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Non-destructive examination of a polychrome wooden sculpture from the 17th century

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Abstract: This study investigates the conservation assessment of a polychrome sculpture from the 17th century depicting San Diego de Alcalá, whose origin and workshop remain unknown. Traditionally characterized by specific iconographic elements such as bread and keys, the examined statue deviates from these norms. Initiated by the Diocesan Mitre in Duque de Caxias, the assessment focused on the structural integrity and pigment composition of the sculpture. Using techniques of Computed Tomography (CT), Digital Radiography (DR), and X-ray Fluorescence (XRF), the sculpture underwent a comprehensive analysis. Portable equipment, such as the ICM CP120B X-ray tube and DXR 250U-W flat panel detector, facilitated both CT and DR scans. The CT scan was segmented due to detector size limitations, using an 80 kV, 1 mA X-ray tube to capture 360 images per segment. XRF analysis focused on 12 specific points, employing the Bruker Tracer III-SD with a rhodium X-ray tube and silicon detector, operating at 40 kV and 35 µA for 60 seconds per point. Imaging techniques revealed imperfections, restorations, and structural details, including high-density fillings and embedded nails in the sculpture. XRF analysis identified characteristic elements of historical pigments, along with indications of more recent restorations, possibly involving 20th-century pigments. These findings significantly enrich the understanding and conservation strategies of this religious artwork, providing valuable insights into its construction history and restoration.

Keywords: X-ray Fluorescence (XRF) analysis, Computed Tomography (CT), Digital Radiography (DR), Polychrome Sculpture

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Exame não destrutivo de uma escultura de madeira policromada do século XVII

Resumo: Este estudo investiga a avaliação de conservação de uma escultura policromada do século XVII de São Diego de Alcalá, cuja origem e oficina permanecem desconhecidas. Tradicionalmente caracterizada por elementos iconográficos específicos como pão e chaves, a estátua examinada se distancia dessas normas. Iniciada pelo Mitra Diocesano em Duque de Caxias, a avaliação focou na integridade estrutural e na composição dos pigmentos da escultura. Utilizando técnicas de Tomografia Computadorizada (TC), Radiografia Digital (DR) e Fluorescência de Raios X (XRF), a escultura passou por uma análise abrangente. Equipamentos portáteis, como o tubo de raios X ICM CP120B e o detector de painel plano DXR 250U-W, facilitaram tanto as varreduras de TC quanto de DR. A varredura de TC foi segmentada devido às limitações do tamanho do detector, utilizando um tubo de raios X de 80 kV e 1 mA para capturar 360 imagens por segmento. A análise de XRF concentrou-se em 12 pontos específicos, utilizando o Tracer III-SD da Bruker com um tubo de raios X de alvo de ródio e um detector de silício, operando a 40 kV e 35 µA por 60 segundos por ponto. As técnicas de imagem revelaram imperfeições, restaurações e detalhes estruturais, incluindo enchimentos de alta densidade e pregos embutidos na escultura. A análise de XRF identificou elementos característicos de pigmentos históricos, juntamente com indicações de restaurações mais recentes, possivelmente envolvendo pigmentos do século XX. Essas descobertas enriquecem significativamente a compreensão e as estratégias de conservação desta obra de arte religiosa, oferecendo insights valiosos sobre sua história de construção e restauração.

Palavras-chave: Análise por Fluorescência de Raios X (XRF), Tomografia Computadorizada (CT), Radiografia Digital (DR), Escultura Policromada

1. INTRODUCTION

San Diego de Alcalá, canonized by Pope Sixtus V in 1588, holds a revered status in Spain and Spanish America [1, 2]. Typically depicted in paintings and images wearing a patched Franciscan lay brother's habit and carrying bread and keys symbolizing his roles as a cook and porter, the sculpture analyzed in this study lacks these customary iconographic elements: neither the keys nor the bread is present. Due to the absence of the left hand in the piece, the attributes that could be found there cannot be determined. Additionally, the number of knots on his cord diverges from the representation of Franciscan brothers, as in this order, the cords usually have only three knots – representing the vows of poverty, obedience, and chastity [3] – rather than four, as observed in this work.

Legendary tales, likely of oral origin, about San Diego de Alcalá depict him as exceedingly generous towards those seeking alms, a trait that caused displeasure among his superiors, who disapproved of his actions and kept a close watch on him. On one occasion, suspicious after finding something in his habit and believing he had already distributed his daily alms, they were about to rebuke him when miraculously, the bread rolls he carried for the poor transformed into roses [4, 5]. This event explains the presence of the bouquet of flowers as an iconic element associated with the saint.

