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Non-invasive characterization of the painting Saint John the Evangelist by means spectroscopic methods

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ABSTRACT

In this work, the pigments and ground layers of the Saint John the Evangelist painting were analyzed using the techniques of computed radiography, X-ray fluorescence (XRF), and micro-Raman spectroscopy. The painting was purchased by a collector at auction as a 19th-century work of art of unknown authorship. XRF analyzes were performed with a voltage of 40 kV, current of 50 µA, and acquisition time of 60 s. Micro-Raman spectroscopy measurements of a black fragment sample were performed with the Thermo Scientific – DXR2 Raman microscope equipment. The sample was excited by the adjusted 785 nm laser source with a power of 4 mW, focused on the sample using a 100x objective. It was possible to characterize the pigments used in the painting of São João Evangelista as Lead White, Vermilion, Carbon Black, and Ocher. No areas of repainting and modern pigments were identified that could suggest any type of intervention.

Keywords: **Archaeometry. 19th century. Pigments. Raman Spectroscopy. XRF. Computed Radiography.**

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1. INTRODUCTION

In the last decades, many scientific techniques have been employed in studies of cultural heritage. Identifying the material content of an art or archeology object provides insight into the painterly process used for creating the painting, helps to distinguish the original compounds from restored or retouched ones, and its state of preservation. It also assists in conservation processes, since depending on their nature, pigments may be sensitive to light, humidity, atmospheric pollutant, or heat, which may require specific storage or display conditions [1].

In particular, pigment characterization can be important for many reasons. Pigment analysis can assist in conservation and restoration processes, it can provide information about the artist's working methods, that is, which pigments the artist used or how the pigments were mixed to obtain a certain hue. Finally, it can also help in confirming a probable date to the painting, reconstructing its past material history, and in detecting forgeries [2].

Many works of art and historical artifacts have a great historical/cultural value, therefore, whenever possible, non-destructive analytical techniques should be used. The use of only one technique may not always be enough to characterize a historical artifact, usually due to its manufacturing process, and to assess its conservation state. Therefore, different techniques and methods have been developed and successfully used for the scientific investigation of cultural heritage, such as X-ray fluorescence (XRF) [4], Raman spectroscopy [4], Radiography [5], and Fourier transform infrared (FTIR) [6].

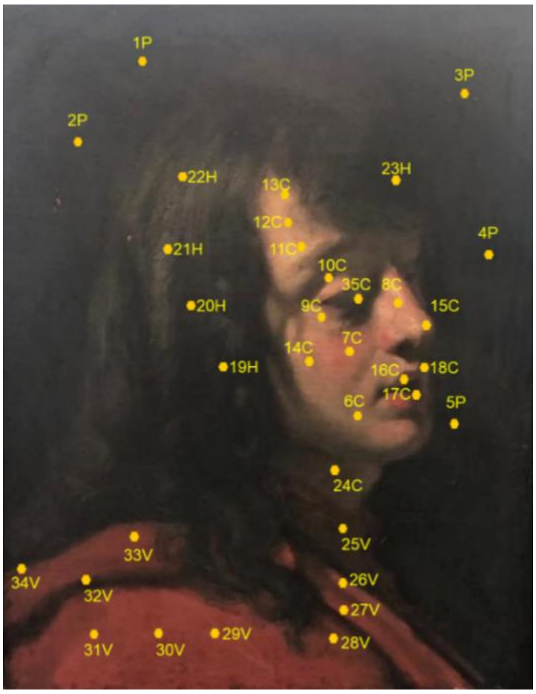
In this work, the pigments and the ground layers of a Saint John the Evangelist painting were characterized by computed radiography, X-ray fluorescence (XRF), and micro-Raman spectroscopy techniques to assist in dating the painting. The painting was purchased by a collector at an auction as a 19th-century artwork of unknown authorship. However, the restoration team responsible for the work suspected that, due to the original canvas and preparation layer, the work could be from the 17th century, being a study or copy, attributed to the Flemish master Pieter Van Mol.

2. MATERIALS AND METHODS

The computed radiography analyses were performed using a 35 µm focal spot size X-Ray tube (Apogee 5500 - Oxford Instruments) operating at a voltage of 23 kV and a current of 1 mA. The source to detector distance was 1000 mm and the exposure time was of 30 seconds per image. It was used a CR scanner (CR50P - GEIT) and a 350 mm x 430 mm imaging plate (IPS - GEIT) for acquiring the images with a 100 µm pixel size. Four exposures were necessary to completely image the whole painting.

