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Analysis of Oval Paintings Attributed to the Painter Leandro Joaquim Using XRF and MA-XRF

Análise de Telas Ovais Atribuídas ao Pintor Leandro Joaquim Utilizando XRF e MA-XRF

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ABSTRACT

Three paintings attributed to the Brazilian artist Leandro Joaquim (1738–1798) were analyzed in situ using X-ray fluorescence (XRF) and macro X-ray fluorescence scanning (MA-XRF) techniques. The artworks belong to the collection of the *Museu Histórico Nacional* in Rio de Janeiro and depict landscapes of the city during the colonial period. Due to their compositional and aesthetic similarities, the paintings have been treated as a collection. The analyses revealed the presence of pigments such as lead white ($2PbCO_3 \cdot Pb(OH)_2$), green earth ($K(Al, Fe^{3+}), (Fe^{2+}, Mg)O_{10}(OH)_2$), raw umber ($Fe_2O_3 + MnO_2$), and vermilion ($HgS$) in all three paintings. It was also observed that all the artworks contain a lead-based ground layer. To further investigate the similarities among the paintings, the XRF data were submitted to Principal Component Analysis (PCA), which confirmed the similarity in their elemental composition. The results suggest that the paintings were created using compatible materials and techniques, reinforcing the hypothesis of a common authorship and production within the same historical and technical context.

keywords pigment analysis, XRF, MA-XRF, PCA

RESUMO

Três pinturas atribuídas ao artista brasileiro Leandro Joaquim (1738–1798) foram analisadas *in situ* por meio das técnicas de Fluorescência de Raios X (XRF) e Macro Mapeamento Elementar por Fluorescência de Raios X (MA-XRF). As obras pertencem ao acervo do Museu Histórico Nacional do Rio de Janeiro e retratam paisagens da cidade no período colonial. Devido às semelhanças compositivas e estéticas, as pinturas vêm sendo tratadas como uma coletânea. As análises revelaram a presença de pigmentos como branco de chumbo ($2PbCO_3 \cdot Pb(OH)_2$), terra verde ($K(Al, Fe^{3+}), (Fe^{2+}, Mg)O_{10}(OH)_2$), sombra natural ($Fe_2O_3 + MnO_2$) e vermelhão ($HgS$) em todas as pinturas. Verificou-se ainda que todas as obras utilizam, como camada de preparação, um pigmento à base de chumbo. Para aprofundar a investigação sobre as similaridades entre as pinturas, os dados de XRF foram submetidos à Análise de Componentes Principais (PCA), a qual confirmou a semelhança na composição elementar entre as obras. Os resultados sugerem que as pinturas foram realizadas com materiais e técnicas compatíveis, reforçando a hipótese de autoria comum e de produção em um mesmo contexto histórico e técnico.

palavras-chave análise de pigmentos, XRF, MA-XRF, PCA

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Introduction

Humans have used pigments since prehistoric times for artistic expression, communication, and symbolic representation. Their presence can be observed in the earliest artistic manifestations, such as cave paintings found around the world, to the masterpieces of great painters like Leonardo da Vinci. Throughout history, this continuous and widespread use has established pigments as an essential tool for the study of artworks, the continuous and widespread use of pigments has established them as an essential tool for studying artworks (Freitas, Ribeiro et al., 2016; Nardes, Silva et al., 2019).

In recent years, studies on the characterization of pigments and other materials that make up a painting, such as binders, have increased significantly. This trend is a consequence of the technological advances of the past decades, which have enabled the development of portable instruments based on various techniques, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Raman Spectroscopy (Brunetti et al., 2016; Mendoza-Cuevas et al., 2023; Miliani et al., 2010).

Another development that has fostered the growth of these studies, and the interaction among different agents from distinct fields of knowledge, is the advancement of imaging techniques, such as Macro X-ray fluorescence scanning (MA-XRF) (Alfeld & de Viguerie, 2017, Freitas, Oliveira et al., 2024). This method produces images showing the distribution of elements present in a painting, revealing details such as underlying compositions and areas of restoration (Parma et al., 2023).