The wooden religious sculpture depicting San Diego de Alcalá, the subject of this study, stands upright, clad in a Franciscan tunic adorned with shallowly grooved drapery, straight folds, sandals, fully exposed feet, and eyes. The sculpture presents a youthful figure without a beard, dressed in a tunic. His right arm is bent forward (without the hand), while his left arm extends across his body, holding a bouquet of flowers.

The origin of the statue remains unknown, and the lack of documentary sources complicates efforts to determine its provenance or the workshop responsible for its creation. It is believed to date back to the 17th century. In light of these uncertainties, assessing the preservation of the religious image of San Diego became a priority for the custodians of the Diocesan Mitre in Duque de Caxias. The Diocesan Commission, entrusted with its care, conducted an evaluation of the conservation status of the polychrome wooden sculpture, which measures 67 cm in height. Techniques such as Computed Tomography (CT) and Digital Radiography (DR) were employed to detect potential structural defects. Additionally, X-ray Fluorescence (XRF) analysis was used to examine pigments and areas of restoration on the artwork.

The radiographic analysis of sculptures relies on X-ray attenuation differences across the object, influenced by factors such as radiation energy, paint layer density, thickness and composition, and the materials used (wood, gypsum, terracotta, bronze, marble, etc.). Higher atomic number (Z) elements, like lead in lead white pigment and metallic components, absorb X-rays more effectively, appearing lighter in images. In contrast, Fe-based pigments and cracks absorb fewer X-rays, appearing darker [6, 7].

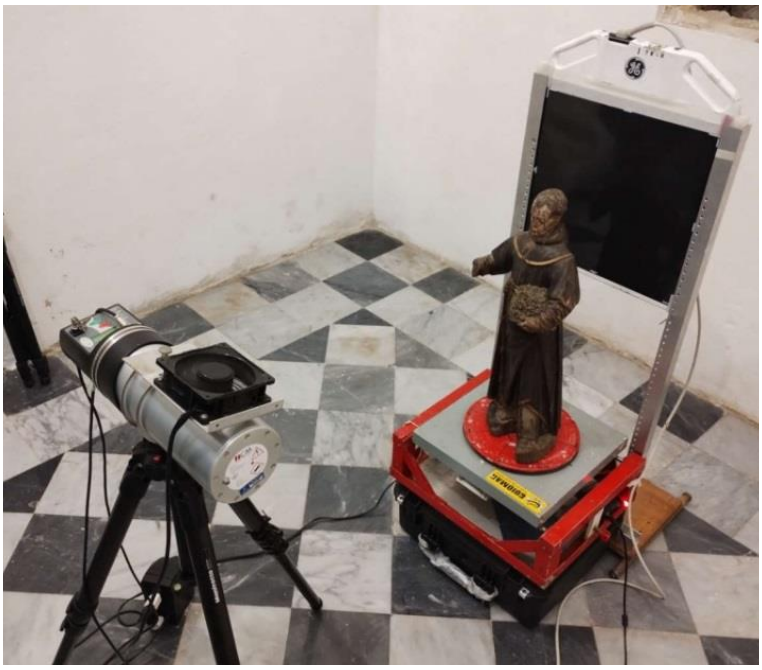
Computed tomography (CT) utilizes X-rays images processed by a computer to create cross-sectional images of a sample. These images, obtained slice by slice, depend on the material's attenuation coefficient, which determines how much radiation is absorbed. By measuring radiation with a detector, the attenuation coefficient can be calculated, producing two-dimensional slices that, when processed by algorithms, form a three-dimensional model of the sample [8–10]. This process is crucial for non-destructive analysis and visualization in various fields, including materials science and cultural heritage preservation [11].

X-ray fluorescence spectroscopy (XRF) is a valuable technique in material characterization, allowing for the non-destructive identification and quantification of elements in samples. It covers a broad spectrum of detectable elements present in various materials [12, 13]. This study focuses specifically on conducting a qualitative analysis, which is essential for understanding the elemental composition and characteristics of the sculpture under investigation.