The X-ray Fluorescence spectra were obtained using the portable Energy Dispersive X-ray Fluorescence (ED-XRF) equipment developed in our laboratory. The portable ED-XRF system used has a low-power X-ray tube (Amptek) with a silver anode [Ag] and a silicon drift detector (Amptek) with an energy resolution of 122 eV @5.9 keV. Figure 1 shows the St. John the Evangelist painting and the analyzed points, which were distributed as 5 points on the background, 5 points on the hair, 1 point on the eye, 14 points on the carnation, 10 points on the tunic, and 1 measurement was performed on the back of the canvas.

Figure 1: *Points analyzed by XRF in the painting of Saint John the Evangelist.*
Source: The authors



The XRF analyses were carried out at 40 kV, a current of 50 µA, and 60 s of acquisition time.

A fragment sample of the background's black pigment was collected and analyzed by micro-Raman spectroscopy. Micro-Raman spectroscopy measurements were performed using Thermo Scientific – DXR2 Raman microscope equipment. The sample was excited by the 785 nm adjusted laser source with a power of 4 mW, focused on the sample using 100x objective. The spectra were collected in the 100-2000 cm^{-1} range, with an acquisition time of 3 s and 10 accumulations were performed.

3. RESULTS AND DISCUSSION

The radiography image (Figure 2) showed the presence of a high-density preparation layer. The high radiopacity of the brighter areas suggests that the high-density material is overlying the carnation.

Figure 2: *Radiography image of Saint John the Evangelist.*
Source: The authors

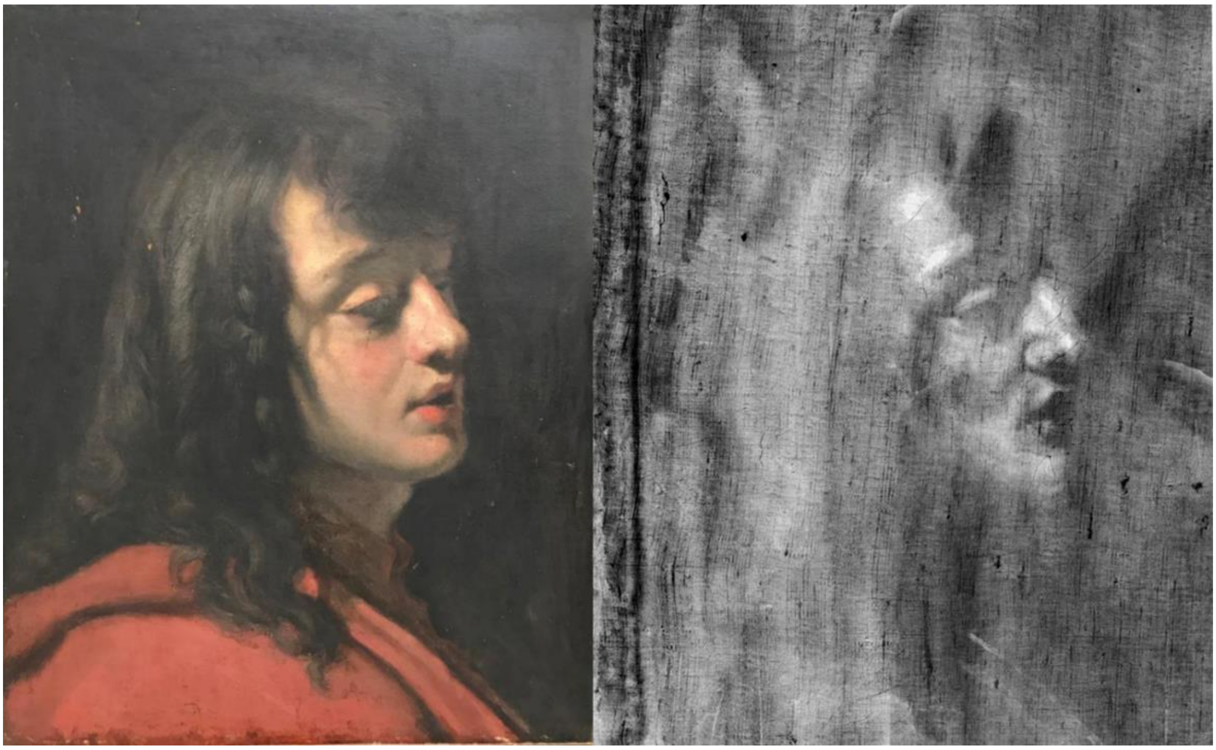
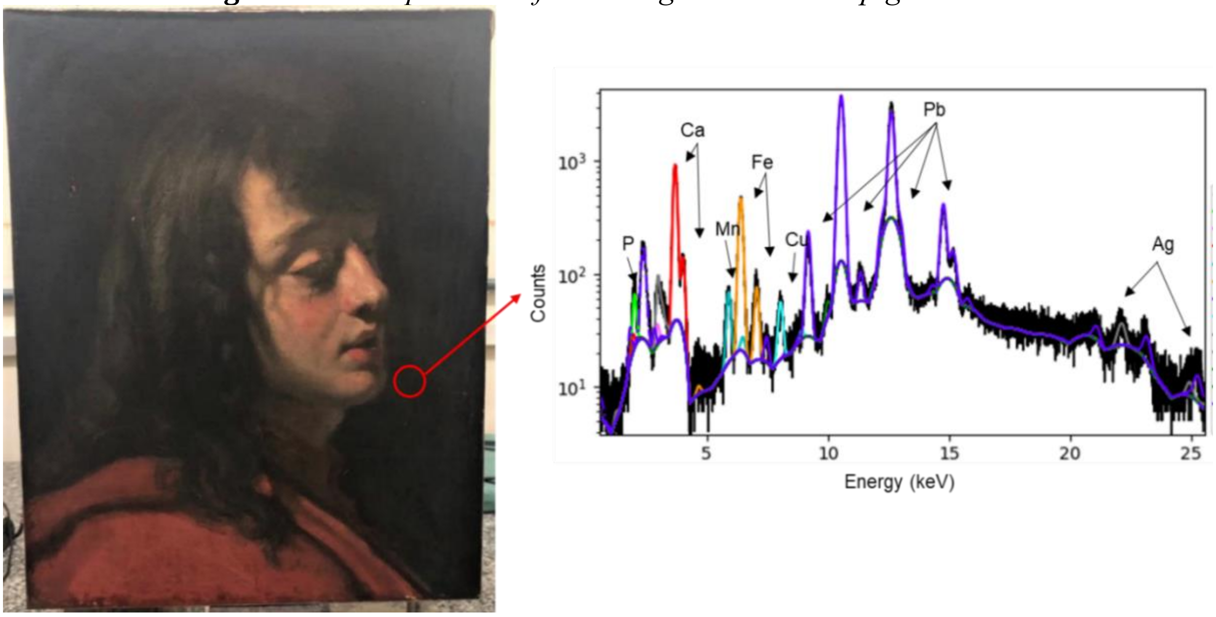


