Characterization of a wooden Brazilian sculpture using µXRF and µCT

Caracterização de uma escultura brasileira de madeira por µXRF e µCT

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Abstract
The scientific characterization of historical pieces reflects the history of a region or country, as it brings countless information about the technology and cultural knowledge of a given civilization. These studies often involve a certain level of interdisciplinarity, as technology and history come together in the search for the characterization of a piece. In many cases it is possible to determine the period in which the artifact was created, identify the techniques used by the artist, provide data of a possible restoration process, in addition to helping to identify possible forgeries in valuable works. In this paper, two non-destructive characterization techniques were used: micro-X-ray fluorescence (µXRF) and X-ray microtomography (µCT), with the aim of characterizing a wooden Our Lady of the Immaculate Conception sculpture. µXRF measurements were carried out at 30 spots on the sculpture to identify the pigments used. It was possible to detect overlapping layers of paint, the presence of gold in some ornaments, and the use of pigments that have not been used since the 19th century, such as vermilion. The images generated by µCT were used to analyze the internal structure of the piece, its fixing points and the techniques used by the artist, in addition to enabling the observation of hollow. From the results obtained, it is concluded that two types of wood were used, the vermilion pigment applied in the mouth area is likely original, and the piece has probably undergone restoration.

Keywords

Ancient sculpture • Painting pigments • µXRF • µCT

Resumo
O estudo de peças históricas reflete a história de uma região ou país, pois traz consigo inúmeras informações sobre as tradições e o conhecimento cultural daquela civilização. Estes estudos frequentemente são interdisciplinares, pois a tecnologia e a história se unem na busca da caracterização de uma peça. Em muitos casos é possível determinar o período em que o artefato foi criado, identificar as técnicas empregadas pelo artista, fornecer dados para um eventual processo de restauração, além de auxiliar na identificação de possíveis falsificações em obras valiosas. Neste trabalho, foram utilizadas duas técnicas de caracterização não destrutivas, microfluorescência de raios-X (µXRF) e microtomografia de raios-X (µCT), para caracterizar uma estátua de madeira de Nossa Senhora da Imaculada Conceição. As medições de µXRF foram realizadas em 30 locais da peça, com o intuito de identificar os pigmentos utilizados. Foi possível detectar camadas sobrepostas de tinta, presença de ouro em alguns ornamentos, e a utilização de pigmentos que desde o século XIX não são mais utilizados, como o vermilion. As imagens geradas pela µCT foram empregadas na análise da estrutura interna da peça, seus pontos de fixação e as técnicas utilizadas pelo artista, além de possibilitar a observação de volumes ocos na obra. Dos resultados obtidos, conclui-se que dois tipos de madeira foram usados, o pigmento vermilion usado na área da boca é provavelmente original e a peça sofreu provavelmente uma restauração.

Palavras-chave

Escultura antiga • Pigmentos de pintura • µXRF • µCT

1 Introduction

Interest in the study of historical and sacred artifacts is steadily increasing, with works of art and archaeological findings captivating the attention of the scientific community [1,2]. Research and a wide range of studies have been developed to reveal information about these pieces from past eras, as they often hold significant insights into the traditions and knowledge of a culture [3,4] besides the history aspects.

When it comes to the characterization of historical pieces in particular, the use of characterization techniques becomes essential for an in-depth study. These tools can reveal a wealth of information, such as the period in which the object was created, its origin, the manufacturing techniques employed, and the structural integrity of the artifact. Additionally, they can assist in identifying forgeries and assessing conservation and restoration efforts [5,6].

Concerning the analysis of historical artifacts, non-destructive characterization techniques are particularly important. These methods involve conducting tests that do not harm the object under study, eliminating the need for any prior preparation of the sample [7]. When dealing with pieces of high historical value, most of the tests performed are non-destructive, since no damage to the piece being studied is desirable, and all aspects of the piece being preserved after the test [8,9].

