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Debret or Not? A Physicochemical Study of Prints from the Castro Maya Museum

Debret ou não? Estudo Físico-Químico de Gravuras do Museu Castro Maya

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ABSTRACT

This study presents a physico-chemical investigation of six watercolor prints attributed to Jean-Baptiste Debret, part of the collection held by the Castro Maya Museum in Rio de Janeiro, Brazil. The authenticity of several works in the museum's Debret collection has been questioned, leading to the formation of a national commission that identified 40 out of 42 disputed pieces as forgeries. To contribute to the technical analysis of these works, this research applied non-invasive methods - macro X-ray fluorescence mapping (MA-XRF) and Fourier-transform infrared spectroscopy (FTIR) - to analyze pigments, binders, and paper fiber composition. Comparative multivariate statistical analyses were performed using principal component analysis (PCA) and component analysis robust (RPCA), aiming to identify chemical patterns distinguishing authentic works from those of unknown authorship. The results suggest significant differences between prints considered authentic and those of uncertain origin, particularly in the distribution and composition of binders and pigments. Similarities found in the use of Prussian blue pigment were not sufficient to establish authorship. This work demonstrates the value of scientific methods in art authentication and highlights the need for further interdisciplinary studies in museum collections.

keywords Debret, watercolor prints, MA-XRF, FTIR, authentication

RESUMO

Este estudo apresenta uma investigação físico-química de seis gravuras em aquarela atribuídas a Jean-Baptiste Debret, pertencentes ao acervo do Museu Castro Maya, no Rio de Janeiro. A autenticidade de diversas obras da coleção Debret do museu foi questionada, o que motivou a criação de uma comissão nacional que identificou 40 de 42 obras como falsificações. Com o objetivo de contribuir com a análise técnica dessas obras, foram aplicadas metodologias não invasivas - mapeamento por fluorescência de raios X (MA-XRF) e espectroscopia no infravermelho por transformada de Fourier (FTIR) - para investigar os pigmentos, aglutinantes e a composição das fibras do papel. Análises estatísticas multivariadas, utilizando análise de componentes principais (PCA) e componentes principais robusto (RPCA), foram conduzidas para identificar padrões químicos que diferenciassem obras autênticas daquelas de autoria desconhecida. Os resultados indicaram diferenças significativas entre as aquarelas consideradas autênticas e as de origem incerta, especialmente na distribuição e composição de aglutinantes e pigmentos. Embora tenham sido observadas semelhanças no uso do pigmento azul da Prússia, isso não foi suficiente para confirmar a autoria. O trabalho demonstra a relevância de métodos científicos na autenticação de obras de arte e reforça a importância de estudos interdisciplinares em acervos museológicos.

palavras-chave Debret, gravuras, MA-XRF, FTIR, autenticação

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Introduction

The Castro Maya Museum, also known as the Chácara do Céu Museum, is in the Santa Teresa neighborhood of Rio de Janeiro and houses a historically and culturally significant collection. According to an inventory conducted in the 2010s, the museum holds more than 27,000 objects, including tapestries, Oriental art, silverware, paintings, and prints. As noted by Batista (2012), this collection was donated by Raymundo Ottoni de Castro Maya shortly before his death to a foundation bearing his name, which was later dissolved in 1983.

Despite its cultural prominence, the museum became notorious following a tragic event. On the afternoon of February 24, 2006 - during Rio de Janeiro's Carnival - four individuals entered the museum while the popular street band "Carmelitas" paraded nearby and executed the largest art theft in Brazilian museum history. Among the stolen items were four paintings by Claude Monet, Henri Matisse, Pablo Picasso, and Salvador Dalí, then valued at over 10 million USD (Tardaguila, 2016). None of the stolen works have ever been recovered.

Among the most remarkable collections in the museum is that of Jean-Baptiste Debret, a French artist who extensively documented 19th-century Brazil through his illustrations. During his stay in Brazil, Debret painted several significant events in the life of the royal court, such as the Acclamation of Dom Pedro I, and faithfully depicted everyday life in the streets of Rio de Janeiro with a documentary approach. Between 1834 and 1839, Debret published in Paris a three-volume collection of prints that combined lithography and watercolor, titled *Voyage Pittoresque et Historique au Brésil* (*Picturesque and Historic Voyage to Brazil*). Castro Maya acquired a set of 551 watercolors and drawings from the Franco-Brazilian art dealer Roberto Heymann, who owned an antiquarian gallery in Paris specializing in Latin American iconography. In pursuit of greater profit, Heymann began to forge watercolors based on Debret's sketches. However, the authenticity of several of these works has been questioned. According to Batista (2012), Pelegrini (2009) and Morais (2020), a commission established by the National Institute of Historic and Artistic Heritage (IPHAN) identified 40 out of 42 disputed works as forgeries, while two required further analysis. These findings introduced the designation "work attributed to Debret" into the discourse surrounding the collection.

Watercolor is a painting technique in which pigments are suspended in a water-soluble medium. When applied to a high-weight paper substrate, the result is a type of wash painting known as watercolor wash. In this medium, water plays a central and dynamic role, demanding precise control, delicacy, and attentiveness from the artist during execution (Almada, 2018).

Watercolor paint is characterized by its inherent transparency, a quality that significantly contributes to its aesthetic value. This transparency allows the underlying paper to actively participate in the final composition by serving as a source of luminosity, enhancing the overall brilliance of the image. The defining features of watercolor painting include its extensive chromatic possibilities, the fluidity of the medium, and the light-transmitting quality of its layered applications.

In recent decades, scientific techniques have increasingly supported the field of art history and cultural heritage by providing objective, non-destructive methods for analyzing the materials and methods used in artworks (Brunetti et al., 2016; Miliani et al., 2010). In 2023, researchers from LISCOMP, under a collaborative agreement between the Brazilian Institute of Museums (IBRAM) and the Federal Institute of Rio de Janeiro (IFRJ), visited the museum with the goal of conducting physico-chemical characterizations of prints attributed to Debret (Pimenta et al., 2023).