In the specific context of painting analysis, the use of investigative techniques has proven essential, as identifying the pigments used in an artwork is a fundamental step toward understanding and its preservation (Molari & Appoloni, 2021; Monico et al., 2020; Rodriguez et al., 2020). The characterization of these materials allows more effective conservation and restoration interventions through the use of compatible techniques and historically appropriate pigments, minimizing risks to the artifact's integrity. Furthermore, the study of the artist's color palette provides valuable insights into their creative process, aesthetic choices, and historical context, which can support painting authentication efforts (Kajiya et al., 2014; Thaumaturgo et al., 2024).

In the present study, three oval paintings attributed to the Brazilian artist Leandro Joaquim (1738–1798) were investigated using XRF and MA-XRF techniques (Joaquim, 1925a, 1925b, 1925c). The results enabled the characterization of the materials present in the artworks and the identification of similarities and differences among them. To further explore these similarities and differences, the XRF data were analyzed using multivariate statistical methods, specifically Principal Component Analysis (PCA). The results confirmed that the paintings were indeed produced using the same materials and are part of a coherent set.

Materials and methods

Paintings

The painter Leandro Joaquim (1738–1798) was one of the leading artists active in Rio de Janeiro during the period when Brazil was a colony of Portugal. His work reflects a strong influence of Portuguese techniques, particularly in the application of pigments and the composition of scenes. He is renowned for depicting landscapes and aspects of daily life in Rio de Janeiro with remarkable precision and is considered one of the pioneers of the city's iconography. His work is essential for understanding Luso-Brazilian art during the colonial period in Brazil.

Currently in the custody of the National Historical Museum in Rio de Janeiro, Brazil, there are six oval artworks attributed to Leandro Joaquim, which depict, in great detail, historical regions of Rio de Janeiro during the Brazilian colonial period. Due to these artworks portraying landscapes of a specific region and sharing similar aesthetic qualities, they have been considered a set.

This study analyzed three paintings from this collection, illustrated in Figure 1: *Lagoa do Boqueirão e Aqueduto da Carioca* (Boqueirão Lagoon and Carioca Aqueduct, 96.0 cm × 126.0 cm), *Revista Militar no Largo do Paço* (Military Review at Largo do Paço, 96.1 cm × 125.3 cm), and *Procissão Marítima diante do Hospital dos Lázaros* (Maritime Procession in Front of the Hospital of the Lazarus, 96.1 cm × 125.3 cm).

Figure 1 - Paintings Attributed to Leandro Joaquim: (a) *Lagoa do Boqueirão e Aqueduto da Carioca*; (b) *Revista Militar no Largo do Paço*; and (c) *Procissão Marítima diante do hospital dos Lázaros*.

(a) (b) (c)

From "*Lagoa do Boqueirão e Aqueduto da Carioca*", by L. Joaquim, (1925a), *Museu Histórico Nacional*, "*Revista Militar no Largo do Paço*", by L. Joaquim, (1925c), *Museu Histórico Nacional*, "*Procissão Marítima diante do Hospital dos Lázaros*", by L. Joaquim, (1925b), *Museu Histórico Nacional*.

Handheld XRF and PCA analyses

XRF spectra were obtained using the TRACER IV, a Bruker handheld X-ray spectrometer, equipped with a miniaturized X-ray generator with a Rh anode, maximum current and voltage of 200 µA and 40 kV, respectively, and a silicon drift detector (SDD), model XFlash (10 mm^2), thermoelectrically refrigerated to –15°C, having an energy resolution of about 145 eV at 5.90 keV, and capable of performing up to 10 kcps. The acquisition parameters used were a voltage of 40 kV, a current of 10 µA, and an acquisition time of 30 s per spectrum.

Principal Component Analysis (PCA) was performed using the full XRF spectra from each sampling point, without any preprocessing. The 2048 channels that make up the XRF spectra were input into the data table for the PCA, with the algorithm executed using The UnscramblerX software.

