4 W, voltage of 0–40 kV and electric current of 0–100 $\mu A)$ with Ag anode and the X-123SDD complete X-ray Spectrometer with silicon drift detector, from Amptek Inc. (with a 12,7 μm Be window and resolution of 139 eV at 5.9 keV), with a 3 mm Ag collimator. The angle between the X-ray tube and the detector was 90° and a pair of low-intensity lasers was coupled to the measurement system in order to indicate the point of analysis [14].

A total of 44 spectra was obtained in several color regions through the pictorial layer (Fig. 2), working at 28 kV and 1 μ A, with 300 s of acquisition time. These excitation conditions were chosen in order to achieve the highest count rate and, at the same time, keeping the dead time as low as possible, due to the very high Cu fluorescence lines (order of 20 times higher than the other peaks of interest) and/or the very high Pb fluorescence lines (order of 10 times higher than the other peaks of interest). The set of spectra was analyzed using the software PyMca [15] and the data was systematized with count rates histograms. These histograms were made for all identified elements, considering only net areas greater than three times the statistical propagated deviation. All histograms present the statistical propagated deviation bars, which in some cases are very small compared with the column values.

The pigments were identified based on the colors associated with the presence of key-elements in the XRF spectra. Because the support is a copper plate, the analysis was also made considering the behavior and the variation of the intensity of the copper lines in all the points measured throughout the painting, which is discussed further.

3. Results and discussion

3.1. Painting's technique

Crossing scientific literature, imaging and XRF measurements was crucial to understand the copper plate manufacture and the painter's technique, bringing valuable information about Saraceni's work.

The copper plate was probably first hammered to achieve 1 mm of thickness by a copper-beater, then cut to the desired format. Indeed, until the late 18th century most plates were produced from hammered copper sheets (though occasionally, from the early 17th century the sheets could have been rolled as well with rolling machines, which became more widespread in the 1770s) [4,6].

Due to its completely smooth surface, copper sheets needed some preliminary treatments before being painted. The plates were sanded and degreased with some abrasive material and an organic substance, in order to improve the adhesion of the painting [3]. Some of the abrasive material used to sand the metallic surface were ashes, stones, emeries, metallic brushes, among others; the goal was to create fine etching on the metallic surface where the painting could physically be attached [4,16]. Concerning the organic material, garlic and onion seem to have been often used, possibly to improve the surface tension of the painting, creating a certain roughness on the metallic surface and acting as siccative [4,16,17]. Although these organic substances are difficult to detect with microchemical analyses, as their components are volatile. The sanding treatment seems to appear in the macro photography of the lacunae (e.g. Fig. 3), which shows the fine scratching created by the abrasion.

XRF helped understand that the ground layer is composed of white lead and a filler (calcium sulfate or carbonate). Indeed, lead and calcium were detected in all the spectra obtained by XRF (table 1). Fig. 4 presents the count rates histograms of Ca-K α and Pb-L α for all measured regions. IRR image (Fig. 5) shows this layer was unevenly



Fig. 2. Photography with visible light of "Venus with Mars and cupids" showing the points analyzed by XRF.



Fig. 3. Macro image of a lacuna before restoration showing scratches from the sanding. .

applied, since among whiter areas, we observe some dark elements. Indeed, the painter seems to have reserved some areas from the ground layer in order to use the copper's natural tonality. This is the case of the trees and the lower register of the painting (with the armor and the vegetation), which are the darkest areas of the composition in the IRR, as they may contain very little white lead. The points measured by XRF spectrometry in these trees (points 3, 13, 15, 16, 20, 21, 28 and 30 at Fig. 4B), shows indeed less quantity of white lead compared to the other spectra measured. In these areas, the color of the copper seems to have been used in purpose, while the rest was grounded with a thicker white lead layer to facilitate the construction of the lighter areas of the composition.