In this study, two non-destructive characterization techniques were used: X-ray fluorescence (µXRF) and X-ray microtomography (µCT). These techniques have been increasingly applied in the analysis of historical artifacts [10-12]. The object of study was an Our Lady of the Immaculate Conception sculpture, a figure of Catholicism. The name "Immaculate" is derived from the Latin word “macula,” meaning stain, as the Catholic Church regards this image as a portrayal of a woman free from any sin, hence the term “Immaculate.” There was lack of information about the piece in question, either regarding its age, its origin, materials or any type of restoration work carried out previously, hence the importance of characterization [13-15]. The curator of the artifact, however, believed it had never undergone any restoration.

The sculpture belongs to the Colégio Anchieta collection of religious objects, located in Nova Friburgo, in the Rio de Janeiro state, Brazil. The school houses an extensive collection of historical and sacred artifacts, including paintings, objects, tools, and laboratory equipment dating back to the 19th century. Colégio Anchieta is a Jesuit school founded on April 12, 1886, originally established in the main house of the old farm “Fazenda do Morro Queimado”, a site of great historical significance in the founding of Nova Friburgo.

The aim of this study was to use µXRF and µCT techniques to characterize the pigments in wooden sculpture paint. Identifying the chemical elements present in the pigments used, as well as an investigation of the entire structural part of the piece, such as its attachment points or possible presence of hollow points or faults.

2 Materials and methods

2.1 Sculpture

The studied object was a painted wooden sculpture as shown in Fig. 1 with four views. The sculpture was carved in wood. The sculpture has four main parts, from bottom to top: a pedestal, a globe, cloud and the female figure of the saint. The sculpture had several physical damages, including broken and chipped parts, as well as paint flaws. Both hands of the sculpture are missing. On the right side, there is a damage on cloud. Near the base, further damage is present, possibly related to the representation of one or more angels, considering that images of Our Lady of the Immaculate Conception often feature depictions of clouds and angels on their bases. A small crack is visible in the neck area of the sculpture, suggesting a possible accident or an unsuccessful restoration attempt. The sides of the piece have several points where the paint is damaged, with some areas quite chipped.

The sculpture has a total height of 210 mm, a common size for images of this kind, and a total mass of 200 g. The base measures 70 mm in length by 60 mm in width. At the top of the sculpture (Fig. 2 (a)), a hole could be observed, likely used to attach the crown, a common adornment in representations of Our Lady of the Immaculate Conception.

The pedestal was firmly attached to the rest of sculpture, without visible gaps. The base is also made of wood, with a nail (Fig. 2 (b)) serving as a connection between the pedestal and the rest of the sculpture. The micro-computed tomography test allowed the determination of the ancillary pieces used for fixing.

Figure 1: Front, side, and back views of the studied sculpture.