PCA was chosen as an unsupervised exploratory tool to investigate patterns and trends in the high-dimensional spectral dataset without imposing any prior classification (Novais Rodrigues et al., 2019). Compared to techniques such as hierarchical clustering or discriminant analysis, PCA is particularly effective in summarizing variance across a large number of correlated variables, such as spectral channels, and provides insight into the main directions of variability (Baddini et al., 2022; Felix, Mello et al., 2020, Shimamoto et al., 2013). This makes it well-suited for detecting structure in complex datasets like XRF spectra, where the goal is to explore intrinsic relationships rather than perform supervised classification.

MA-XRF system

The MA-XRF analysis was carried out with CRONO, a Bruker portable system. It consists of a detection head mounted on a motorized XYZ stage, allowing it to scan an area of up to 450×600 mm^2 (Alberti et al., 2017). The source operates with a maximum current and voltage of 200 µA and 50 kV, respectively. The spectra acquisition was made by means of an SDD with an energy resolution below 130 eV at 5.9 keV for a 100 kcps input rate. The measurements of three paintings were made by using a 1 mm spot size, 40 kV, and 200 µA without a filter. XRF spectra were collected every 1 mm of the painting surface with a dwell time of 40 ms, resulting in a total acquisition time of approximately 8 hours per painting. The collected data cubes were analyzed using PyMca and Datamuncher (Alfeld & Janssens, 2015; Solé et al., 2007).