Technical studies of other copper paintings show that most of the grounds are thin, whitish and made with oil media, often containing lead compounds, as lead carbonate or lead oxides (and sometimes a certain amount of pigments) [4]. It is also known Saraceni used this kind of ground in other paintings [8]. However, we can also find situations where the painters exploited the optical potentialities of the copper by using simple and transparent oil or oil and resin layers (containing sometimes very little amounts of extender or pigments) only to isolate the support [4,16,18]. Consequently, in the case of the MASP's painting, we observe a sort of hybrid situation, as the painter seems to have played with both the thicker and the thinner white ground layer.

These oil ground layers – transparent or pigmented – have an isolation function because of their hydrophobic properties, giving to the

copper surface a certain degree of protection from humidity penetration [19]. Also, combined with lead pigments, the oil medium has a tendency to form lead soaps that increase even more the hydrophobia of the layer [20]. Finally, the fatty acids of the oil and resin layers would react with the ions formed with the natural oxidation of the copper in the surface of the metal, creating a translucent green layer of copper oleate or resinate soaps [21]. It has been suggested that these soap layers would have an impact on the adhesion of the paint layer, yet their consequences are still not certain [19].

The IRR image also allowed us to analyze the preparatory drawing, which seems to have been made first with a dry media, like charcoal, then with a humid media – possibly oil painting – applied with a brush (by comparison with other underdrawing description [12]). The first drawing appears more synthetic, with darker and rapid outlines, describing mainly the contours of the figures. The wet drawing seems to link these dry outlines in a subtler manner and give more details. It is important to note that similar underdrawing has been studied in another painting of Saraceni [8].

Another remarkable fact about the painters' technique that could be observed thanks to IRR image is the innumerous modifications the artist made to his drawing to achieve the final composition. Most of the "pentimenti" are readjustments of the figures body outlines or even bigger changes in the composition made during the painting stage. For example, the positions of the bodies of the gods and some of the cupids were totally rethought, as well as the place of Mars' armor, which was mended to be placed at the right lower corner instead of its actual central position (Fig. 6). We can assume that Saraceni elaborates his composition while he is painting, spontaneously, as he had shown in other cases [8].

Imaging examination allowed revealing a particular feature that also contributes to characterize Saraceni's production: the presence of an unachieved area. The little musician cupid represented next to Mars, on the floor next to a sort of rock, is supposed to hold a flute in his hands, which is absent in the final composition (Fig. 7). We could notice that these characters' paint layer is thinner, and it appears greener than the other figures in visible light photography. It can be assumed that some final brushstrokes are lacking. Together with the cupid, the rock near it also appears unfinished. We can notice in the IRR image that the rock seems to be a reserved area with very little white lead. With visible light, we see it very flat, without any depth (besides its bad condition, which we will describe later). Considering all these elements, we can conclude this part of the composition was left unfinished, as the cupid and the rock are lacking some final paint layers intended to detail and give more reality to the scene.

The paint layer is in general thin and translucent, due to the glazes used to construct the shadows. Delicate and precise brushwork represents the highlights, as it is shown in the raking light photography (Fig. 8). These lightest areas have more body, resulting in little impasto typical of Saraceni's technique [8].

Table 1
Pigments identified by XRF in the painting "Venus with Mars and cupids", by Carlo Saraceni.

	Key-elements	Pigments	Chemical composition [27,28]
Underlying layers	Pb	White lead	2PbCO ₃ .Pb(OH) ₂
	Ca	Calcium carbonate and/or Calcium sulfate	CaCO ₃ and/or CaSO ₄
Whites	Pb	White lead	2PbCO ₃ .Pb(OH) ₂
Blacks	Ca	Bone black	$C + Ca_3(PO_4)_2$
Yellows	Pb, Sn	Lead-Tin Yellow	Pb_2SnO_4
	Fe	Yellow ochre	$Fe_2O_3.H_2O$
Blues	Cu*, Ba**	Azurite	2CuCO ₃ .Cu(OH) ₂
Greens	Cu	Malaquite and/or Verdigris	CuCO ₃ .Cu(OH) ₂ and/or Cu(C ₂ H ₃ O ₂) ₂ .2Cu(OH) ₂
Reds	Hg	Vermilion	HgS
	Fe	Red ochre	Fe_2O_3
Browns	Fe	Brown ochre	Fe ₂ O ₃ .MnO ₂ .nH ₂ O + clay

^{*} Inconclusive;.