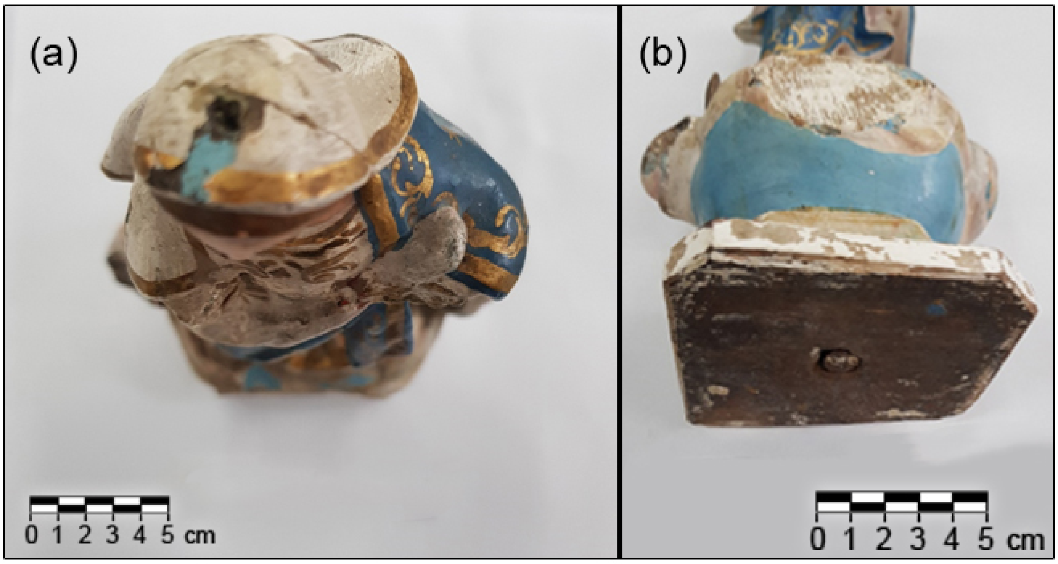

Figure 2: (a) Top and (b) Pedestal of the sculpture.

2.2 µX-ray Fluorescence Analysis

The X-ray fluorescence tests were conducted using a portable Artax 200 spectrometer (Bruker). This equipment performs non-destructive tests with a spatial resolution of up to 70 µm and is suitable for the simultaneous detection of elements within the range of Na (11) to U (92), i.e., $11 \leq Z \leq 92$, where Z represents the atomic number. The device was equipped with an X-ray tube with a fine molybdenum focus, operating at a maximum voltage of 50 kV and a maximum current of 1000 µA [16].

The Artax spectrometer was equipped with an integrated CCD camera with a resolution of 500 x 582 pixels, providing an enlarged image of the region of the sample under analysis, aided by a white light that improves the quality and contrast of the image. Photographs can be taken for documentation and illustration purposes of the

research. All system control and interpretation of the acquired data, presented in the form of spectra, were performed using the manufacturer proprietary software (Bruker), Spectra, version 5.3.21.0.
Thirty spots on the surface were selected for analysis by µXRF. These sites are indicated in Fig. 3. The selection was made to ensure that all colors of the piece were examined, including damaged areas or areas that presented only the preparation layer, or a layer of paint under the main layer. The colors are given by pigments made from different compounds.

Figure 3: Spots selected for µX-ray fluorescence analysis.

The main operating parameters of the equipment were established, as presented in Table 1.

Table 1: Operational parameters Artax 200.

Operational Parameters	**Data**
Anode	Molybdenum
Voltage	40 kV
Current	200 µA
Live time	100 s
Dead time	1.1%

With the spots and the operational parameters defined, the piece was positioned on the bench then the Artax 200 equipment could perform the µX-ray fluorescence for all indicated locations, as illustrated in Fig. 4. Prior to the test, a calibration was performed to ensure consistency in the measured data.

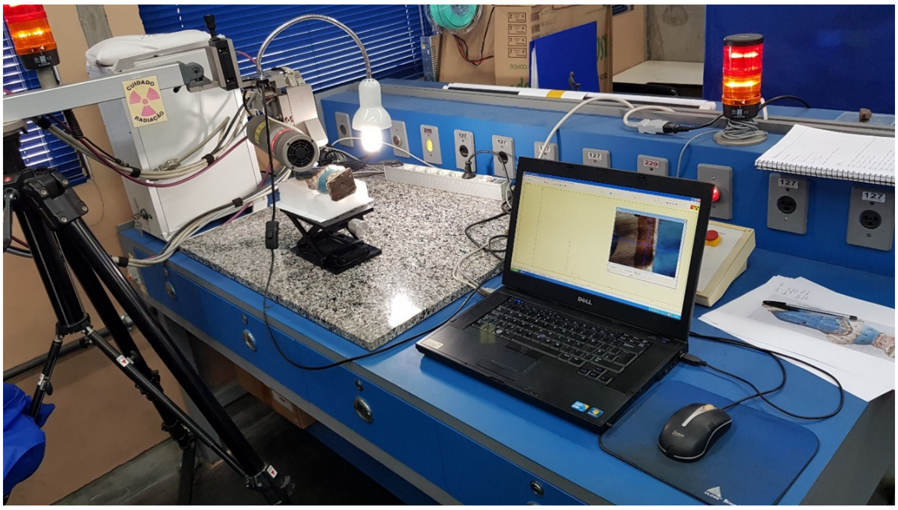

Figure 4: Sculpture positioned for µXRF analysis with Artax 200.