This study focuses on six watercolors previously flagged for stylistic inconsistencies but never subjected to scientific analysis. Two advanced, non-invasive techniques were employed: Macro X-ray Fluorescence Mapping (MA-XRF), which enables spatially resolved detection of inorganic elements in pigment matrices, and Fourier Transform Infrared Spectroscopy (FTIR), which identifies molecular vibrations associated with organic and inorganic materials. By applying these techniques in situ, the team was able to investigate the chemical composition of pigments, binders, and paper fibers without compromising the artworks' integrity (Haddad et al., 2023). Moreover, multivariate statistical tools such as Principal Component Analysis (PCA) and Robust Principal Component Analysis (RPCA) were employed to compare the chemical profiles of prints considered authentic with those of uncertain authorship. The combination of these methodologies not only aids in the authentication process but also contributes to the preservation and understanding of Brazil's cultural heritage.

Material and methods

This study is based on the analysis of six historical watercolor prints, selected for their iconographic relevance in representing aspects of everyday life and social dynamics in Brazil during the 19th and early 20th centuries. The images were chosen for their thematic and authorial diversity, including works by Jean-Baptiste Debret and anonymous artists. Each print was identified with a specific code and characterized by title, dimensions, authorship, date, and technique, and described as summarized in Table 1.

Table 1 - Analyzed works: code, title, authorship, dimensions, and status.

Code	Title (English) – Original (Portuguese)	Author / Date	Dimensions (cm)	Authorship status
3CM	Itinerant Barbers – *Barbeiros Ambulantes*	Jean-Baptiste Debret, 1826	18.7 × 23.5	authentic
4CM	Black Bird Sellers – *Negros Vendendo Galinhas e Peru*	Jean-Baptiste Debret, 1826	18.8 × 27.6	authentic
1CM	A Brazilian Lady in her Home – Uma Senhora de Algumas Posses em sua Casa	Jean-Baptiste Debret, 1826	16.2 × 23.0	authentic
8CM	Acclamation of Dom Pedro I, Emperor of Brazil: at the Campo de Sant' Ana – *Aclamação de D. Pedro I, Imperador do Brazil no Campo de Sant'Anna*	Unknown, 1901/1950	25.7 × 18.9	attributed
6CM	Olinda, Brazil – *Olinda*	Unknown, 1901/1950	19.2 × 27.0	attributed
7CM	Village of Caboclos in Cantagalo – *Aldeia de Caboclos no Cantagalo*	Unknown, 1901/1950	20.5 × 27.6	attributed

The respective images are presented in Figure 1. The methodology applied in the analyses was developed in collaboration with expert members of the Carlos Eboli Forensic Institute of the Civil Police of Rio de Janeiro. This same methodology has been employed in various forensic reports issued by the Civil Police of Rio de Janeiro and in one report by the Federal Police. In addition to these reports, the methodology has also been applied in several publications (Kajiya et al., 2025; Pimenta et al., 2023; Thaumaturgo et al., 2024). This study was conducted under the following experimental conditions: Macro X-ray Fluorescence Mapping (MA-XRF), Fourier Transform Infrared Spectroscopy (FTIR), Principal Component Analysis (PCA), and Robust Principal Component Analysis (RPCA).

Macro X-ray Fluorescence Mapping

This method enables the identification of the inorganic components of pigments by scanning the elemental distribution across the artwork. The MA-XRF analysis was carried out using CRONO, a portable system developed by Bruker. It consists of a detection head mounted on a motorized XYZ stage, allowing for the scanning of areas up to 450×600 mm^2 (Alberti et al., 2016), and was adapted by the mobile laboratory of the Federal Institute of Rio de Janeiro (IFRJ). An alternative configuration of the detection head, also mounted on a motorized XYZ stage, allows for scanning areas up to 900×900 mm^2 (Kajiya et al., 2025). The X-ray source operates at a maximum voltage of 50 kV and a current of 200 μA. Spectral acquisition is performed using a silicon drift detector (SDD) with an energy resolution below 130 eV at 5.9 keV, at an input count rate of 100 kcps.

Measurements on six paintings were conducted using a 1 mm spot size, with an excitation voltage of 40 kV and a current of 200 μA, without the use of filters. An XRF spectrum was collected at every 1 mm interval across the surface of each painting, with a dwell time of 40 ms per point, resulting in a total acquisition time of approximately eight hours per artwork. The resulting data cubes were processed and analyzed using Bruker's CRONO software, in conjunction with PyMca and Datamuncher (Alfeld & Janssens, 2015; Solé et al., 2007).

Figure 1 - Description of the images of the watercolor prints: (a) Itinerant Barbers; (b) Acclamation of Dom Pedro I, Emperor of Brazil: at the Campo de Sant' Ana, in Rio de Janeiro; (c) A Brazilian Lady in her Home; (d) Olinda, Brazil; (e) Black Bird Sellers; (f) Village of Caboclos in Cantagalo.

From "Itinerant Barbers" by J.-B. Debret, 1826, Museu Castro Maya; "Acclamation of Dom Pedro I, Emperor of Brazil: at the Campo de Sant' Ana" 1901, Museu Castro Maya; "A Brazilian Lady in her Home", by J.-B. Debret, 1823, Museu Castro Maya; "Olinda", 1901, Museu Castro Maya; "Black Bird Sellers" by J.-B. Debret, 1820, Museu Castro Maya; "Village of Caboclos in Cantagalo" 1901, Museu Castro Maya.

Fourier Transform Infrared Spectroscopy

The FTIR measurements were made using the portable system Alpha II model from Bruker. Using an external reflectance accessory, the spectra were collected by the pseudo-absorbance $\log(1/R)$ method in the mid-infrared region (360–6000 cm^{-1}), using a resolution of 4 cm^{-1} and 32 scans. This technique identifies organic and inorganic molecular structures through vibrational analysis. It allows for spot analysis on selected regions and was employed to identify pigments and binders.

Principal Component Analysis and Robust Principal Component Analysis

Multivariate statistical analysis using PCA, which allows for the evaluation of similarities and differences among analytical datasets, was performed using FTIR data collected from both the suspect paintings and original works attributed to Debret (Baddini et al., 2022). The objective of the analysis was to investigate potential similarities in the creative processes behind the artworks. Raw pseudo-absorbance data, expressed as $\log(1/R)$, from the six analyzed prints were input into a spreadsheet without any preprocessing, forming a data matrix that was subsequently processed using *Unscrambler X* software.