^{**} Lake substrate, contamination or restoration.

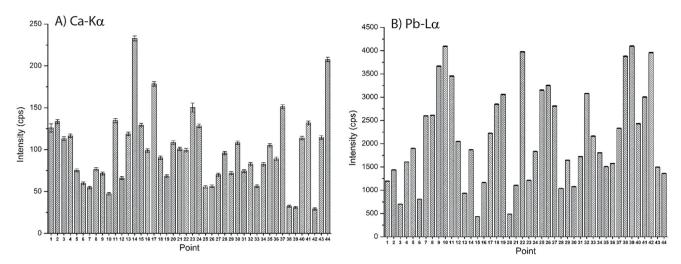


Fig. 4. Line count rates histogram, showing the net area for each analyzed point determined by XRF: A – Ca-Kα; B – Pb-Lα.

Concerning the paint layer composition, XRF analyses brought interesting results. In the whitish tonalities, for the bodies and the clouds, white lead was found, for example points 9, 10, 38, 39 and 42 (Fig. 4B). Moreover, the histogram of the lowest energy Pb-M α line, at Fig. 9A, shows higher peak intensities at the points where the white lead is present in the uppermost paint layers. At this graph, the same points mentioned above also stand out.

In the reddish colors, like the red drapery (points 29, 31, 34, 35 and 36) and the pink tonalities of the flesh tones, peaks of mercury show the use of vermilion (e.g. Fig. 9B). This pigment was probably mixed with earth and/or ochre pigments, rich in manganese and iron, shown at Figs. 9C and 9D, respectively, (points 8, 24, 27 and 40). Some bone or ivory black could be used as well for darker colors, as shown by the calcium intensity on Fig. 4A, at point 44, for example. Earth and/or ochre pigments were also employed in brownish regions, such as points 2, 4 and 5 (Fig. 9C).

Fig. 10 shows an example of the color spectra of the blue drapery hold by Venus (points 37 and 41). These spectra show elements such as Ca, Ba, Mn, Fe, Cu, Hg and Pb. The copper peaks could suggest a

copper-based pigment, probably azurite (typical pigment at that time). However, the Cu/Pb ratio for these points (Fig. 11A) does not have a high value, which may be due to the high amount of Pb present in these points. The same low value of Cu/Pb ratio appears in the other two light blue points (11 and 22).

The presence of the other elements in Fig. 10 can suggest a mixture of pigments intended to obtain certain nuances. The blue pigment was combined with lead white for the lighter areas, or with earths and/or black pigment (considering the presence of iron, manganese and calcium), for the darker or brownish areas. It is interesting to observe also the presence of barium in these spectra, which could indicates old restorations or a contaminant present in the blue pigment, because barium sulfate is a mineral of paragenesis (mineral association) with azurite. This is one further indicator of the mineral origin of the pigment [22]. Barium could also suggest the use of a blue or a red/purple lake. Prepared from naturally occurring organic dyestuffs, lakes are extracted from plant or animal sources and precipitated onto a suitable inorganic substrate as alumina, calcium, potassium or barium [23]. Blue indigo – coming from *Indigofera* plants – was found to be used in



 $\textbf{Fig. 5.} \ \ \textbf{General IRR image before restoration.} \ .$





Fig. 6. Details in the IRR image showing modifications in the composition: A - The position of the legs of the couple of gods and the veil of Venus were completely modified during the painting process, as we can see in the difference of density of the figures in the image. This difference is due to the addition of paint layers by the painter when he decided to change the composition; B - Some dancing cupids and Mars's armor were modified during the painting process. The armor was initially represented on the lower right corner, but was later changed to the center of the composition.

some cases as underlayer for azurite to obtain blue nuances [23]. Potassium was also detected in many areas as shown at Fig. 11B, particularly in blue points 11, 22, 37 and 41. In some purple areas (for example, in the purple drapery, for points 32 and 33, which also has a high value area), this element seems to indicate the use of a red lake – as madder, cochineal or kermes – as potassium has been found in other paintings from Italian painters of the period as a lake substrate [24]. Barium traces were observed at all measured points (Fig. 11C). The use of lakes for purple or dark tonalities in blue or red colors would be a hint of refinement, characteristic of Saraceni's technique [8]. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