2.3 Computed Microtomography Analysis

To perform the computed microtomography tests, the Phoenix V|tome|x M equipment was used, as shown in Fig. 5.

Figure 5: Phoenix V|tome|x M equipment.

The X-ray tube of this equipment uses a tungsten filament to generate electrons, with all X-ray production occurring at a tungsten target. A nanofocus transmission through a diamond window allows the precise positioning of the selected area. The use of a diamond output window significantly improves data quality compared to beryllium windows, commonly used in similar equipment. This improvement enables the generation of highly detailed images, achieving detectability of features smaller than 1 µm. Detectability refers to the smallest size of an object that can still be distinguished in an image, even if it is smaller than the voxel size. The detector array is temperature stabilized, with a pixel size of 200 µm and a resolution of 2,024 x 2,024 pixels [17]. The main operating parameters of the equipment used in our tests are presented in Table 2.

Table 2: Operational parameters of Phoenix V|tome|x M apparatus.

Operational Parameters	Data
Voltage	110 kV
Current	400 μA
Acquisition time	250 ms
Integration	5 frames
Filter	0.4 mm Al
Number of projections	1800
Effective pixel size	126 μm

Phoenix datos|x CT software was used for data acquisition and processing including volume processing. This software enables the entire μCT process to be fully automated, significantly enhancing the repeatability and reproducibility of data. Once the appropriate programming has been configured, the entire scanning and reconstruction process is carried out.

3 Results and Discussion

3.1 μX-ray Fluorescence Results

The most relevant pigments identified in the piece were analyzed, along with their respective spectra. In the head region of the image, detailed in Fig. 6, four points of interest were analyzed: forehead, mouth, eyes, and hair.

Figure 6: Face of the sculpture.

The forehead displayed a characteristic beige tone of the skin, where the presence of Zn was detected, together with a very low concentration of Pb and Fe (spot 1 of Fig. 3). The intensity of the fluorescence peaks is proportional to the quantity of the analyzed element, thereby enabling its semiquantitative estimation [18]. This indicated a predominant mixture of zinc white (ZnO) with a small amount of brown ochre ($Fe_2O_3{\cdot}H_2O$, along with clay and silica), creating a lighter brown that results in the beige coloration. The presence of lead was probably due to the preparation layer using lead white ($2PbCO_3{\cdot}Pb(OH)_2$).

In the representation of the eyes (spot 3), in addition to Zn, Fe was also found, indicating a possible use of zinc white for the white color of the eyes, combined with the pigment black iron oxide (Fe_3O_4) in a top layer to create the dark appearance of the eyes. In the analysis of the mouth (spot 4), Zn was also detected together with a low concentration of mercury, which possibly resulted from a mixture of zinc white with the pigment vermilion (HgS), aiming to obtain a lighter reddish color and a softer appearance. Vermilion can become unstable in the presence of chloride, forming white calomel (Hg_2Cl_2), discoloring the painting. Subsequently, the pigment undergoes by a photoreaction, resulting in a black color [19]. However, chlorine was not detected in the μXRF analysis, indicating that the softer appearance is original and not due to white deterioration caused by calomel formation.

On the surface of the hair of the piece (spot 2), Zn, Pb and Fe were detected, indicating the use of a mixture of zinc white with brown ochre, with a preparation layer using lead white. The pigments used in the representation of the garments (Fig. 7) in the sculpture were identified.

Figure 7: Details of the representation of the garments.