2. MATERIALS AND METHODS

CT, DR, and XRF examinations were comprehensively conducted across all sections of the sculpture using portable and compact equipment. Specifically, the ICM CP120B X-ray tube from Teledyne ICM and the DXR 250U-W flat-panel detector from General Electric were employed for both CT and DR. Figure 1 illustrates the setup of the imaging techniques used for the analyses.

Figure 1: DR and CT setup



The tomography process was segmented into three parts due to the size limitations of the detector, utilizing an 80 kV, 1 mA X-ray tube. Each segment involved acquiring 360 images (3 frames every 3 degrees) with a 1.5-second exposure time per frame at a source-detector distance (SDD) of 1,170 mm and a source-object distance (SOD) of 970 mm.

For pigment analysis, 12 specific points on the sculpture were chosen (Figure 2). XRF measurements were conducted using the portable commercial equipment Tracer III-SD from Bruker, equipped with a rhodium-target X-ray tube and a silicon detector (Si PIN diode). Operating at 40 kV and 35 μA, each point was analyzed for 60 seconds. The resulting spectra were analyzed using Bruker's Artax software, and graphs were generated using OriginPro 8.5 software.

Figure 2: Identification of the points analyzed by XRF on the sculpture of San Diego de Alcalá.

The identification of pigments in the sculptures relied on detecting their key elements and analyzing the characteristic color of the examined regions. Rhodium was detected in the spectra due to the X-ray tube anode; argon peaks were present because measurements were conducted without a vacuum, and nickel's presence was attributed to the equipment used. Additionally, certain paint shades were achieved through palette mixing, influencing the inferred pigments identified through the analysis.

All on-site XRF measurements, CT scans, and DR image acquisitions were conducted at the Church of Our Lady of Pilar in Duque de Caxias, Rio de Janeiro state, Brazil.

3. RESULTS AND DISCUSSIONS

3.1. Digital Radiography and Computed Tomography

Digital radiography of the San Diego de Alcalá sculpture revealed significant details about its structural condition and artistic history. Analysis of the head region showed specific areas with signs of restoration and structural reinforcement. A brighter area at the top of the head indicated dense material fillings, suggesting previous repair work to stabilize the sculpture. Additionally, within the facial region, areas with higher pigment density were identified, possibly indicating original paint application or later retouching. The radiographic images of the right arm clearly displayed the presence of three nails, strategically placed within the sculpture's structure (Figure 3). This finding provides insights into the original assembly techniques or subsequent repairs and damages over the sculpture's history.

Figure 3: Defects and components identified through digital radiography images.