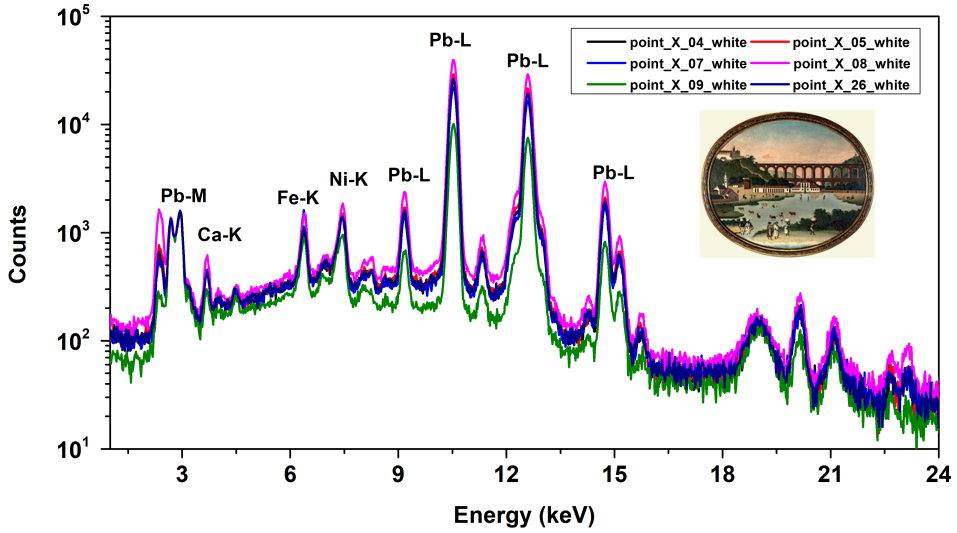
Results and discussion

XRF results

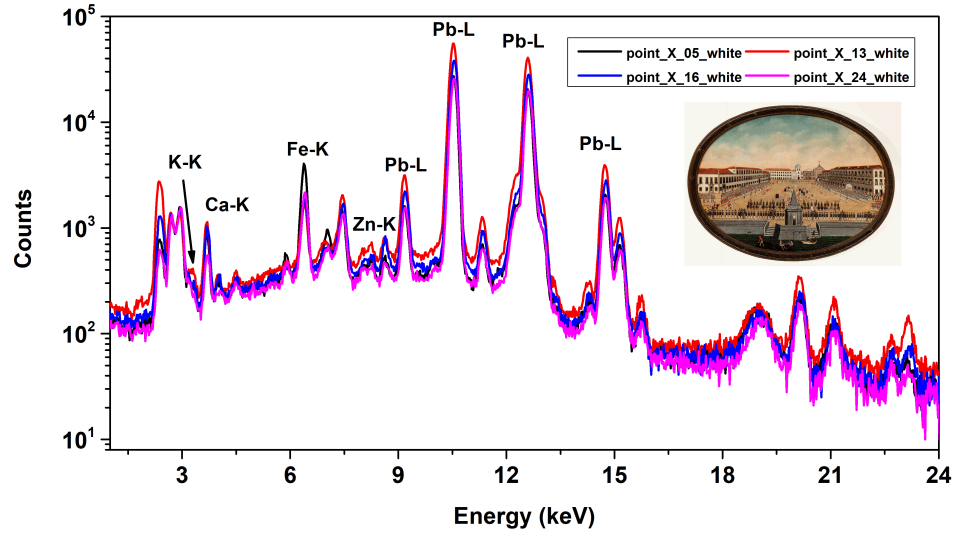
The three analyzed paintings predominantly feature white, green, brown, and red tones, as shown in Figures 1(a)-1(c). In all XRF spectra collected from the artworks, regardless of the region's tone, Pb was predominantly detected, as presented in Figure 2.

Figure 2 - XRF spectra collected from a white region of the painting: (a) *Lagoa do Boqueirão e Aqueduto da Carioca*; (b) *Revista Militar no Largo do Paço*; and (c) *Procissão Marítima diante do hospital dos Lázaros*.

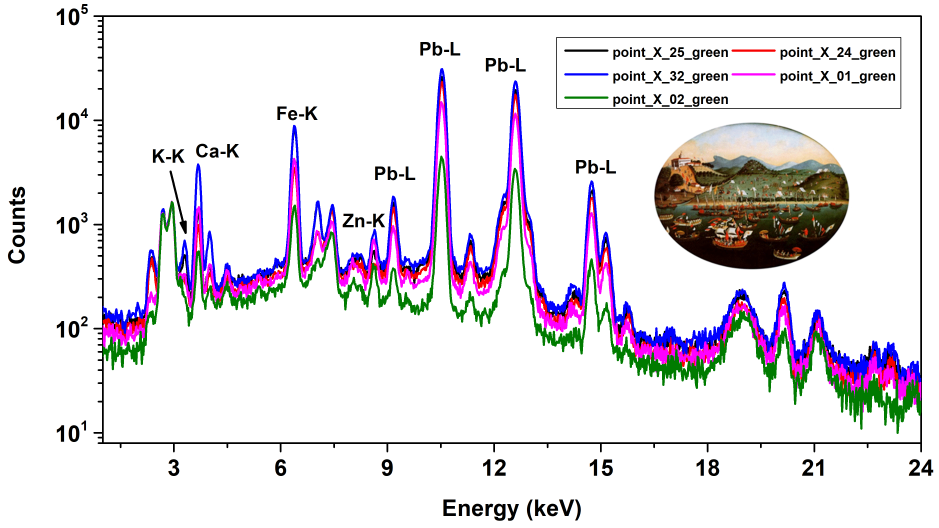
(a)



(b)



(c)