RPCA, a variant of PCA designed to manage datasets containing noise, outliers, or anomalies, was also employed (Felix et al., 2020). Unlike conventional PCA, which assumes a Gaussian distribution and represents data as a linear combination of principal components, RPCA decomposes the data matrix into two components: a low-rank matrix representing the underlying data structure, and a sparse matrix that captures anomalies or outliers. This approach has proven especially effective in contexts where noise can compromise statistical interpretation, such as in the spectroscopic analysis of artworks (Daffara & Parisotto, 2021). RPCA was performed using raw pseudo-absorbance FTIR spectra and implemented via Antropofágico, a software developed by the mobile laboratory of the Federal Institute of Rio de Janeiro (IFRJ).

Results and Discussion

Paints consist of pigments or dyes mixed with a binder of animal or plant origin and dispersed in aqueous or oily media. Water-based paints were commonly employed on paper, parchment, or cardboard. In painting manuals from the 17th and 18th centuries, these materials were referred to as “illuminating inks, ”while paints intended for canvas or wood panels were known as “tempera”.

Considering the historical and technical characteristics of watercolor materials, the following subsections present the results of the physico-chemical analyses performed on six selected works, representing both authentic and attributed authorship, see Table 1 and Figures 1(a)-(f).

MA-XRF analysis was applied to Itinerant Barbers (3CM, authentic) and Olinda, Brazil (6CM, attributed), whereas FTIR analysis was conducted on all six prints. The FTIR datasets were subsequently examined using multivariate statistical methods (PCA and RPCA) to compare chemical profiles and identify patterns that support the distinction between authentic and attributed works.

MA-XRF Mapping Results

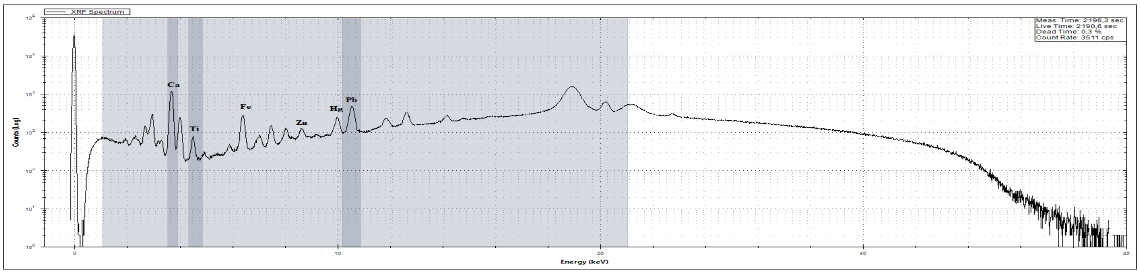
Figure 2 presents the MA-XRF investigation of the watercolor Itinerant Barbers (3CM), performed with the commercial Crono system.

The elemental maps indicate the presence of mercury (Hg), Figure 2(d), in walls, clothing, and rooftops, with the strongest signals concentrated in vivid red areas, such as the cloth tied around the seated man’s waist. Lead (Pb) is associated with white pigments, with particularly high intensities in the arms, legs, and backs of the shaved men, Figure 2(e). In addition to Hg and Pb, calcium (Ca), iron (Fe), and zinc (Zn) were also detected, Figures 2(b), 2(c) and 2(f). Calcium is uniformly distributed across the work, consistent with its role in the paper substrate. Iron is localized in red-pigmented areas, while zinc appears together with mercury and lead, suggesting its function as an extender or filler in the paint formulations.

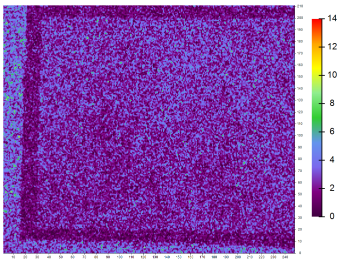
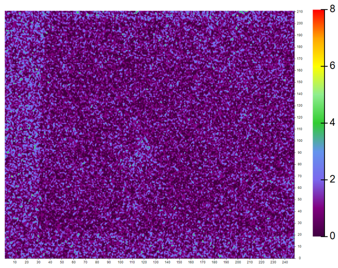
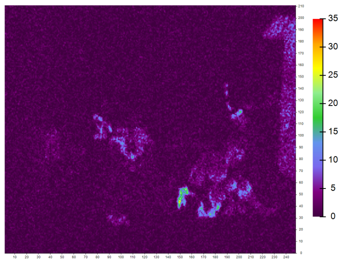
Figure 3 presents the results of the MA-XRF investigation of the watercolor Olinda, 6CM, acquired using equipment from IFRJ and processed with *PyMca* software.

Figure 2 - MA-XRF analysis of the engraving Itinerant Barbers (3CM):(a) Average X-ray fluorescence spectrum; (b) Calcium (Ca) distribution; (c) Iron (Fe) distribution; (d) Mercury (Hg) distribution; (e) Lead (Pb) distribution; (f) Zinc (Zn) distribution; (g) Count spectrum.

(a)



(b) (c) (d)

(e) (f) (g)