Figure 3 shows the XRF analysis of the black pigment present in the background and the eye. The elements phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), and lead (Pb) were detected.

Figure 3: *XRF spectrum of the background's black pigment.*



The Pb element was identified in all analyzed points, suggesting that this work was painted over a preparation layer made of Lead White [$PbSO_4.PbO$]. The variation of Pb-M lines in all spectra and the radiography image support this hypothesis. Table 1 shows the Pb counts and the L-M lines ratio of the Pb obtained by XRF analyses.

Table 1: M and L lines ratio (M/L) of the Pb element presents in the black pigment.

	Points	Pb_L	Pb_M	Pb (M/L)
Dark hues	19	445066 ± 754	9237 ± 118	0.02
	23	442043 ± 748	7138 ± 108	0.02
Lighting hues	20	488524 ± 784	13237 ± 138	0.03
	21	520407 ± 809	22977 ± 174	0.04
	22	522092 ± 811	26553 ± 188	0.05

It is possible to notice that in the shadow areas of the black pigment the M-line count is lower than the Pb-M count in the brighter areas, indicating that in this region the white lead pigment is present in a layer under the surface. [7].

The Lead White pigment was used from antiquity to the 19th century, after which it was replaced by less toxic pigments such as Titanium White and Zinc White [8-11].

The presence of the elements P and Ca found in the analysis of the black pigment suggests that this pigment may be the Carbon Black/Bone black [$Ca_5(OH)(PO_4)_3$], which is a pigment used since pre-history, and is obtained by the carbonization of animal bones, containing about 10 to 20% of carbon. The remainder of the material consists of hydroxyapatite [$Ca_5(OH)(PO_4)_3$] and calcium sulfate [8]. In the Raman spectroscopy analysis of the black pigment (Figure 4), the wavenumber bands detected were 1582 and 1320 cm^{-1}. These bands correspond to the Carbon Black pigment, corroborating XRF results [12].