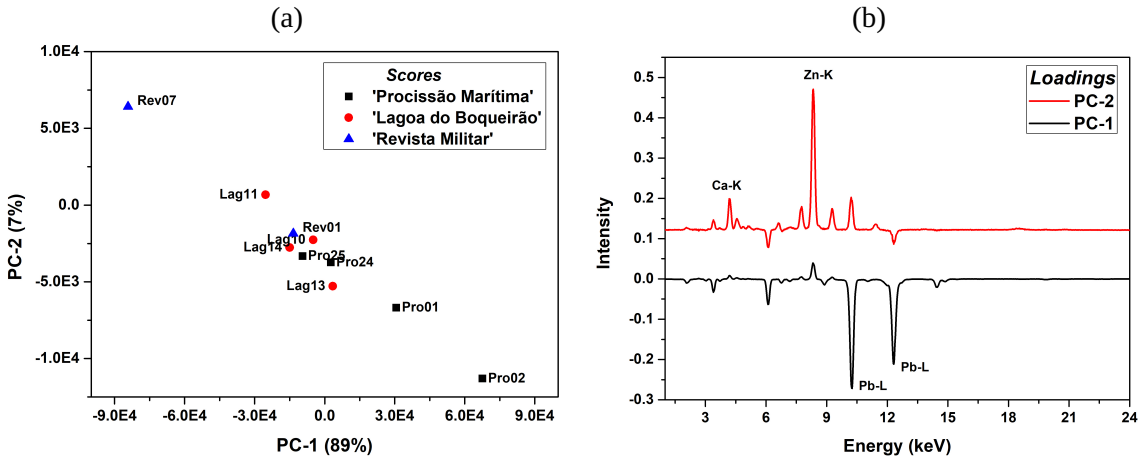


The consistently high intensity of Pb in all spectra, Figures 2(a)-2(c), suggests the presence of lead-based pigments, such as lead white ($2PbCO_3 \cdot Pb(OH)_2$), in the preparation layer (Nardes, Sanches et al., 2023; Pimenta et al., 2023). Lead-based pigments are known for their drying and sealing properties, which is why they are commonly applied in the preparation layer of artworks, particularly before the 20th century (Felix, Pereira et al. 2018). Ca was also detected in all the XRF spectra; however, the intensity of the element varied, being characterized by low intensity in most of the spectra. Calcium can be associated with materials such as calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4 \cdot 2H_2O$), and due to its consistent presence in all spectra, it may also be linked to the preparation layer (Birelo & Appoloni, 2024).

In XRF spectra collected from the green and brown regions, an increase in the intensity of Fe was observed. In the spectra collected from the green areas, the presence of K was also detected, Figure 2(c), which is a key element of the pigment Green Earth $K(Al, Fe^{3+}), (Fe^{2+}, Mg)O_{10}(OH)_2$ (Freitas, 2023). In the brown regions, in addition to Fe, Mn was detected, which can be attributed to the presence of the pigment umber $Fe_2O_3 + MnO_2$ (Appoloni et al., 2023).

It is noteworthy that the spectra collected from all the green-toned regions of the paintings presented the same elements, with variations only in the intensities of the characteristic peaks. Principal Component Analysis (PCA) of the data collected from these areas revealed a strong similarity between the spectra obtained from the different artworks. A total of 11 spectra from green regions were used: five from *Lagoa do Boqueirão e Aqueduto da Carioca*, two from *Revista Militar no Largo do Paço*, and four from *Procissão Marítima diante do Hospital dos Lázaros*. These spectra were subjected to the PCA algorithm without any prior treatment, a similar approach to that used by Freitas & Calza et al., (2010) in the investigation of archaeological artifacts. For simplicity, the scores are labeled as Lag, Rev, and Proc in Figure 3.

Figure 3 - Method from the XRF spectra collected at the green points of the three paintings: (a) graph of the scores represented by Proc, Lag, and Rev; and (b) loadings obtained by the PCA.



As shown in the PCA score plot obtained from the XRF spectra collected in the green regions, the first two principal components (PC1 and PC2) explain 96% of the variance among the samples (89% and 7%, respectively). This substantial value is attributed to the mixture of materials employed by the artist or possibly the use of distinct pigments during restoration processes. The score plot, Figure 3(a), reveals a predominant cluster formed by most of the samples from the three artworks, *Procissão Marítima diante do Hospital dos Lázaros* (Pro01, Pro24, and Pro25), *Lagoa do Boqueirão e Aqueduto da Carioca* (Lag10, Lag13, and Lag14), and *Revista Militar no Largo do Paço* (Rev01). This grouping indicates a strong similarity in the elemental composition of the green pigments used in these paintings.