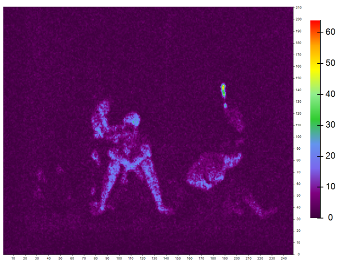
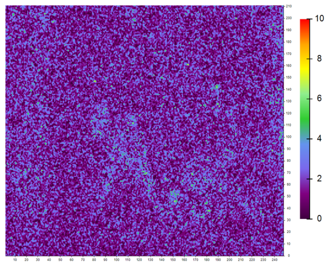
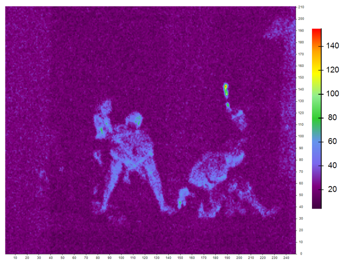
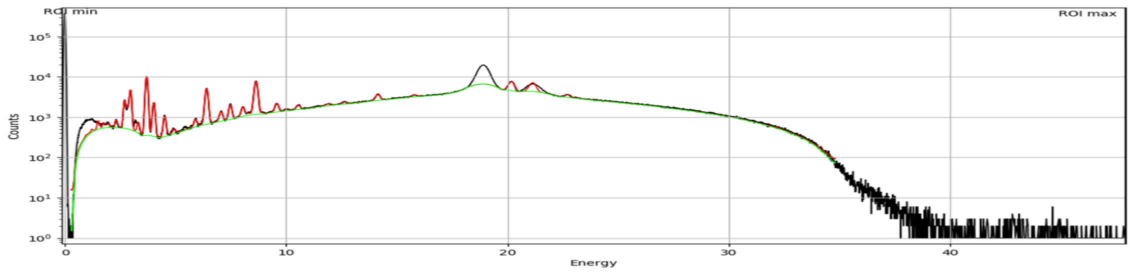
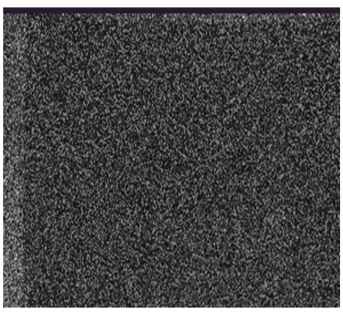
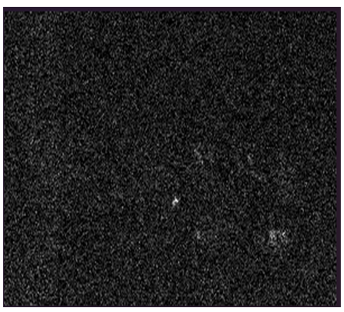
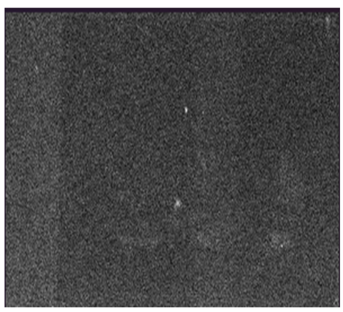




Figure 3 - MA-XRF analysis of the engraving *Olinda* (6CM): (a) Average X-ray fluorescence spectrum; (b) Calcium (Ca) distribution; (c) Lead (Pb) distribution; (d) Count spectrum.

(a)



(b) (c) (d)

The Figure 3 shows that the detected elements include Zn, Fe, Ca, Ti, Hg, and Pb, with calcium, iron, and zinc showing the highest count rates. These elements are consistently distributed across the entire print, similarly to what was observed in watercolor Itinerant Barbers (3CM).

Comparing the average spectra in Figure 2(a) and Figure 3(a), it becomes clear that the latter has lower overall count rates. As a result, the elemental distribution maps in Figures 3(b) and 3(c), corresponding to the Olinda watercolors, are of lower quality, making it difficult to observe any meaningful information. This same behavior was observed in samples Acclamation of Dom Pedro I, Emperor of Brazil and Village of Caboclos, 7CM and 8CM, respectively, both of which have disputed authorship.

The limitations encountered in the mapping were anticipated, as a simple visual inspection of Olinda, and the other questioned works clearly shows that pigment deposition on the substrate is significantly lower than that of the other paintings, such as Figures 1(a), 1(c) and 1(e). As reported by Haddad et al. (2023) and Kogou et al. (2015), the inherent fragility of watercolors on paper and the low pigment concentration are factors that hinder the study of this type of artwork.

Due to the low count rates observed in the elemental mapping, spot measurements were conducted using the Bruker equipment. Although the spectra exhibited significant interference from the organic matrix (Kogou et al., 2015), the results revealed that zinc appeared with higher intensity in the white areas, suggesting the use of zinc white (ZnO). This finding contrasts with the non-disputed prints, where white regions predominantly showed the presence of lead, indicative of white lead (Pb-based pigments).

Additionally, a slight increase in the intensity of the Kα peak of iron (Fe) was observed in the blue-colored areas compared to the rest of the watercolor. This may indicate that, in addition to being present in the paper substrate, iron may also contribute to the composition of the blue pigment in these regions, particularly where higher count rates were recorded.

FTIR Analysis and Multivariate comparison of binders in watercolor paintings

In watercolor paintings, one of the most commonly used binders is gum arabic, a mixture of polysaccharides and oligosaccharides that are partially or fully water-soluble and may exhibit cyclic or acyclic structures with alcoholic hydroxyl and acetal/hemiacetal groups. In FTIR spectra, these structures correspond to bands in specific regions.

The distinctive shape of the C–H bond stretching bands is particularly characteristic and can therefore be used to differentiate between binders. This is one of the advantages of applying FTIR using the pseudo-absorbance mode (Rosi et al., 2016).

To assess the degree of similarity between the attributed and authentic prints, FTIR spectra were collected from regions with different color tones in the watercolors.

Figure 4 shows the analyzed points: 18 in the 1CM print, 12 in the 3CM, 14 in the 4CM, 16 in the 6CM, 14 in the 7CM, and 13 in the 8CM, see Table 1 for the identification of the watercolors. FTIR data from both authentic and unknown-authorship prints were compared to identify similarities and differences. These comparisons were performed using Principal Component Analysis (PCA) and Robust Principal Component Analysis (RPCA), multivariate statistical methods that allow for comparison between analytical datasets through graphical representations (Felix et al., 2018; Freitas et al., 2010; Jolliffe, 1986; Thaumaturgo et al., 2024).

The FTIR spectra corresponding to the paper support showed no significant difference, indicating a minimization of differences due to chemical treatment for whitening or that all the prints were made on similar papers.

Figure 5 shows the FTIR analysis results of the paper support, indicating a high degree of similarity between the prints considered suspect (7CM, and 6CM) and those regarded as authentic (3CM and 4CM). This result was not unexpected, given that, according to Bortoli (2014), who sold several works attributed to Debret to Brazilian collectors, including Prince Dom João de Orleans e Bragança, great-grandson of Dom Pedro II, hired European specialists known for artificially aging fabrics and papers commonly used in reproductions. Additionally, the English manufacturer Whatman began producing a specialized line of papers for watercolor use as early as 1780. As such, both Debret and any other artist based in Europe at the time could have had access to this type of paper.

Figure 4 - Description of the images showing the points analyzed by FTIR in the watercolor prints. Prints considered authentic: (a) 3CM, (c) 1CM, and (e) 4CM; and prints considered suspicious: (b) 8CM, (d) 6CM, and (f) 7CM.