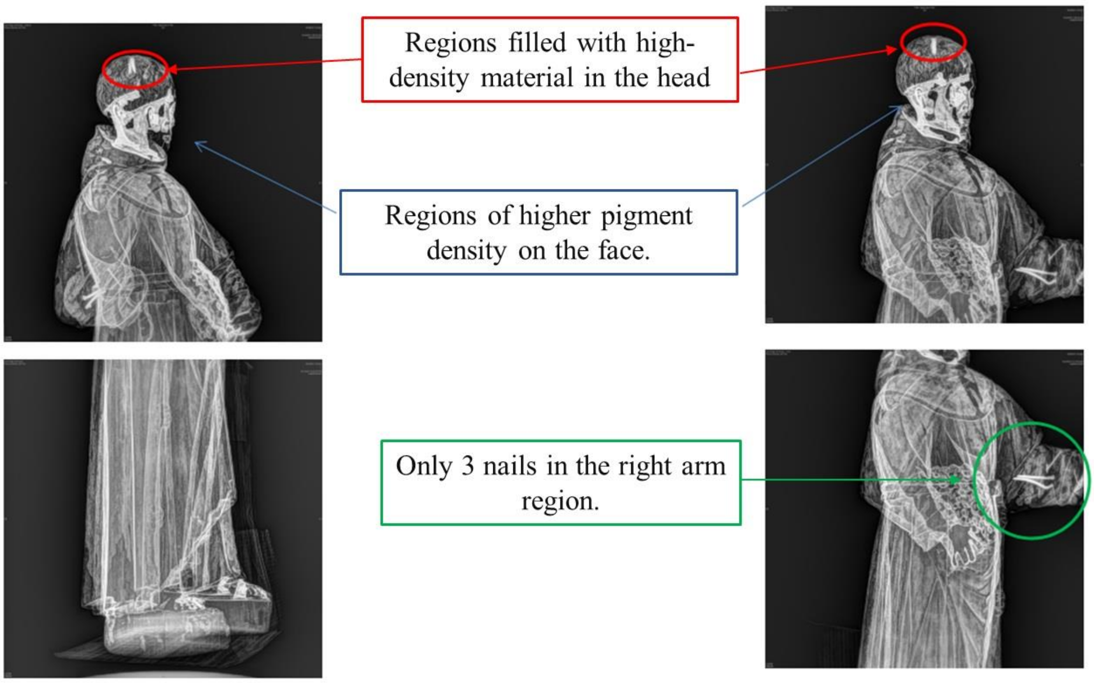


Figure 4 depicts a sculpture carved from a single block of wood, featuring a prominent crack that spans nearly the entire length of the statue. This structural detail is clearly visible in the radiographic image, where void areas, including cracks, appear darker due to the imaging technique employed. In contrast, regions containing pigments with higher density elements exhibit brighter shades. This brightness contrast in the image is attributed to the differential absorption of X-rays: denser materials, such as those in pigments containing elements like lead, absorb more X-rays and appear brighter, while less dense voids and materials allow more X-rays to pass through, resulting in darker areas.

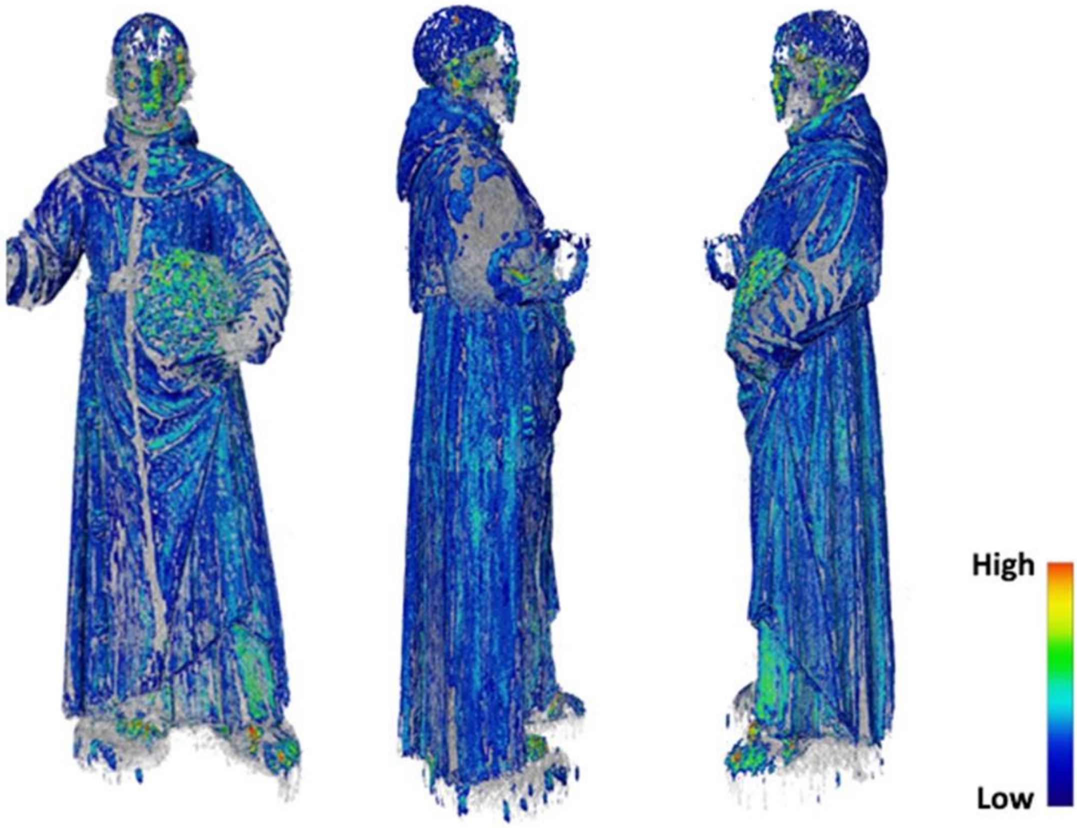
Figure 4: Frontal digital radiograph displaying a lengthy crack in the sculpture.

Computed tomography (CT) provided high-resolution images of the sculpture's interior. Figure 5 depicts the analyzed tomographic slices. A cross-section at the base revealed cracks and voids, indicating potential structural weaknesses or damage likely caused by environmental conditions, long term handling, or original construction issues. In the central region slice, voids and the outline of superficial layers hinting at high-density elements were visible. Voids observed may signify material degradation or insufficient substance.