In the white region of the garment, only the element Zn was identified, indicating the use of zinc white. In the areas where the blue color predominates, a strong presence of Zn and a lower concentration of Fe suggest the application of zinc white overlaid with Prussian blue ($Fe_4[Fe(CN)_6]_3 \cdot 14\text{-}16H_2O$). The golden details visible in Fig. 7 show the elements Zn, Fe, Pb and Cr. The presence of chromium and lead suggests the use of chrome yellow pigments ($PbCrO_4$ or $PbCrO_4 \cdot 2PbSO_4$). Lead was also identified in high concentration in the peeled region, highlighted in Fig. 7, reinforcing the hypothesis of the use of lead white in the preparation of the piece, a common technique until the 19th century.

One point of particular interest in the study was a peeled region at the base of the piece. The image was enlarged using the Artax-200 camera. Figure 8 shows the spectrum of this area, and the image captured by the Artax-200.

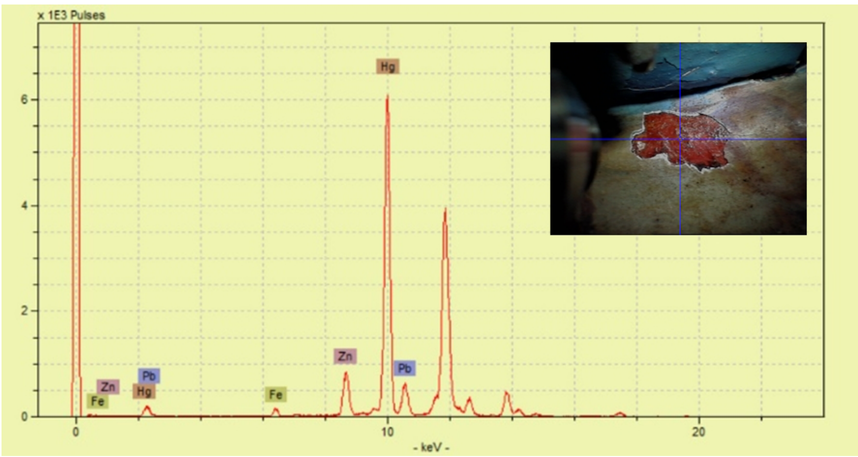

Figure 8: Spectrum with the identification of Hg and the analyzed region.

The spectra display, on the Y-axis, the unit of pulses (pulse counts), which refers to the fluorescence intensity, and on the X-axis, the unit of keV, which represents the energy. In this region, there was a high concentration of Hg, with low concentrations of Zn, Pb, and Fe. The high concentration of mercury indicated the use of vermilion in a substantial portion of the base coat, with some red ochre likely due to the presence of iron. The lead is probably due to the white lead used in preparation and the zinc in a small quantity of some white trace of zinc, most of which was lost due to chipping in the paint. Another region where a more in-depth analysis was necessary is shown in Fig. 9, where a large area without the outermost layer of paint can be observed.

Figure 9: Peeling area in the veil region.

In this region it was possible to observe the presence of ornaments with a star shape in gold color below the layer of white paint with a different appearance from the other star shapes observed in the region of the garment's clothing. Noticing these differences, an X-ray fluorescence test was performed at this point for a more detailed analysis, the spectrum of this area and the image captured by Artax 200 are shown in Fig. 10.