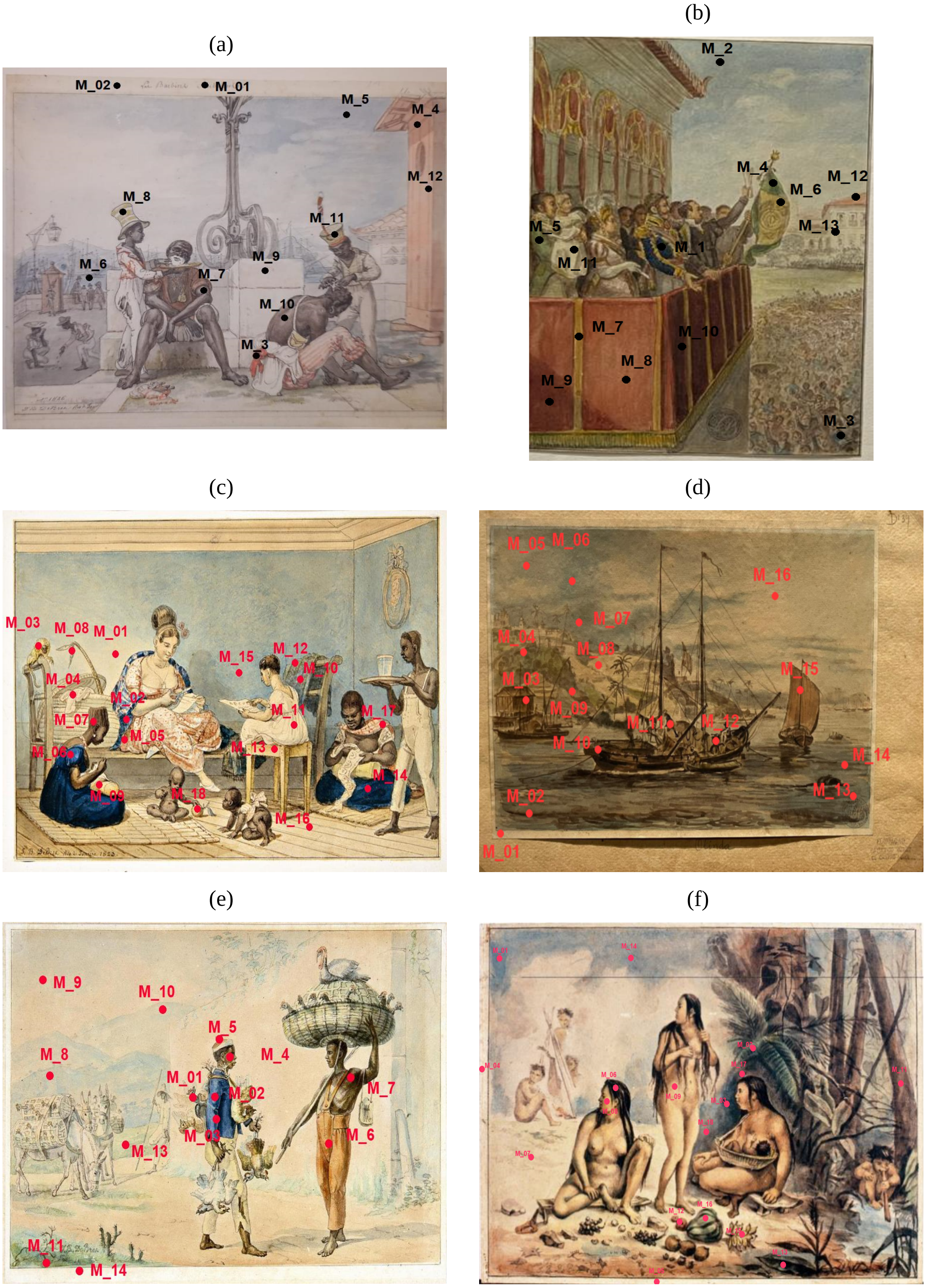
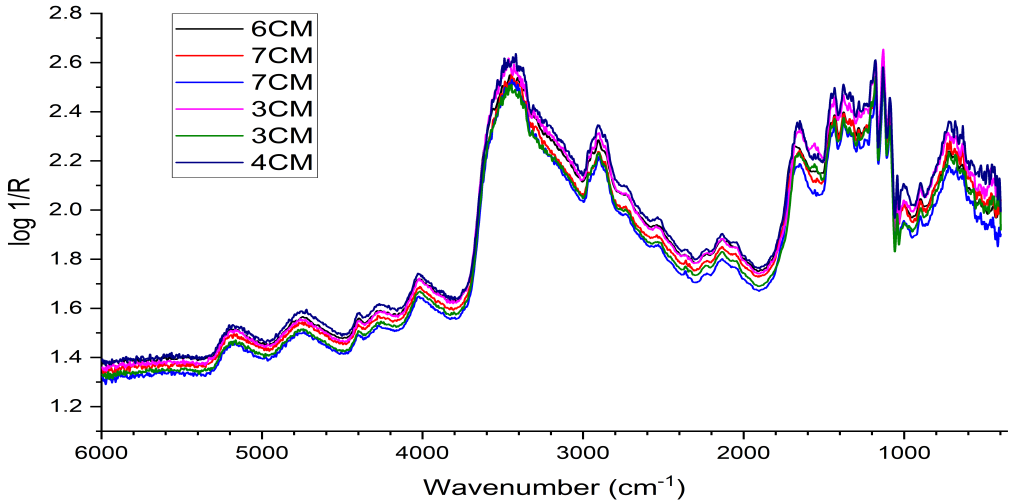


Figure 5 - Image of FTIR spectra obtained in the analysis of the support of paintings 6CM, 7CM, 3CM and 4CM.