Figure 4: *Raman shift of the black pigment.*

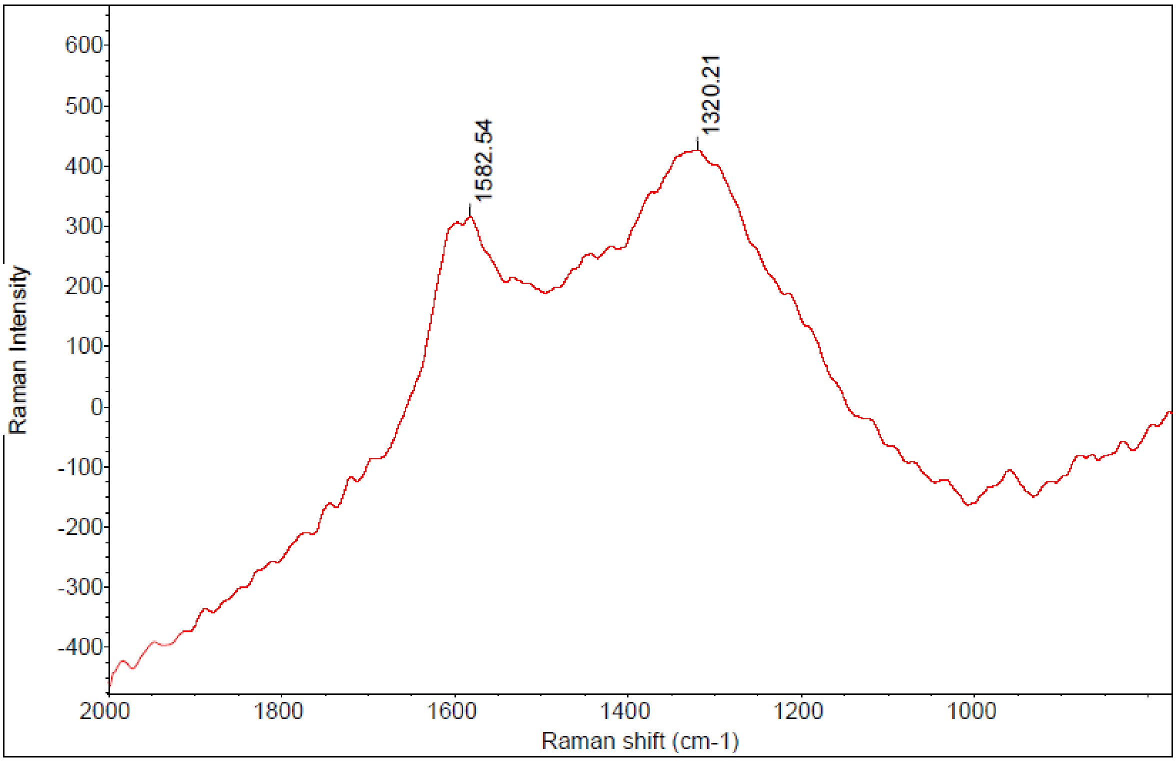
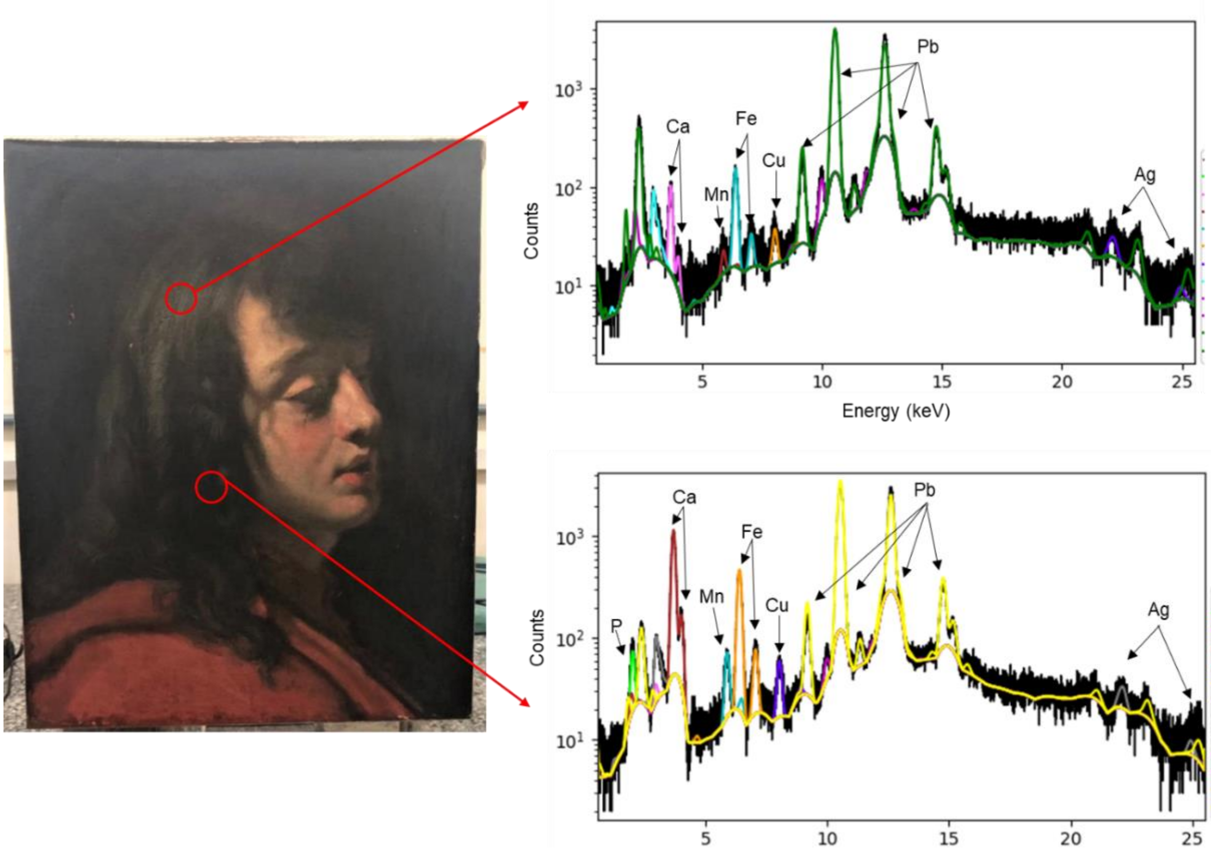