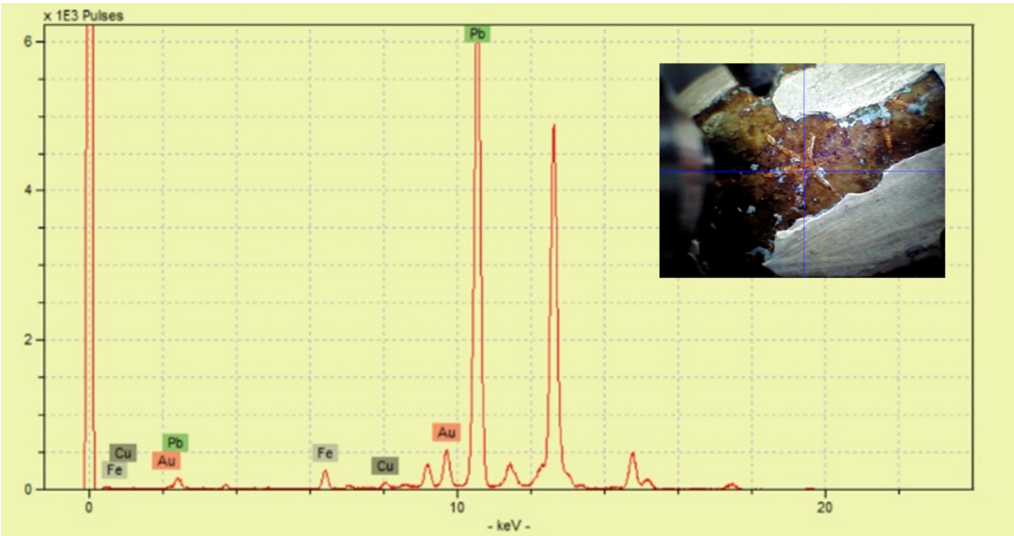

Figure 10: Spectrum with the identification of Au and the analyzed region.

In the star, a high concentration of Pb was detected, followed by Au and a low concentration of Fe, as indicated by the generated spectrum (Fig. 10). The high concentration of lead is probably due to preparation with lead white, while the gold may be the result of the use of gold foil or gold powder, a common technique in the past.

Two-star shapes exist in the sculpture, with different appearances and elemental compositions, as shown in Fig. 11. The star shown on the left in Fig. 11 has gold as its main element and is only visible in the areas where the white paint has peeled off in the veil region. The star on the right has a different shape, and does not have gold, but chromium, indicating the use of chrome yellow. This difference provides strong evidence of restoration on the piece, involving different chemicals, in this case less expensive, and artistic techniques.

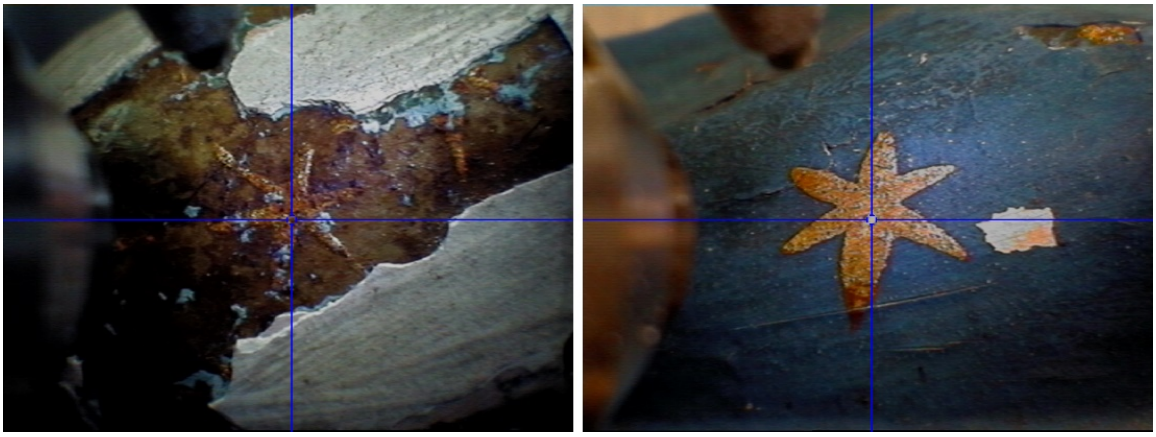

Figure 11: The two star shapes in the sculpture, the intersection point of the blue lines is the exact location of the analysis.

The equipment used cannot detect elements with an atomic number lower than 11. The hypotheses raised about the pigment compounds were based on the heavier elements identified by µXRF together with the data of pigments available in the literature.