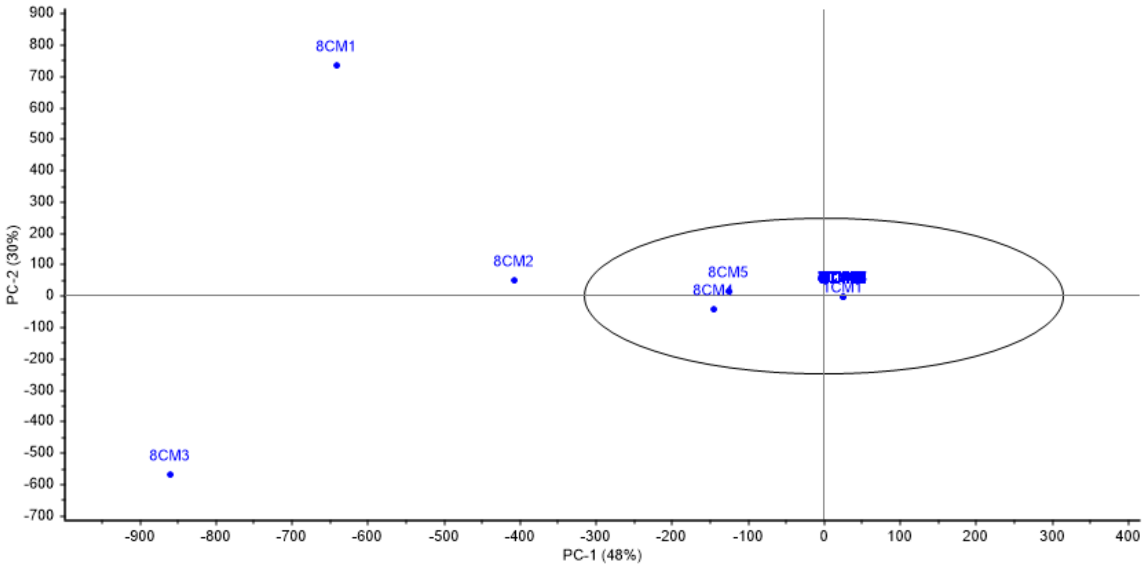


The FTIR spectra in Figure 5 exhibits characteristic features of cellulose-based paper. A broad band around $3420\,\mathrm{cm}^{-1}$ corresponds to the O–H stretching vibration. Bands related to C–H stretching vibrations in the cellulose backbone are observed at $2943\,\mathrm{cm}^{-1}$, $2904\,\mathrm{cm}^{-1}$, and $2866\,\mathrm{cm}^{-1}$. Around $1670\,\mathrm{cm}^{-1}$, a C=O stretching band is present, which is commonly associated with the hydrolysis and oxidation (i.e., aging) of the 1–4 glycosidic bonds in cellulose. A weak band at approximately $1230\,\mathrm{cm}^{-1}$ corresponds to the C–O stretching vibration of acetyl groups, while the C–O–C stretching vibration from the glucopyranose rings appears at $1029\,\mathrm{cm}^{-1}$ (Gorassini et al., 2016; Zhbankov et al., 2002).

FTIR Analysis and Multivariate comparison of colors in watercolor paintingss

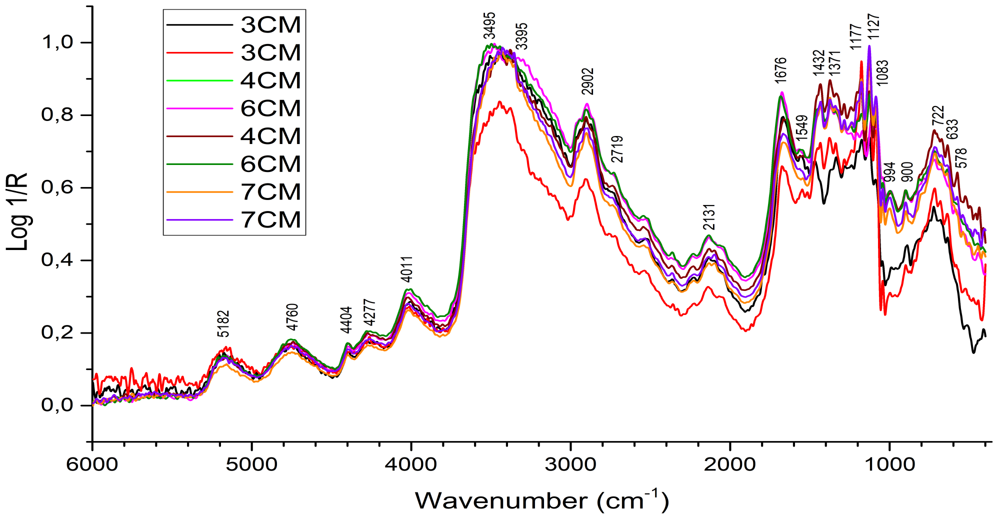
Figure 6 presents the PCA scores of the FTIR spectra using pseudo-absorbance. It shows that the PC-1 and PC-2 values accounted for 78% of the total variance. The analysis reveals that the points corresponding to print 8CM (The Acclamation of D. Pedro I at Campo de Sant'Anna) form a distinct group, clearly separated from all other evaluated points, along with three outliers. This separation suggests a very low spectral similarity with the other paintings, including prints 6CM and 7CM, which are also considered suspect.

Figure 6 - PCA scores of the FTIR spectra of green regions analyzed in the prints.



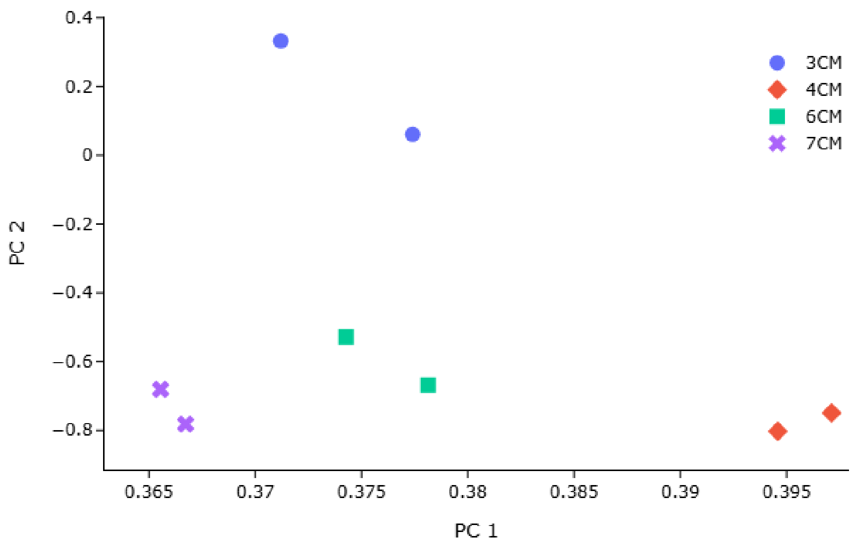
The comparison between the FTIR spectra corresponding to the brown-colored regions in samples 3CM, 4CM, 6CM, and 7CM is presented in Figure 7. This is evidenced by the shape of the bands corresponding to C–H bonds located between 2780 and 3001 cm^{-1}, which exhibit a pattern consistent with (Rosi et al., 2016) that found in watercolor paint standards prepared by the LISCOMP team. Additionally, the carbonyl stretching observed at 1676 cm^{-1}, which is commonly associated with saccharides, further supports this finding.