Figure 5 shows the XRF analysis performed on the St. John the Evangelist's hair. It is possible to notice shadow areas and brighter areas. The elements detected in the black pigment used in the hair were phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), and lead (Pb).

In the brighter areas of the hair, it was not possible to detect the P element. Furthermore, both the Pb intensities and the ratios between the Pb-M and Pb-L lines increased, suggesting that a layer of Lead White was applied over the black pigment to produce this light effect.

Figure 5: *XRF spectrum of the hair's black pigment.*



In the XRF analysis of the pigments used in the carnation (Figure 6), the elements calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), mercury (Hg), and lead (Pb) were detected. It can be highlighted the elements Fe, Hg, and Pb as key elements of the earth pigments, called Ocher [Fe2O3], Vermilion/Vermilion [HgS], and Lead White [PbSO4.PbO], respectively. The presence of Fe, Pb, and Hg suggests that the pink flesh tones on the face contain these pigments. The redder region, like the lips, contains the same pigments found in the carnation, however, with a greater contribution of the vermilion pigment, as inferred from the XRF spectrum.

Vermilion is a pigment of mineral and synthetic origin widely used from antiquity to the 18th century [11].

Figure 6: *XRF spectrum of the carnation pigment.*

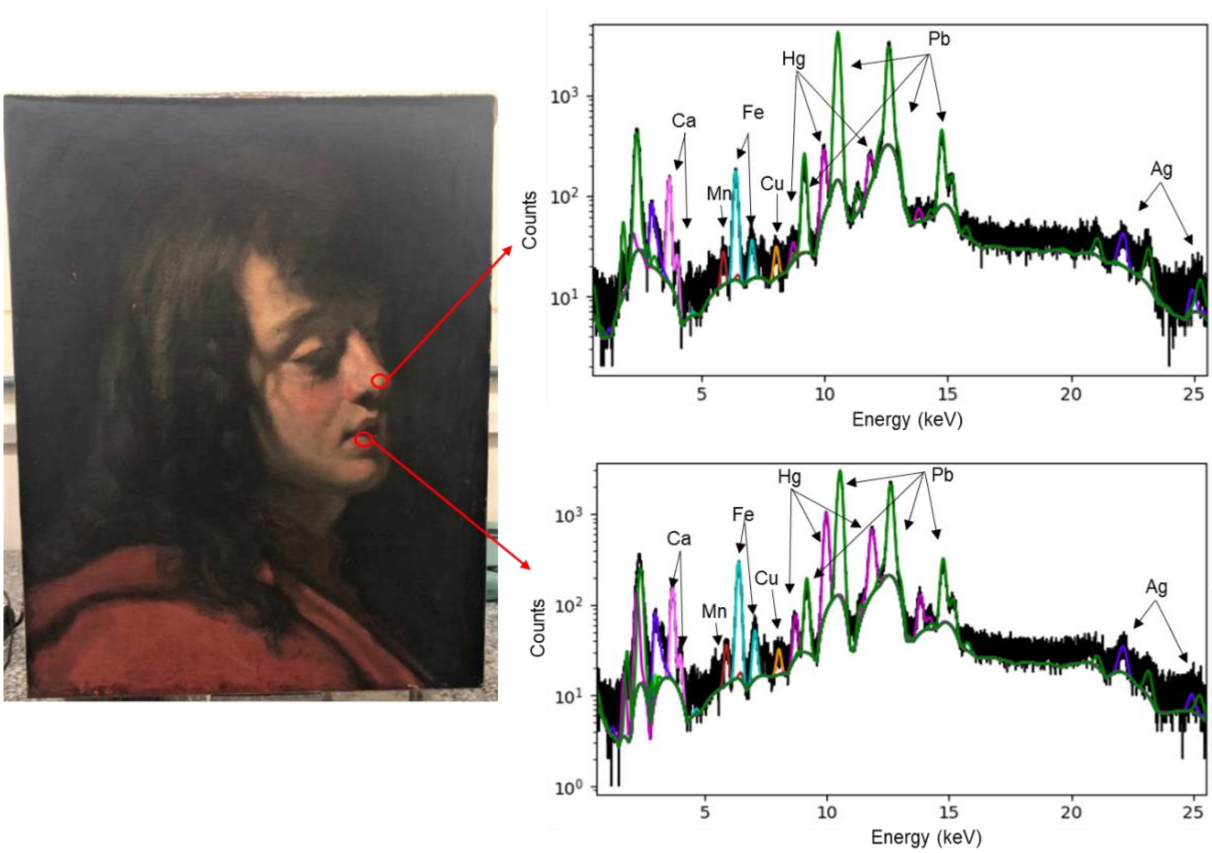
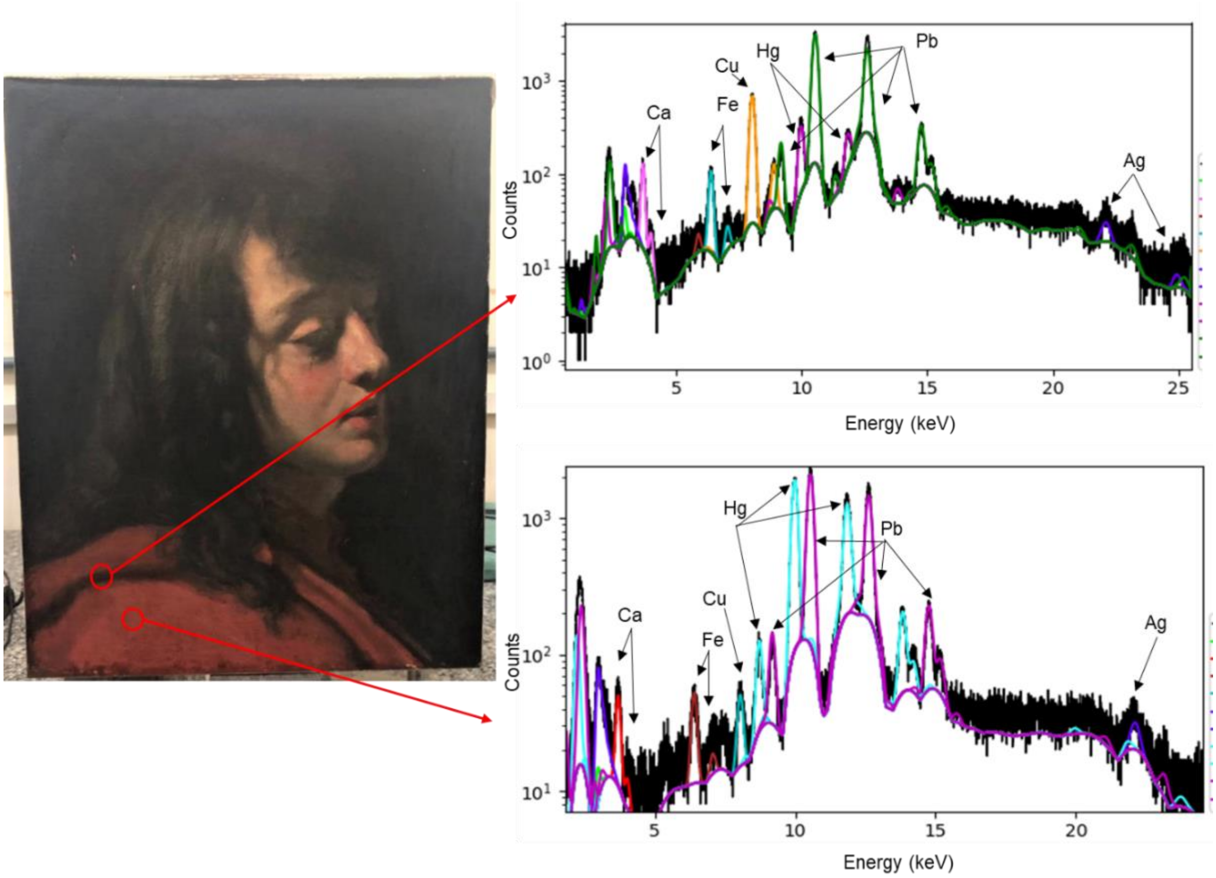