Copper based pigments – as azurite, malachite and verdigris – were possibly also used in green tonalities (like rocks, trees, foliage) and they were probably mixed with yellow ochers, brown earths and black natural pigments (due to the presence of manganese, calcium and iron in the spectra). This can be verified at Fig. 11A, which presents the Cu-K α /Pb-L α ratio, where points 1, 3, 13, 15, 16, 20, 21 23, 28, 30 and 44 at green regions clearly stand out. Other than yellow ochers, the painter used lead-tin yellow for the brightest yellow tonalities of the foliage, as is suggested by the small peaks in the spectra of some of the points (1 and 23, at Fig. 12).

In conclusion, most of the pigments could be detected with XRF (Table 1) and all of them correspond with Saraceni's period. XRF analyses of another work of Saraceni gave similar results [8].

3.2. Painting's condition

Imaging and close examination allowed us to determine that the painting was in a poor condition. These analyses permitted also assume that the painting was restored before arriving to the museum at least two times. Indeed, several damages on the metallic support and the pictorial layer – as areas of lacunae and corrosion – had led to interventionist treatments, as large inpainting.

The corrosion phenomenon presented in the painting and support layers is mainly due to the interaction between the metallic pigments, the copper plate surface and humidity. In high relative humidity conditions, water can be condensed in the metallic surface, activating reduction-oxidation reactions that produce copper oxides. Pollutant agents (as ammonia salts, sulfides and carbon dioxide) contained in the air, the dust or in soil surface layers can also produce reduction-oxidation reactions, catalyzed with water [19]. The copper oxides emerge from the metallic surface and reach the paint layer especially through opened areas as cracks and lacunae. This phenomenon creates, at the same time, more lifting and paint loses as it spreads out across the paint layer and remains a permanent risk of corrosion's expansion [4,17].

The corroded areas appear as green, brownish or dark rough spots scattered all over the composition (Fig. 13). Imaging helped us to characterize and distinguish them from other damages and from inpainting, leading to a precise map of alterations (Fig. 14). As represented in the map, the extension of the corroded areas indicates a direct relationship with the lacunae and the old inpainting, realized by



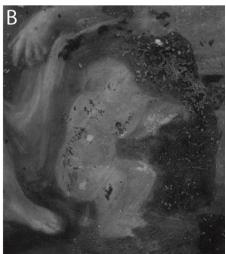
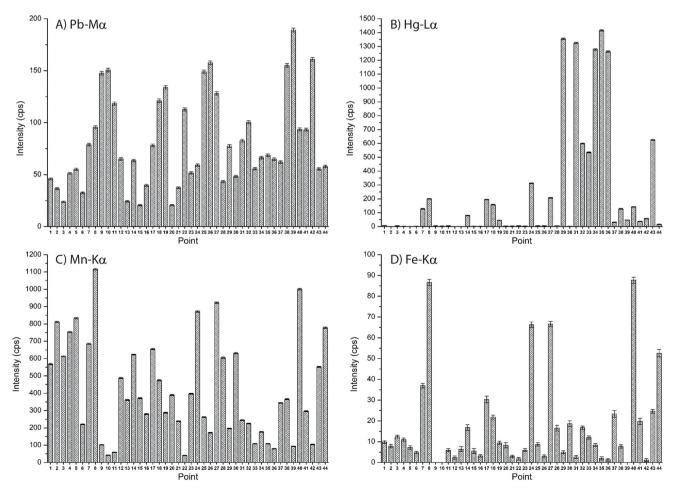


Fig. 7. Images of the unachieved musician cupid seated next to a rock, in the middle of the composition: A – with visible light; B – in the IRR.



Fig. 8. General raking light photography showing all the reliefs formed by the brushwork and the superposition of glazes.