Figure 7 - FTIR spectra of brown-colored regions present in samples.



The graph in Figure 8 displays various points, each representing an FTIR spectrum collected from the brown-toned regions of the watercolors. In the graph, points that are closely clustered indicate data similarity, while points that are more distant reflect differences. It can be observed that the FTIR data from Olinda (6CM) and Village of Caboclos in Cantagalo (7CM) are closely grouped together but are distinctly separated from those of the authentic watercolors, such as Black Bird Sellers (4CM) and Itinerant Barbers (3CM).

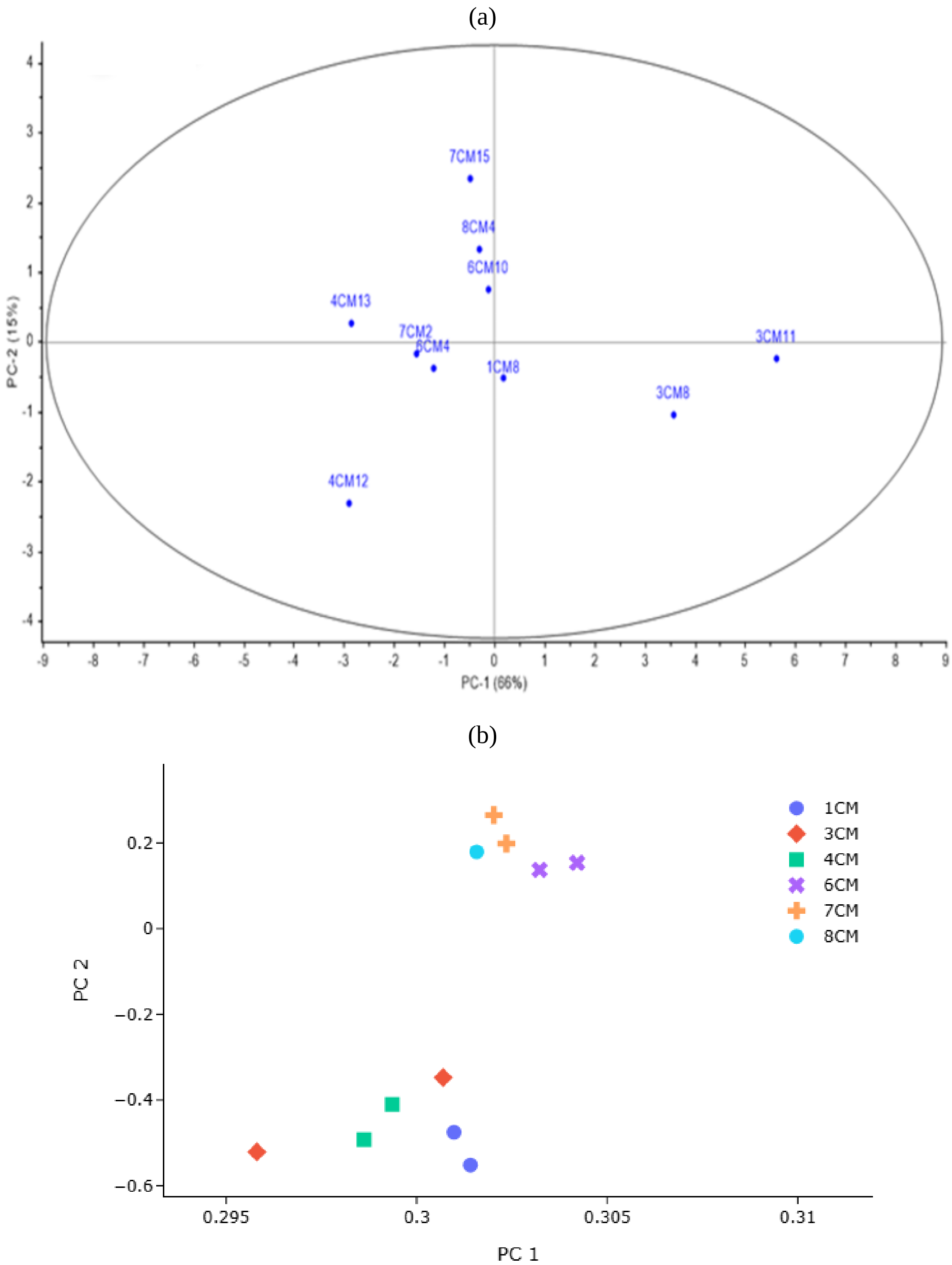
Figure 8 - RPCA plot comparing FTIR data collected from “brown” regions.



The distribution shown in Figure 9(a) and 9(b) represents data points associated with FTIR spectra from the green-toned regions of the watercolors. Again, proximity between points denotes similarity, while distance indicates dissimilarity. In Figure 9(b), we can clearly observe an organization of the questioned watercolors (6CM, 7CM, and 8CM) and the watercolors considered authentic (1CM, 3CM, and 4CM).

The result may be directly related to the methodology used for obtaining the green color. According to Almada (2018), green coloration was commonly achieved by mixing Prussian blue pigment with a white pigment.

Figure 9 - FTIR data from green regions compared using multivariate analysis: (a) PCA plot; (b) RPCA plot.



The graphs presented in Figures 10 and 11 display the RPCA distribution and the average FTIR spectra of the blue-toned regions.

In Figure 10, the point corresponding to the outlier, 1CM1, refers to the area between the seated woman on the bench and the lid of the basket, as shown in Figure 4.

In Figure 11, three distinct sample groups and one outlier are identified. The blue regions present in the watercolors 8CM, 7CM, and 6CM formed a very homogeneous group, along with point 3CM5, where the blue region is not as intense (see Figure 4). Except for these points, it is observed that the RPCA was sufficiently effective in assessing the degree of similarity between the suspect prints and those considered authentic.

Figure 10 - RPCA plot comparing FTIR data collected from "blue" regions.