Figure 5: 3D model and CT slices of the sculpture

Another cross-section at the upper part showed the contours of superficial layers, possibly indicating areas with high-density materials. At the neck, the CT scan highlighted a significant crack and the outlines of superficial layers, suggesting the presence of dense material. A cut at the head, particularly the upper part, displayed voids and high-density material, with varying contours of superficial layers indicating areas where pigments or surface materials have degraded. Additionally, a 3D model of the sculpture (Figure 6) showcased the thickness of pigment layers, depicted in colors.

Figure 6: 3D model with a color map, highlighting thickness of the pigment layer.



The overall radiographic examination depicted the sculpture as a cohesive wooden block, revealing extensive cracks spanning its surface. Areas with denser pigments appeared brighter in the images, indicating either original pigmentation or later interventions with more concentrated materials. Conversely, void areas and spaces devoid of dense materials appeared darker, highlighting areas of potential structural weakness or loss of original material.

3.2. X-Ray Fluorescence

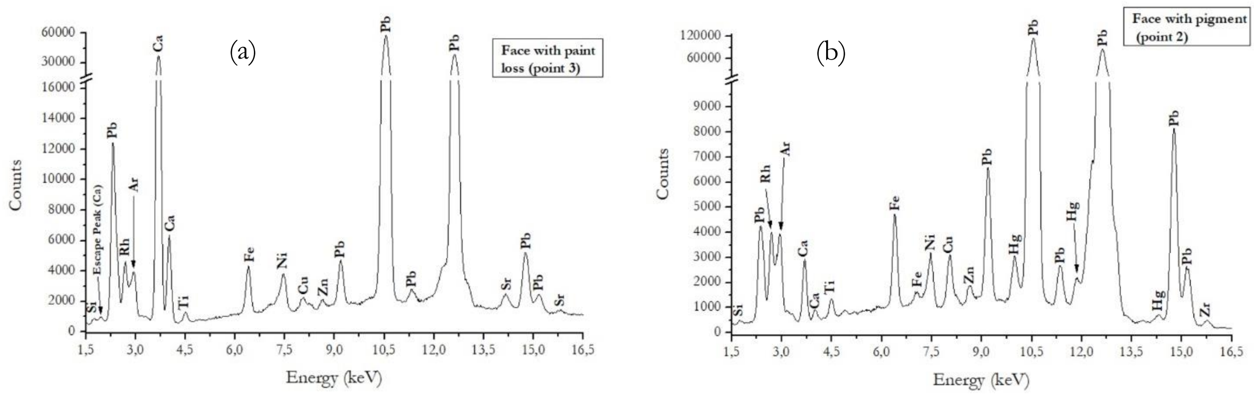
Twelve X-ray fluorescence measurements were conducted on the sculpture: 4 measurements for the identification of pigments composing the carnation (face and feet), 1 evaluating the hair, and 7 points analyzed for the drapery (tunic, tunic's yellow stripe, belt and cord). The elements found in the multi-elemental XRF analysis are indicated in Table 1.

Tabela 1: The multi-elemental XRF results for regions of the San Diego deAlcalá sculpture.

REGIONS OF THE SCULPTURE	NUMBER OF POINTS	ELEMENTS DETECTED
Carnation (face and feet)	4	Si, Ca, Ti, Fe, Cu, Zn, Hg, Pb, Sr, Zr
Hair	1	Si, K, Ca, Ti, Mn, Fe, Cu, Zn, Hg, Pb, Sr
Tunic	4	Si, K, Ca, Ti, Ba, Mn, Fe, Cu, Zn, Au, Pb, Sr, Zr
Tunic's yellow stripe	1	Si, K, Ca, Ba, Fe, Cu, Zn, Au, Pb
Belt and cord	2	Si, K, Ca, Ti, Ba, Mn, Fe, Cu, Zn, Au, Hg, Pb, Sr

The XRF analysis of the San Diego de Alcalá sculpture was conducted to infer the original pigments used in its paint, as well as to identify any subsequent repainting. By comparing the results from areas with paint loss to those from more pigmented regions, it was possible to make these determinations. This comparison can be made in the analysis of the points on the flesh tone and the tunic.