3.2 Computed Microtomography

The structural analysis of the piece was conducted using computerized microtomography to identify potential regions affected by pests, as well as to verify the fixing points and construction techniques used by the artist. Figure 12 shows the image generated to gather information about the materials used in the construction of the work. By examining the image and the wood grain arrangement, it is revealed that two different species of wood were used, one for the base and another for the rest of the sculpture. The wood grain pattern in the upper section is aligned vertically and is finer than that of the pedestal, where the grain is oriented at approximately 45°. Two types of wood were used; however, they were not identified. Wood from slow-growing trees has finer grain, is denser, and more resistant to degradation, being used in sophisticated pieces.

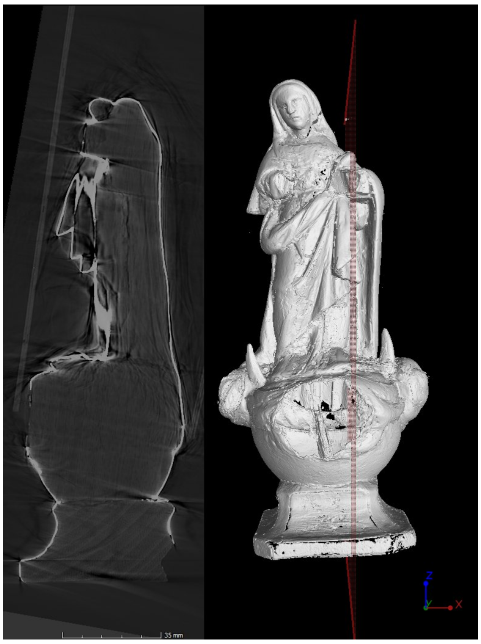

Figure 12: Analysis of the types of wood used.

Further analysis of the integrity of the sample, in Fig. 13, it was possible to observe voids found in the piece. In the lower part of the piece (highlighted in green circle in Fig. 13), near the area where the base is attached to the rest of the sculpture, there is a hollow. The origin of this hollow could be a flaw in the wood during the construction of the piece, at the time of attachment, or even caused by pests over the years. Although, it is not possible to determine the true cause. Another void was found on the face of the sculpture, which allows us to state that the saint in question does not have glass eyes, a very common technique in century-old sacred works; here the eyes were painted. Continuing the analysis in the head region, we could see the presence of a nail, which probably served to attach a crown to the piece, since representations of Our Lady of the Immaculate Conception usually feature a crown on top of her head. However, the piece analyzed did not have this ornament, which indicates that it was probably lost over time. Figure 14 displays all the fixing points present in the piece.

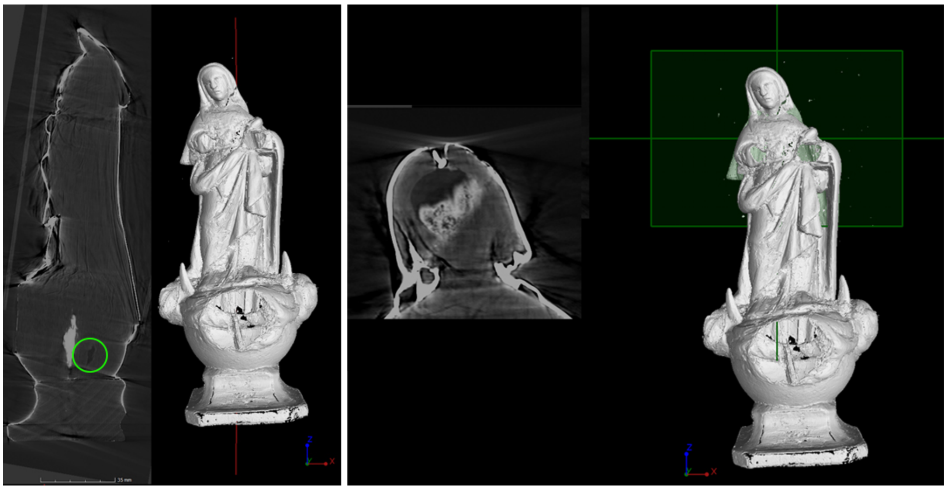

Figure 13: Voids detected in the piece.