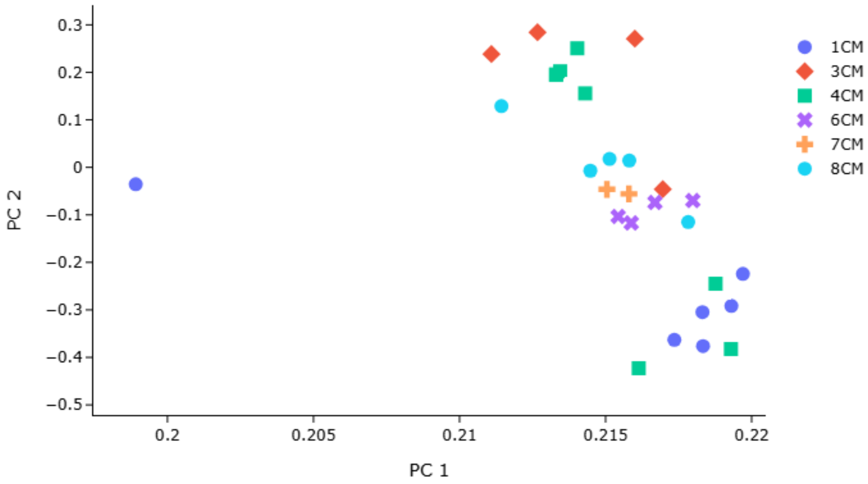
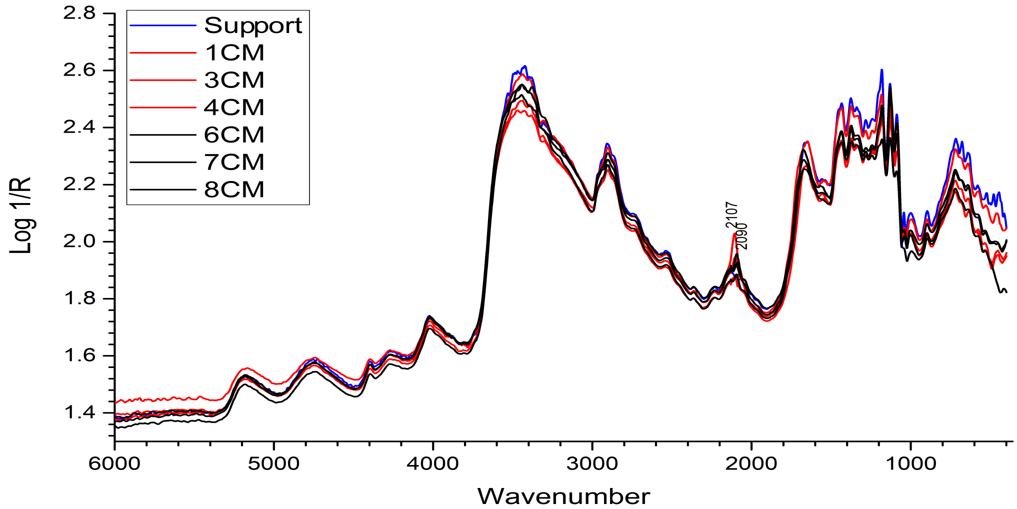


Figure 11 - Average FTIR spectra of the blue-colored regions present in the samples.



When analyzing the average FTIR spectra of the blue regions in Figure 11, we note that both spectra, when compared to the spectrum of the cellulose matrix, present a medium- to low-intensity band between 2200 and 2000 cm^{-1}. In the prints considered original, the band appears at 2107 cm^{-1} with medium intensity, while in the suspect prints, the band occurs at 2090 cm^{-1}. Considering that both bands fall within the region corresponding to the stretching of the C–N bond, we can suggest that the artists used Prussian blue pigment. However, the shift of approximately 17 cm^{-1} in all spectra of the 6CM, 7CM, and 8CM groups suggests that the Prussian blue used in these prints presented some differences in its composition.

Conclusions

The physico-chemical study of these watercolors was particularly complex due to several factors: the fluidity of the applied paint, the low concentration of deposited pigments, overlapping pigment layers, interference from the paper substrate, the fragility of the support, and the absence of standardized analytical references. Despite the challenges, the results supported the findings of the technical report issued by IBRAM, which raised doubts regarding the authenticity of some of the watercolors in the museum's collection.

The PCA and RPCA analysis results indicate that the watercolors of unknown authorship, The Acclamation of D. Pedro I at Campo de Sant'Anna, Olinda, and Aldeia de Caboclos no Cantagalo, differ significantly from the authentic works. In most tests, the FTIR data collected from these attributed prints were clearly distant from those obtained from verified originals. The only notable similarity was found in FTIR data from blue-toned regions. In this case, the identified pigment was Prussian blue ($Fe_4[Fe(CN)_6]_3 \cdot xH_2O$), which appeared in both authentic and attributed prints. This finding is historically consistent, as Prussian blue began to be widely used in watercolors starting in the 18th century. However, the presence of a common pigment alone is not sufficient to establish authorship.

The spectral profile formed by the axial stretching of C, H bonds and the appearance of carbonyl absorption bands further supports the use of gum arabic as the binder, confirming that the prints were executed using the watercolor technique on paper.

The results consistently demonstrate chemical differences in composition, particularly in binder and pigment distribution, between the authentic and the attributed works. Moreover, the strong similarities between Olinda and Aldeia de Caboclos no Cantagalo suggest that these two paintings may have originated from the same production context.

This research underscores the importance of integrating scientific and historical approaches for the authentication and preservation of cultural heritage. The use of non-invasive techniques such as MA-XRF and FTIR, combined with statistical tools like PCA and RPCA, has proven highly effective in supporting museum studies and preventing the misattribution of artworks.

It is important to extend these analyses to other prints from the Castro Maya Museum collection and from other institutions under IBRAM's management, with the aim of refining and validating the proposed methodology. Additionally, incorporating hyperspectral imaging and infrared reflectography will contribute to the generation of more robust and accurate results.

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Author contributions

V. S. Felix participated in: conceptualization, formal analysis, investigation, methodology, resources, programs, validation, writing. **A. R. Pimenta** participated in: conceptualization, projects managements, investigation, methodology, resources, validation, visualization, writing. **Y. R. R. Felix** participated in: conceptualization, methodology, resources, validation, writing. **R. A. Mesquita** participated in: programs, validation, writing. **R. P. Freitas** participated in: conceptualization, formal analysis, investigation, methodology, resources, programs, validation, writing, projects managements, supervision.

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Conflicts of Interest

The authors certify that no commercial or associative interest in the manuscript represents a conflict of interest.

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