Figure 7: Characteristic X-ray spectra of the Carnation (face region): (a) Carnation (face with paint loss), (b) Carnation (face with pigment)



The analysis depicted in Figures 7a and 7b presents X-ray spectra obtained from distinct points on a facial sculpture: one exhibiting paint loss and the other with visible pigment. Comparing these spectra reveals a more pronounced calcium peak at the unpainted point compared to the painted area, alongside intense lead peaks in both cases. This observation suggests the presence of lead white in the ground layer, possibly with underlying calcium carbonate or gypsum, consistent with documented practices regarding multiple ground layers in sculptures [14, 15]. Figure 7a's spectrum from the unpainted point provides a clearer insight into the composition of the ground layer, whereas the pigment spectrum likely reflects results influenced by radiation attenuation effects within the paint layer.

Traces of titanium detected may be attributed to previous restorations involving titanium white, developed in the 20th century [16], which could have already degraded over time, reflecting the current condition of the sculpture. Furthermore, titanium's presence serves as a potential indicator for identifying the mineralogical origins of the ochres used in polychromy, acting as a distinctive "fingerprint" [17, 18]. Strontium is likely present in the spectra due to its association with celestine, a mineral commonly found in gypsum rock [19]. This explains its detection in the absence of chromium, thereby excluding the possibility of strontium yellow [20] being used in the polychromy.

The ochres, pigments used since prehistory, consist of iron oxide along with clay and silica. Therefore, the detection of silicon, potassium, calcium, titanium, iron, strontium, and zirconium may be closely associated with the clay [21] present in the pigment, as evidenced by the trace elements identified in all spectra.

To achieve the observed flesh tone, it is inferred that white pigments were mixed with red and yellow pigments, although dirt and wear on the pictorial layer of the piece obscure a clearer visualization of these tones. The presence of a lead (Pb) peak suggests the use of pigments such as massicot, litharge, and red lead. The detection of iron (Fe) indicates the presence of an ochre pigment, which can vary in hue from yellow to dark red, including brown. The presence of mercury (Hg) confirms the use of vermilion in the mixture, contributing to the flesh tone of the sculpture.

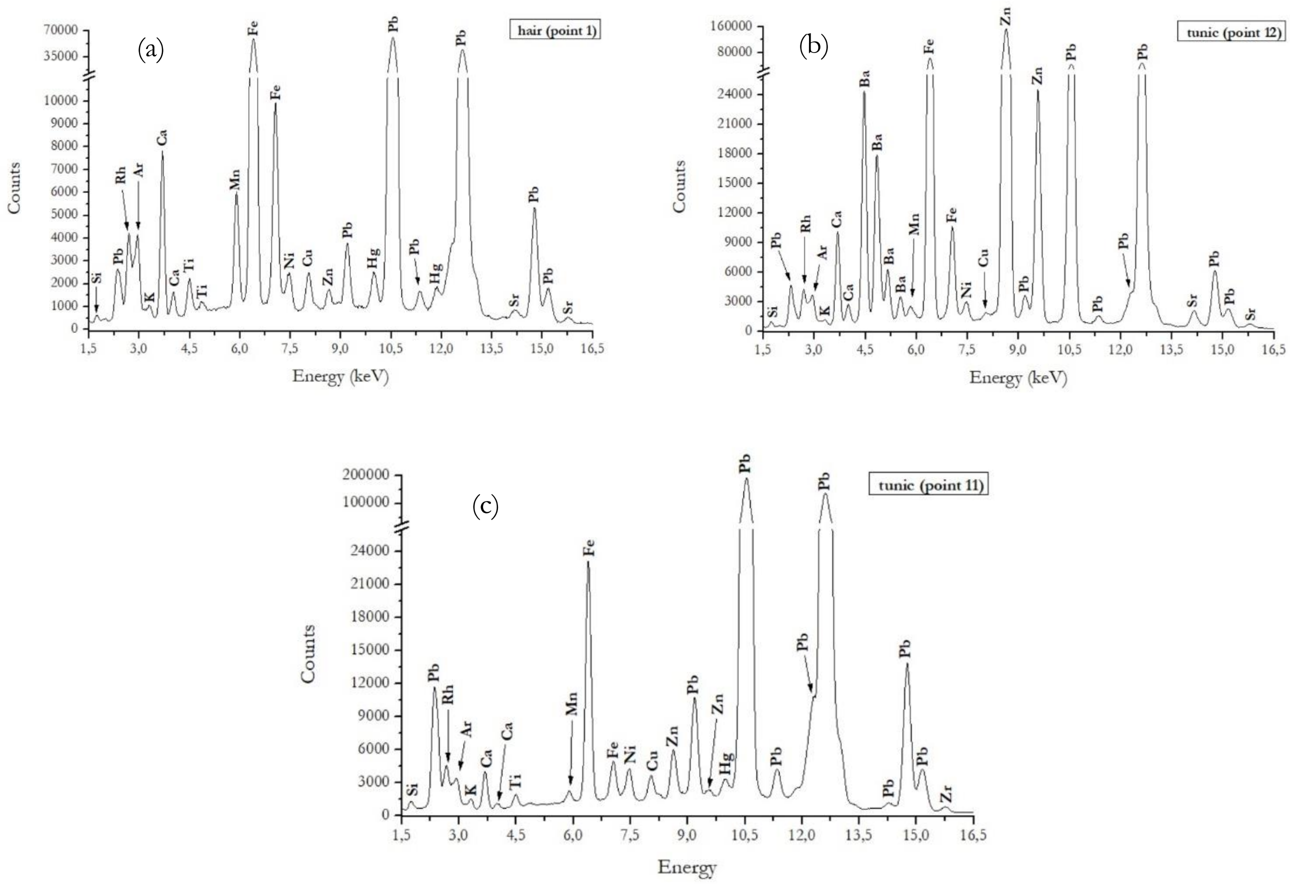
The presence of copper (Cu) suggests, counterintuitively, the use of blue and green pigments in the piece. However, copper residues in lead ores occur due to the geochemical properties and geological settings of polymetallic deposits, where copper often coexists with lead in sulfide minerals like galena [22]. Complex geological processes result in the formation of these ore bodies containing multiple metals, like zinc, as found in the deposits of the Alcudia Valley mineral field (Eastern Sierra Morena, Spain) [23]. The unexpected presence of copper in the analyzed artifact may not exclusively signify deliberate utilization of blue and green pigments, but rather may also be ascribed to the inherent geochemical conditions of the lead ore employed in the fabrication of Pb-based pigments. An alternative explanation for the presence of copper in the artifact may stem from contamination of the paint employed during the fabrication process. To achieve a more comprehensive understanding of the copper's presence, employing additional analytical techniques would be necessary to validate these hypotheses.