Figure 7 shows XRF analysis of the red pigment from the tunic of Saint John the Evangelist. In this region, the elements calcium (Ca), iron (Fe), copper (Cu), mercury (Hg), and lead (Pb) were detected. Pb and Hg indicate the presence of Lead White and Vermilion pigments. In the St. John the Evangelist's tunic there are two shades of red. A darker one and a lighter one.

In the XRF analysis was possible to notice that the Cu intensity was higher in the darker red hue. Cu can also be found in the black pigment Tenorite [CuO], which is a mineral origin pigment [11]. It is possible that the shadow areas of the tunic were painted with Tenorite.

Figure 7: *XRF spectrum of the red pigment.*



Through the XRF technique, it was to detect the elements S, Ca, Mn, and Pb, present on the back of the canvas (Figure 8). On the other hand, a great contribution of these elements was identified in the pigments of the painting. However, it is possible to conclude that these elements are not characteristic elements of the canvas material, but rather of the pigments. So, the presence of S and Ca elements may suggest the presence of gypsum ($CaSO_4$) as a thin layer of preparation on the canvas of the frame.

Figure 8: XRF spectrum of the canvas' back.

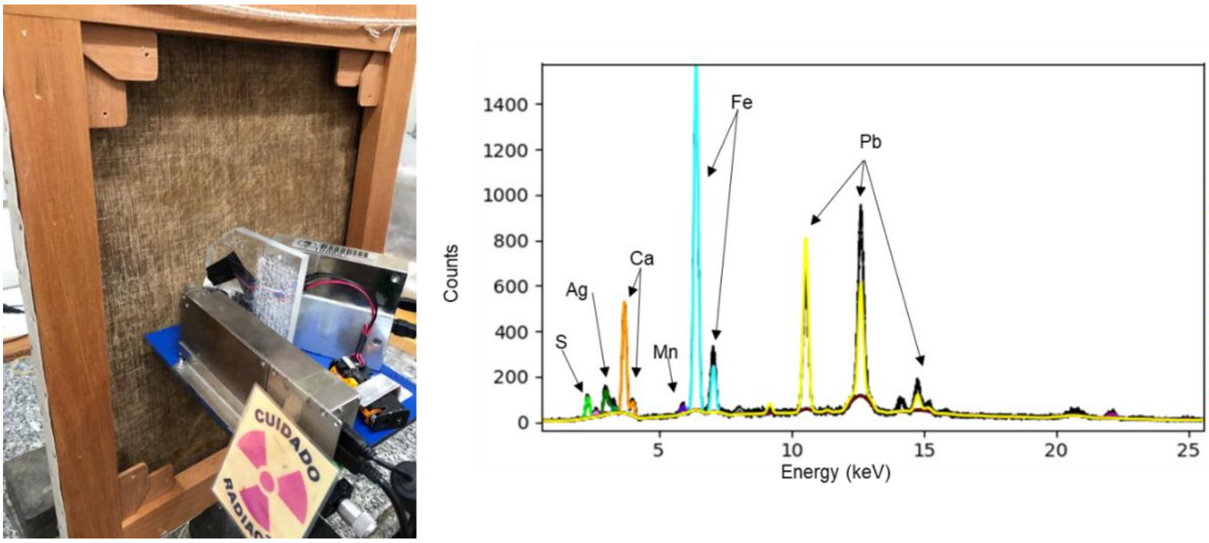


Table 2 presents all the elements found in the analyzed regions and the suggested pigments for these regions. The underlined elements are the characteristic elements of each pigment.