 $\textbf{Fig. 9.} \ \, \textbf{Line count rates histogram showing the net area for each analyzed point determined by XRF: A - Pb-M\alpha; B - Hg-L\alpha; C - Mn-K\alpha; D - Fe-K\alpha. . . }$

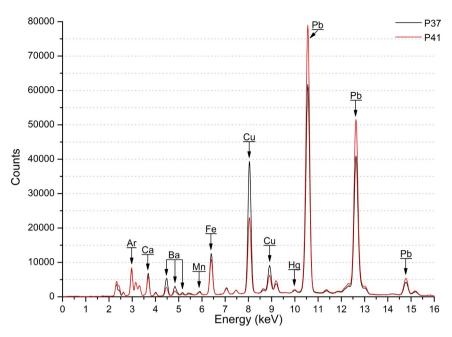


Fig. 10. Overlapping of XRF spectra obtained in the blue drapery hold by Venus.

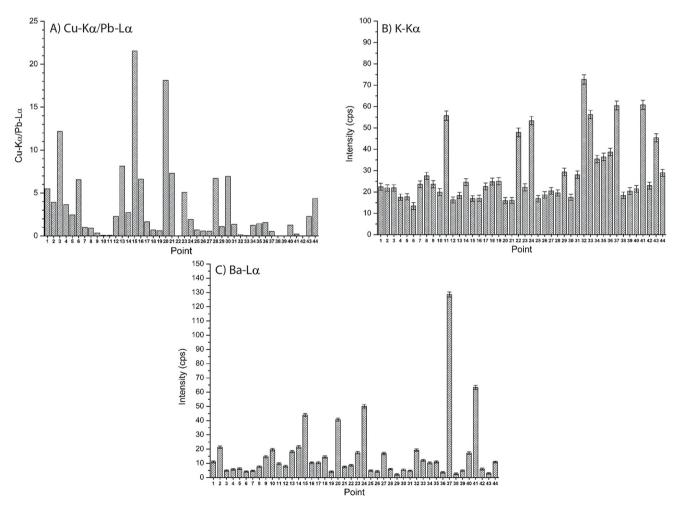


Fig. 11. A – Cu-K α /Pb-L α ratio histogram, showing the net areas ratio for each analyzed point by XRF; B – K-K α count rates histogram, showing the net area for each analyzed point by XRF; C – Ba-L α count rates histogram, showing the net area for each analyzed point by XRF.

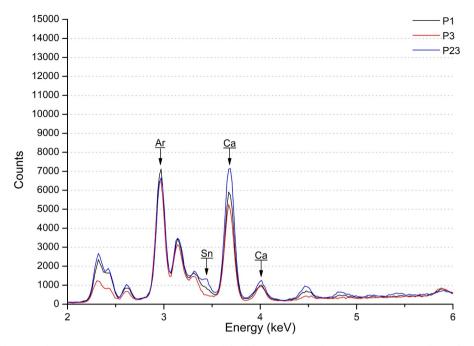


Fig. 12. Zoom of the overlapping of XRF spectra obtained in some points of the foliage. Spectra of points 1 and 23 were obtained in the yellow foliage, while spectrum of point 3 was obtained in standard green foliage.

previous restorers to hide the disturbing oxidized dark spots and paint loses.

One figure was particularly affected by corrosion: the little cupid musician and the rock described earlier (Fig. 7). As we observe in the IRR, the cupid shows several green corrosion spots (Fig. 13B) – which is a typical reaction between copper and white lead [17] – that appear as black stains, while the rock is very lacunar, full of loses that look as lighter stains. This part of the composition has a thinner paint layer, as it was probably not finished, remaining possibly more fragile to oxidation reactions.

Other than corrosion, multispectral examination revealed large overpainted zones related to past accidents, as we can see in the arm of Venus and in the upper right corner (Fig. 15–16). These examples show how confronting different imaging is important to locate and delimitate inpainting areas with precision. Additionally, the painting was presenting an oxidized, cracked and uneven varnish, as shown by the UV fluorescence photography (Fig. 17).

These alterations were disturbing the reading of the image and the esthetical features of the painting, and they were compromising its conservation. By consequence, an aesthetic and conservative treatment was collectively decided and realized in the MASP's studio, with the help of specialized scientific conservation literature [4,17,25,26].