Similar to copper, the presence of zinc traces can be understood through two potential mechanisms: the historical application of zinc white in restoration efforts, possibly degraded due to inadequate maintenance of the artwork, or the presence of zinc residues originating from lead ores [23]. In the spectral analysis of the brown color observed on the saint's tunic, the prominent intensity of zinc peaks may indicate the prior application of zinc white in those areas, suggesting past restoration interventions. Zinc white, also known as zinc oxide (ZnO), became prevalent in the 19th century due to technological advancements, displacing earlier white pigments like lead white and chalk [24]. The simultaneous detection of zinc and barium indicates the utilization of lithopone, a pigment introduced from the late 19th century onwards [25, 26].

Regarding the brown color observed on the sculpture, specifically in the hair (figure 8a) and areas of the tunic (figure 8b), the key elements detected were lead, iron, calcium, manganese, and mercury for the hair, and lead, iron, zinc, and barium for the tunic.

Therefore, it can be inferred that the brown color is primarily derived from ochre pigment. In the hair, the detected elements suggest the use of umber and vermilion pigments in the mixture to achieve the observed color. In the tunic, the combined presence of barium and zinc indicates the use of lithopone, pointing to the repainting of the garment.

Figure 8: Characteristic X-ray spectra for the brown hue: (a) hair, (b) tunic repainted, (c) tunic with paint loss



At analysis point 11 (figure 8c), a region where the loss of the outermost pictorial layer (repainting) was observed, the presence of vermilion pigment was detected. This finding indicates that the original painting of the piece included vermilion in the composition of the tunic's brown color.

In the analysis of spectra obtained from the belt and cord of the Franciscan sculpture, the detection of gold indicates that the piece underwent gilding (figure 9). Table 2 presents the potential pigments constituting the polychromy of the San Diego de Alcalá sculpture, as determined through XRF analysis.