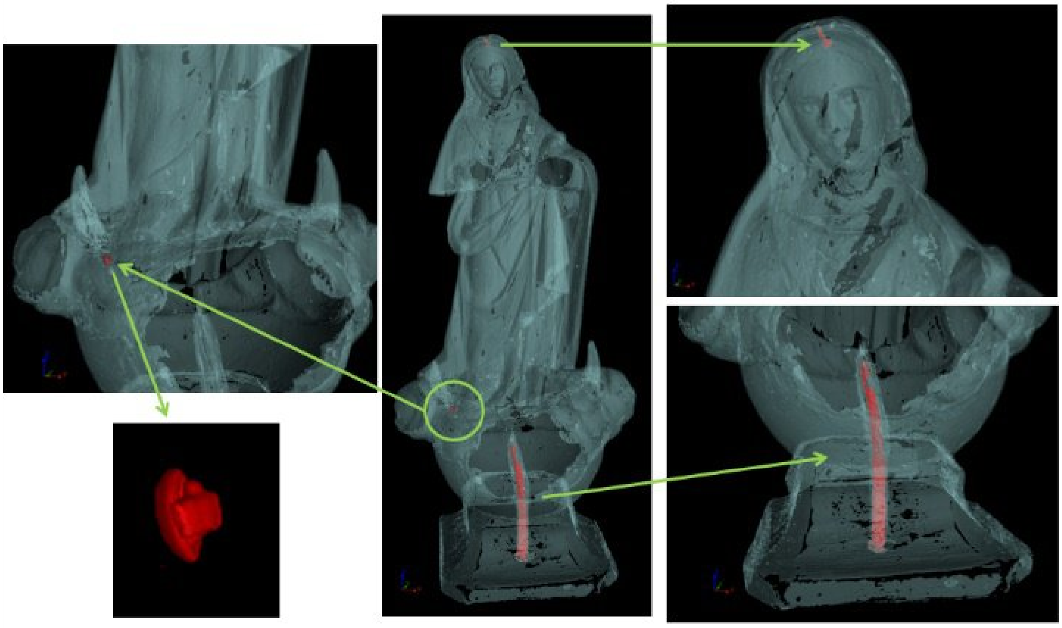

Figure 14: Attachment points in the sculpture.

In the region of the ornaments known as the half-moon, it was possible to identify a small attachment, which indicates that the ornament was carved separately and later integrated into the main piece. A large nail used to attach the base to the rest of the sculpture is also visible. The presence of a nail, and not a stud, is indicated by the circular shape of the head and the shape between the head and the body of the nail. Its appearance suggests it was made using a less sophisticated fastening technique, likely one available to the wood sculptor.

4 Conclusions

The analysis of the results obtained using micro-X-ray fluorescence and computed microtomography techniques demonstrated their great effectiveness in the study of a sacred wood sculpture. It was possible to identify the chemical compositions of the pigments used, as well as to evaluate the structural integrity of the piece and its attachment points.

Based on the identification of the pigments used, it was found that some representations on the piece, such as the stars, present different conception techniques, as well as different pigmentation, suggesting that the piece underwent some kind of restoration process. The images captured by the Artax-200 camera revealed regions where there are overlapping layers of paint, further supporting the indication that the piece has already undergone restoration. The analysis of the pigments revealed the presence of vermilion, a pigment used until the 19th century, which provides clues about the period in which the work was conceived. Furthermore, the use of zinc white was identified, which began to be used in works from 1835 onwards. Based on the identification of the pigments, it is possible to estimate an age range for the production, between the 18th and 19th centuries.

The images generated by computerized microtomography revealed that the sculpture is made from wood, and the eyes is not made of glass. The presence of a small nail on top of the sculpture head indicated the attachment point for a crown, which the image originally had, but was lost over time. The attachment points use elements consistent with the historical estimate era raised in the analysis of the pigments.

This study highlighted the value of non-destructive techniques for obtaining relevant information about the piece, the techniques used by the artist, and its integrity without causing any damage.

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