IRR, UV fluorescence and visible light photographs were made after the cleaning and the corrosion treatment, in order to register the painting without the main old restoration coatings and the corroded spots. Finally, visible light photographs were done to register the painting after treatment. Multispectral imaging is indeed essential to register conservation processes.

4. Conclusions

The Saraceni's copper painting was a particular case of study for the MASP's conservation studio, because of its particular technique and materials, and because of its specific alterations. An in-depth technical

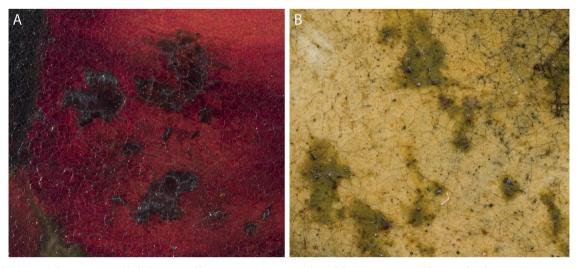


Fig. 13. Details of corroded areas: A – Visible light image of brown corrosion spots in the red drapery; B – Macro-photography showing the green corrosion spots in the body of the musician cupid.

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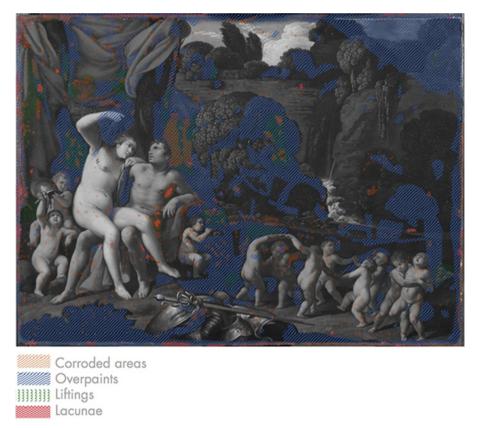


Fig. 14. Map showing the corroded areas, the old inpainting, the liftings and the lacunae present on the painting.







Fig. 15. Detail of an overpainted area in the arm of Venus: A – with visible light; B – with UV fluorescence; C – with IRR. We observe that in the three images the inpainting appears as a darker area, especially in the UV fluorescence and the IRR. In the IRR we observe that the overpainted cracks appears clearly outlined in black, while the original cracks slightly appear. In the visible image, the fake cracks appears green and are very visible as they differ from the original surrounding cracks.

study was indispensable, realized thanks to a methodology involving interdisciplinary examination. Technical imaging, XRF, close examination and scientific literature allowed us to characterize Saraceni's technique and provided unprecedented information about the painter's oil on copper production, given the fact that jut few Saraceni's paintings seem to have been examined in such complete way. IRR showed us the painter's firsts intentions and how he progressively composed his image. XRF gave us valuable information about the ground and the paint composition, as summarized at Table 1.

All analyses helped also to discriminate between past restorations, actual alterations and original technical features. Different analyses approaches were indeed extremely useful to detect, identify and map all the damages presented in the painting, allowing us to define appropriate diagnosis and treatment approaches. UV fluorescence and IRR were particularly valuable tools to distinguish corrosion spots and old interventions. Imaging was also essential to record every technical feature and all the conservation processes.

In conclusion, crossing the technical information given by the scientific analyses with scientific literature and with practical observation was fundamental to understand the painting's technique and condition,

and to enhance our knowledge of Carlo Saraceni's work. Discussions between art historians, conservators and scientists were valuable tools to interpret the results and to bring interdisciplinary approaches, enriching the museum's conservation methodology.