Figure 9: Characteristic X-ray spectra displaying the detection of Au: (a) belt, (b) cord

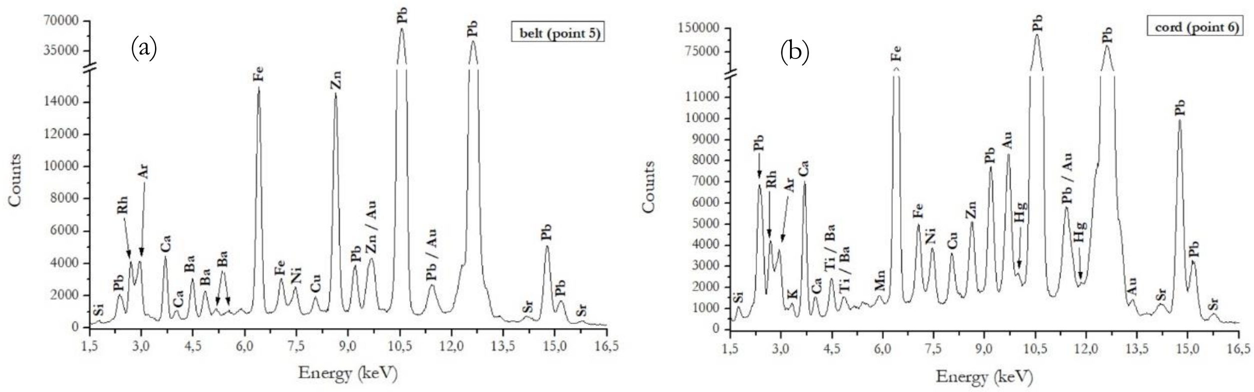


Tabela 2: Possible pigments identified by XRF, colour, composition, period of use

PIGMENT	COLOUR	COMPOSITION	PERIOD OF USE
Calcium Carbonate	White	$CaCO_3$	Antiquity / Still in use
Gypsum	White	$CaSO_4$.2H2O	Antiquity / Still in use
Lead White	White	$2PbCO_3.Pb(OH)_2$	Antiquity / 20th century
Lithopone	White	$ZnS + BaSO_4$	1874 / Still in use
Titanium White	White	TiO_2	1923 / Still in use
Zinc White	White	ZnO	1835 / Still in use
Yellow Ochre	Yellow	$Fe_2O_3.H_2O$	Prehistory / Still in use
Massicot	Yellow	PbO	Antiquity / 20th century
Red Ochre	Red	$Fe_2O_3.H_2O$	Prehistory / Still in use
Red Lead	Red	Pb_3O_4	Antiquity / 20th century
Litharge	Red	PbO	Antiquity / 20th century
Vermilion	Red	HgS	Antiquity / 19th century
Brown Ochre	Brown	$Fe_2O_3.H_2O$	Prehistory / Still in use
Sienna	Brown	Fe_2O_3 + clay	Antiquity / Still in use
Umber	Brown	$Fe_2O_3.MnO_2$	Prehistory / Still in use

4. CONCLUSIONS

Based on the detailed cross-sectional analysis using CT, several critical observations about the San Diego de Alcala´ sculpture have been highlighted. The examination revealed structural vulnerabilities such as cracks and voids, particularly evident at the base and neck regions. Additionally, the presence of high-density materials in superficial layers suggests deliberate structural elements or repair interventions, impacting both the sculpture's stability and its aesthetic integrity.

The XRF results highlighted a diverse array of elements present in the analyzed regions, revealing the use of pigments such as lead white, ochres, vermilion, and potentially later additions like zinc white and lithopone. The comparison of spectra from areas with intact pigmentation versus those showing paint loss provided crucial evidence of the original color palette and subsequent repainting interventions. For instance, the detection of vermilion in areas with paint loss on the tunic underscores its historical application, contributing to the brown hues observed.

Furthermore, the presence of trace elements such as titanium and strontium provided insights into the mineralogical characteristics of pigments. The presence of these elements gives clues about the mineral composition or specific types of minerals involved in the manufacture of the pigments. The unexpected presence of elements like copper in all spectra raised questions about their origins, potentially linked to geological conditions of lead ore or later restoration efforts using modern pigments.

The combined analyses of CT, DR, and XRF techniques applied to the San Diego de Alcalá sculpture have significantly advanced our knowledge of its original pigment composition, restoration history, current conservation condition, and construction methods. These investigations have also provided valuable insights into the sculpture's conservation trajectory. Further research employing complementary analytical approaches will be essential to corroborate and deepen these findings, thereby enriching our understanding of the sculpture's artistic and historical context.

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CONFLICT OF INTEREST

We have no conflicts of interest to disclose.

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