As illustrated in Figure 3(a), the score plot displays the distribution of the different XRF spectra in the space defined by the first two principal components. PC1, which accounts for 89% of the variance, is strongly influenced by lead (Pb), as evidenced by the negative Pb-L peaks in the loading plot, see Figure 3(b). This indicates that the position of the points along the PC1 axis is directly related to the Pb intensity in the XRF spectra. Samples such as Rev07, Pro02, and Pro01, which deviate toward the positive or negative extremes of PC1, likely have significantly different lead intensity compared to the other samples, explaining their distant placement from the main cluster.

PC2, which accounts for 7% of the variance, is primarily influenced by elements such as calcium (Ca) and zinc (Zn), whose peaks appear prominently in the loading plot, Figure 3(b). Variations in these elements distinguish samples that are similar in Pb content but differ in other aspects of their elemental composition. For example, Rev07, an outlier in the score plot, is positioned high along the PC2 axis, indicating a greater contribution of Ca and Zn compared to the other samples.

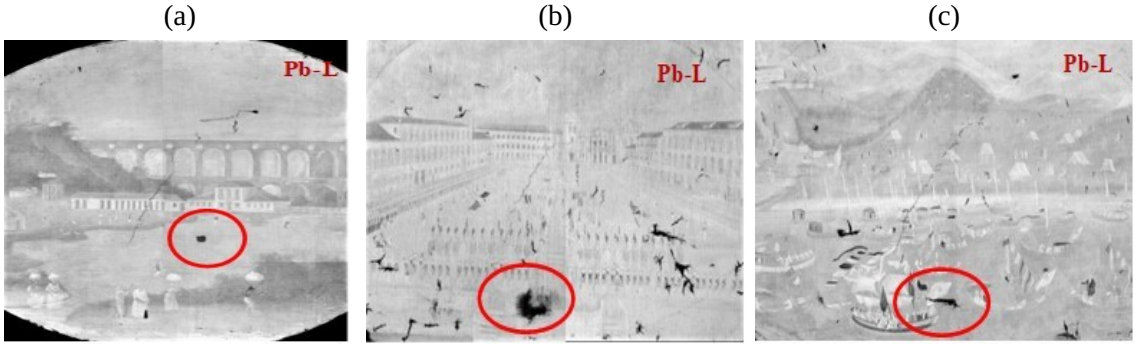
Thus, the loadings not only identify the most relevant elements for each component but also help explain why certain samples cluster together or appear as outliers in the score plot. The combined analysis of these plots suggests that the chemical differences and similarities among the green pigments are primarily related to variations in Pb, Ca, and Zn concentrations, which may reflect both original material choices and restoration interventions.

Thus, the results show that the trends observed in the score plots are corroborated by the loading plot, which indicates that PC1 is strongly influenced by the presence of lead Pb, and PC2 is associated with elements such as calcium (Ca) and zinc (Zn). This suggests that the distribution of these elements plays a central role in differentiating the samples. Similar patterns were observed in the PCA analyses of the brown and red regions, where XRF spectra also revealed consistent groupings across different paintings. These consistent results across multiple color regions support the interpretation that the artist, or the restorers, employed a shared palette or pigment source for the studied artworks.

MA-XRF results

The Pb-L elemental maps of the paintings, presented in Figure 4, were constructed in grayscale, where areas with higher contrast indicate higher intensity of the detected element.

Figure 4 - Photographs of the artworks and lead (Pb-L) elemental maps, where (a) *Lagoa do Boqueirão and Aqueduto da Carioca*, (b) *Revista Militar no Largo do Paço*, and (c) *Procissão Marítima diante do Hospital dos Lázaros*.