CRediT authorship contribution statement

S. Hennen Rodriguez: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. C.R. Appoloni: Validation, Formal analysis, Investigation, Resources, Data curation, Writing - review & editing, Visualization. P.H.O.V. Campos: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing, Visualization. B. Gonçalves: Validation, Writing - review & editing, Visualization. E.A.M. Kajiya: Methodology, Formal analysis, Resources, Data curation, Writing - review & editing, Visualization. R. Molari: Validation, Formal analysis, Investigation, Resources, Data curation, Writing - review & editing, Visualization. M.A. Rizzutto: Conceptualization, Methodology, Validation, Formal analysis,

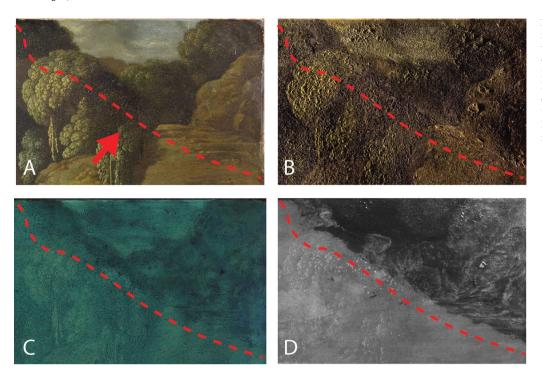


Fig. 16. Details of an overpainted area in the right corner of the painting: A – with visible light; B – with raking light; C – with UV fluorescence and D – with IRR. We can observe that in visible light, fluorescence UV and IRR the overpainted zone appears darker than the original painting. In the raking light, the area appears with a different relief.



Fig. 17. UV fluorescence photography, showing the thick and old oxidized varnish.

Investigation, Resources, Writing - review & editing, Visualization. **C. Winter:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing, Visualization.

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.

Acknowledgments

We are grateful to all our colleagues of the Curatorial and the Collection departments of MASP, who participated in the study and the conservation process in many ways. We would like to specially thank Erick Santos, Nalu Maria de Medeiros, Paula Coelho, Erika Litsumi Uheara and Przemyslaw Kosierkiewicz for their participation in the discussion, their practical assistance and their valuable presence in the daily life at the conservation's studio. We would also like to thanks Olivia Ardui and Mariana Lemefor their support and their great interest for the project. XRF analyses were part of the project INCT-FNA CNPq Proc. No. 464898/2014–5.

References

- L. Marques, Catálogo do Museu de arte de São Paulo Assis Chateaubriand, MASP (1998)
- [2] M.G. Aurigemma, Carlo Saraceni, Carlo Saraceni 1579-1620 un Veneziano tra Roma e l'Europa, Catalogue of the exhibition hold in Saloni Monumentali del Palazzo di Venezia, Rome, 2013.
- [3] M.K. Komanecky, Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575-1775, Phoenix Art Museum, 1999.
- [4] I. Horovitz, The materials and techniques of European paintings on copper supports, Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575-1775, Phoenix Art Museum, 1999, pp. 63–92.
- [5] E.P. Bowron, A brief history of European oil paintings on copper, 1560-1775, Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575-1775, Phoenix Art Museum, 1999, pp. 9–30.
- [6] J. Wadum, N. Streeton, History and use of panels or other rigid supports for easel paintings, Conservation of Easel Paintings, Routledge, 2012, pp. 49–115.
- [7] C. Bargellini, La pintura sobre cobre en los virreinatos de la nueva españa y perú, Anales Del Instituto De Investigaciones Estéticas 21 Universidad Nacional Autonoma de México, 1999, pp. 79–98.
- [8] M.B. De Ruggieri, M. Cardinali, G.S. Ghia, A.I. Idelson, G. Leone, C. Serino, Carlo Saraceni e la tela di San Carlo Borromeo in San Lorenzo in Lucina, Kermes: La Rivista Del Restauro 91 (2013) 47–64 julho-setembro.
- [9] R. MacBeth, The technical examination and documentation of easel paintings, Conservation of Easel Paintings, Routledge, 2012, pp. 291–305.
- [10] E.A.M. Kajiya, P.H.O.V. Campos, M.A. Rizzutto, C.R. Appoloni, F. Lopes, Evaluation of the veracity of one work by the artist di cavalcanti through non-destructive techniques: XRF, imaging and brush stroke analysis, Radiation Physics and Chemistry 95 (2014) 373–377, https://doi.org/10.1016/j.radphyschem.2013.03. 027
- [11] P.H.O.V. Campos, E.A.M. Kajiya, M.A. Rizzutto, A.C. Neiva, H.P.F. Pinto, P.A.D. Almeida, X-ray fluorescence and imaging analyses of paintings by the Brazilian artist oscar pereira da silva, Radiation Physics and Chemistry 95 (2014) 362–367, https://doi.org/10.1016/j.radphyschem.2013.05.029.
- [12] D. Bomford, R. Billinge, Art in the Making Underdrawings in Renaissance Paintings, National Gallery, 2002.
- [13] P.S. Parreira, F.L. Melquiades, F. Lopes, V.F. Oliveira, C.R. Appoloni, Sistema portátil de Fluorescência de Raios X. BRPatent 0801331- 4, (2019).
- [14] R. Molari, C.R. Appoloni, A PXRF and TXRF study of The Portrait of a young gentleman (1539), by Lucas Cranach the elder, Radiation Physics and Chemistry 165 (2019) 108413, https://doi.org/10.1016/j.radphyschem.2019.108413.
- [15] V.A. Solé, E. Papillon, M. Cotte, P. Walter, J. Susini, A multiplatform code for the