Table 2: Elements detected in the analyzed regions and the suggested pigments for these regions.

Analyzed region	**Elements**	**Suggested pigments**
Carnation	Ca, Mn, Fe, Cu, Hg, and Pb	Ocher [Fe_2O_3], Lead White [$PbSO_4.PbO$] and Vermilion [HgS]
Hair (black)	P, Ca, Mn, Fe, Cu, and Pb	Carbon Black [$Ca_5(OH)(PO_4)_3$] and Lead White [$PbSO_4.PbO$]
Background and Eyes (black)	P, Ca, Mn, Fe, Cu, and Pb	Carbon Black [$Ca_5(OH)(PO_4)_3$]
Tunic (red)	Ca, Fe, Cu, Hg, and Pb	Vermilion [HgS], and Lead White [$PbSO_4.PbO$]

4. CONCLUSION

This work carried out for the first time for the non-invasive characterization of the painting St. John the Evangelist, allows for defining some aspects of the preparation layer, pigments, and indirect dating. The radiographic analysis showed the presence of a preparation layer composed of a high-density material, which was also present in a thick layer on the carnation. These data associated with XRF analyses indicate it may be lead white. According to the results obtained in the XRF and Raman spectroscopy analyses, it was possible to characterize the pigments used in the Saint John the Evangelist painting as Lead White, Vermilion, Carbon Black, and Ocher. No repainting areas and modern pigments were identified that could suggest any kind of intervention. The presence of Lead White pigment in the preparation layers and the lighting of other pigments suggests that the work predates the 19th century. The Vermilion pigment, on the other hand, had been in use from antiquity to the 19th century, suggesting that this artwork had been made until the end of the 19th century.

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REFERENCES

[1] MOLARI, R. et al.. Non-destructive portable X-ray fluorescence analysis of the Portrait of a Young Man with a Golden Chain (c. 1635) by Rembrandt and/or atelier. **Applied Radiation and Isotopes**, v. 165, 2020.

[2] KLOCKENKÄMPER, R., VON BOHLEN, A. and MOENS, L. Analysis of Pigments and Inks on Oil Paintings and Historical Manuscripts Using Total Reflection X-Ray Fluorescence Spectrometry. **X-Ray Spectrom.**, v.29, p. 119–129, 2000.

[3] SANCHES, F.A.C.R.A. et al. Characterization of a sacred statuette replica of "Nossa Senhora da Conceição Aparecida" using X-ray spectrometry techniques. **Radiation physics and chemistry**, v.167, p.108266, 2020.

[4] FREITAS, R.P. Analysis of a Brazilian baroque sculpture using Raman spectroscopy and FT-IR. **Spectrochim. Acta - Part A Mol. Biomol. Spectrosc**, v. 154, p. 67-71, 2016.

[5] EVENO, M., RAVAUD, E., CALLIGARO, T. et al. The Louvre Crucifix by Giotto – Unveiling the original decoration by 2D-XRF, X-ray radiography, Emissiography and SEM-EDX analysis. **Heritage Science**, v. 2, p 2-9. 2014.

[6] BONIZZONI, L. et al. Use of integrated non-invasive analyses for pigment characterization and indirect dating of old restorations on one Egyptian coffin of the XXI dynasty. **Microchemical Journal**, v. 138, p. 122-131, 2018

[7] DELANEY, J.K. et al. Mapping the pigment distribution of Vermeer's Girl with a Pearl Earring. **Heritage Science**, v. 8, 2020.

[8] COLOURLEX website. Available at: <https://colourlex.com>. Last accessed: 21 Sept. 2021.

[9] HAYEZ, V. et al. Identification of pigments on a 16th-century Persian manuscript by micro-Raman spectroscopy. **J. Raman Spectrosc**. v. 35, p. 781–785, 2004.

[10] DOOLEY, A.K. et al. **Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting**. Angew. Chem. Int. Ed., v. 53, p. 1 – 6, 2014.

[11] SILVA, W.D. and APPOLONI, C.R. **Pigmentos: propriedades físicas, químicas e o período histórico de utilização.** Publicação Técnica PT - Laboratório de Física Nuclear Aplicada Depto. de Física – Universidade Estadual de Londrina, Londrina, 2009, v. 13.

[12] CASTRO, K. et al. Noninvasive and nondestructive NMR, Raman and XRF analysis of a Blaeu colored map from the seventeenth century. **Anal Bioanal Chem**, v. 391, p. 433–441, 2008.