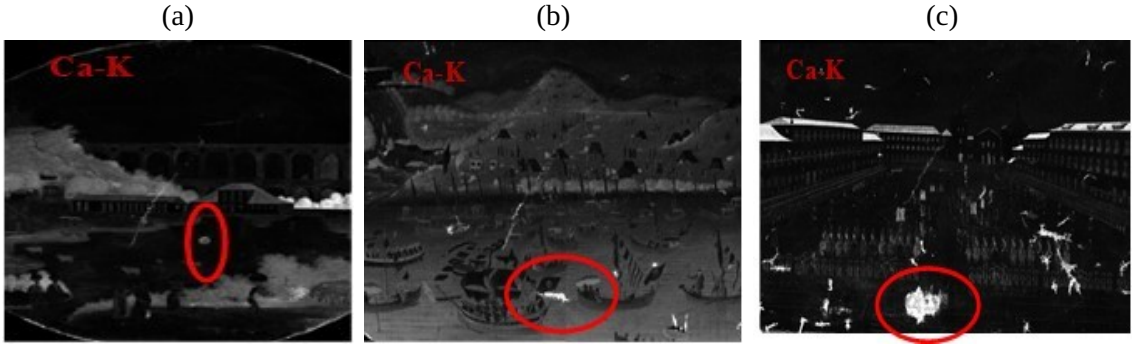


In all the analyzed artworks, a high contrast is observed across almost the entire surface of the canvases, highlighting a significant distribution of lead (Pb) in the paintings, Figures 4(a)-(c). This result is consistent across the different paintings, suggesting a common pattern in the application of this element.

The recurrent presence of lead with high intensity in all the mapped regions reinforces the conclusion obtained through XRF, indicating that lead-containing compounds were used as a preparation layer. This type of application was a common practice in certain artistic contexts, especially with the use of lead white, a pigment that provided better adhesion and stability to the painting. The convergence of data obtained through MA-XRF images and point XRF analysis strengthens the interpretation regarding the materials and the position of the layer where the element is found.

The Pb-L elemental maps also help identify regions with low gray intensity, highlighted by red circles in Figures 4(a)-4(c), indicating possible areas of loss in the original pictorial layer. In these locations, a significant reduction in lead presence is observed, suggesting that the preparation layer has been removed. This interpretation is further supported by the calcium elemental maps (Ca-K), illustrated in Figures 5(a)-5(c), which show high contrast in the same regions, also highlighted by red circles, indicating an accumulation of calcium-rich material, possibly associated with restoration processes.

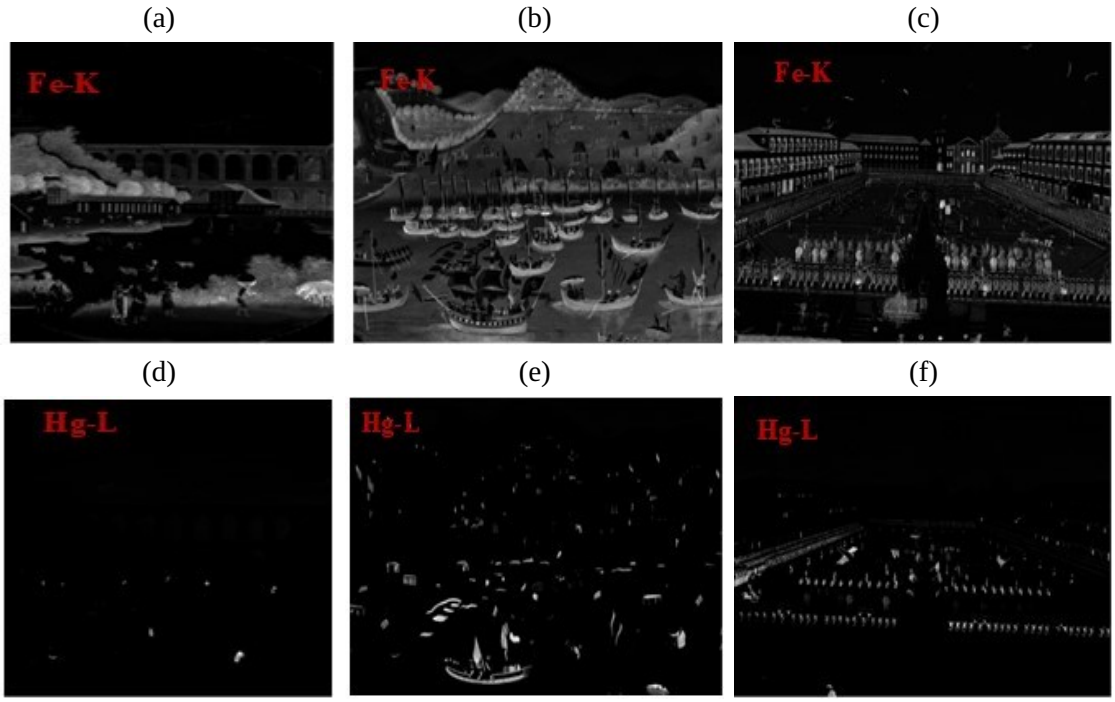
Figure 5 - Elemental maps of calcium (Ca-K), iron (Fe-K), and mercury (Hg-L) collected from the three artworks, where (a) *Lagoa do Boqueirão and Aqueduto da Carioca*, (b) *Revista Militar no Largo do Paço*, and (c) *Procissão Marítima diante do Hospital dos Lázaros*.