- analysis of energy-dispersive X-ray fluorescence spectra, Spectrochimica Acta Part B: Atomic Spectroscopy 62 (1) (2007) 63–68, https://doi.org/10.1016/j.sab.2006. 12.002.
- [16] M. Stols-Witlox, A Perfect Ground: Preparatory Layers for Oil Paintings, 1550-1900, Archetype, 2017.
- [17] I. Horovitz, Paintings on copper supports: techniques, deterioration and conservation, The Conservator 10 (1) (1986) 44–48, https://doi.org/10.1080/01410096. 1986.9995017.
- [18] S. Bergeon, Les supports de métal et de pierre, Science et Patience Ou La Restauration Des Peintures, Réunion des musées nationaux, 1990, pp. 97–103.
- [19] L.-.C. Pavlopoulou, D. Watkinson, The degradation of oil painted copper surfaces, Studies in Conservation 51 (1) (2006) 55–65, https://doi.org/10.1179/sic.2006.51. Supplement-1.55.
- [20] J.A.van De Graaf, Development of oil paint and the use of metal plates as a support, Conservation and Restoration of Pictorial Art, Butterworth-Heinemann, 1976, pp. 48–51.
- [21] G. Chottard, M. Gunn, E. Riviere, J.-.J. Girerd, J.-C. Chottard, Chemical reactions between copper pigments and oleoresinous media, Studies in Conservation 47 (1) (2002) 12–23, https://doi.org/10.1179/sic.2002.47.1.12.
- [22] N. Salvadó, S. Butí, M.A.G. Aranda, T. Pradell, New insights on blue pigments used in 15th century paintings by synchrotron radiation-based micro-FTIR and XRD, Analytical Methods 6 (11) (2014) 3610–3621, https://doi.org/10.1039/ C4AY00424H.
- [23] R. Ashok, L. Campbell, J. Dunkerton, S. Foister, J. Kirby, J. Pilc, A. Roy, M. Spring, R. White, Methods and materials of northern European painting in the National Gallery, 1400-1550, Technical Bulletin Volume, 18 National Gallery Technical Bulletin, 1997, p. 18.
- [24] H.C. Santos, C. Caliri, L. Pappalardo, R. Catalano, A. Orlando, F. Rizzo, F.P. Romano, Real-time MA-XRF imaging spectroscopy of the Virgin with the child painted by Antonello de Saliba in 1497, Microchemical Journal 140 (2018) 96–104, https://doi.org/10.1016/j.microc.2018.04.015.
- [25] I. Horovitz, The consolidation of paintings on copper supports. Triennial Meeting; 11th, International Council of Museums: ICOM Committee for Conservation, James & James, 1996, pp. 276–281.
- [26] I. Horovitz, Fourteen March 2002: 'to those who like their pictures in pristine condition..., techniques and conservation of paintings on copper, The Picture Restorer 22 (2002) 16–19.
- [27] R.J. Gettens, G.L. Stout, Painting materials: a short encyclopedia, Courier Corporation. 1966.
- [28] J.P. Cabral, Exame científico de pinturas de cavalete, Colóquio/Ciências, 1995, p. 16.