These findings from the Pb-L and Ca-K maps, Figure 4 and Figure 5, are consistent with the PCA results, which identified these elements as having the greatest influence on the distribution pattern observed in the score plot. As shown in the elemental maps of the painting Revista Militar no Largo do Paço, there is a large area of lead loss filled with calcium-containing material. This result explains the outlier behavior of the Rev07 point, suggesting that its spectrum was likely collected from a region that underwent restoration.

Figure 6 shows the elemental maps of iron (Fe-K) and mercury (Hg-L) obtained from the three analyzed artworks: *Lagoa do Boqueirão e Aqueduto da Carioca*; *Revista Militar no Largo do Paço*; and *Procissão Marítima diante do Hospital dos Lázaros*.

Figure 6 - Elemental maps obtained from the three artworks: (a)–(c) iron (Fe-K) and (d)–(f) mercury (Hg-L).



In Figures 6(a)-6(c), the presence of iron is observed with greater intensity in the green and brown areas, confirming the use of green earth and shadow pigments. Additionally, the Hg-L maps indicate the presence of mercury in the red-toned regions, suggesting the use of the vermilion pigment (HgS) (Freitas, Felix et al., 2019).

Conclusions

Based on the results obtained through XRF and MA-XRF analyses, the presence of the pigments lead white ($2PbCO_3 \cdot Pb(OH)_2$), green earth ($K(Al, Fe^{3+})$, $(Fe^{2+}, Mg)O_{10}(OH)_2$), umber ($Fe_2O_3 + MnO_2$), and vermilion ($HgS$) was identified in the three paintings studied. All of these materials were characterized in areas whose tones are consistent with the pigments used, such as green earth in green areas and vermilion in red zones, corroborating the correspondence between the chemical composition and the apparent coloration of the pictorial layers in the three paintings.

The MA-XRF maps also revealed that all the artworks share the same lead-rich ground layer, indicating a common technical procedure during the initial creation stage. This uniformity is further reflected in the results obtained through Principal Component Analysis (PCA), which highlighted a strong similarity between the pigments applied across the three works, including the methods used to create subtle tonal variations within a single color. These findings, combined with the observed stylistic coherence, support the hypothesis that the three paintings were produced during the same period, using a common pigment palette and likely executed by a single artist.

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Author Contributions

A. L. C. de Oliveira, A. R. Pimenta, V. de S. Felix, M. G. Parma, and **I. M. de C. Mendes**: Formal Analysis, Investigation, Methodology, Writing – original draft. **R. P. de Freitas**, and **M. J. dos Anjos**: Supervision, Formal Analysis, Investigation, Validation, Visualization, Project Manager, Writing – revision and editing.

Conflicts of Interest

The authors declare no conflict of interest.

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