Material and Imaging Analysis Procedure for the Investigation of Paintings in the Archbishop's Palace of Seville

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Abstract: The Archbishop's Palace of Seville harbours an important art collection with mostly works by great Renaissance and Baroque artists. However, the authorship of some paintings is unknown, and, in a few cases, there is an interest in discovering the painter due to the quality of the artwork. As a first step for this purpose, a systematic analysis procedure has been established using non- destructive techniques, such as UV photography and IR reflectography, to locate interventions and underpaintings, as well as X-ray fluorescence to identify original pigments and those of later interventions. The study following this established protocol is presented with the example of two paintings by unknown authors. They were made in different centuries representing, consequently, different styles. UV images showed several retouches, while IR reflectography revealed under- drawing and composition corrections (*pentimenti*). Furthermore, XRF identified the pigments applied in the production of the different colours and tonalities, allowing to characterise the artist's palette, whose pigments generally agree with the dates when the artworks were produced. This study resulted in valuable information on painting materials and techniques, which will be useful in the search for authorships, among others.

1. Introduction

The Archbishop's Palace of Seville has started a project dedicated to the conservation of its patrimony. It has an important art collection with many artworks by the great Renais- sance and Baroque authors. However, there are also many paintings whose authorship is unknown and, in a few cases, of high quality, which arouses an interest in discovering the painter. In this work, two paintings of different centuries and styles are studied.

The first painting represents *The Virgin and Child* (Figure 1). It is a panel painting that art historians date to the first quarter of the 16th century and attributed to the circle of Alejo Fernández [1,2]. After 1508, Alejo was called to Seville to paint for the Cathedral. He was a famous Spanish painter, educated in the Hispano-Flemish style, mixed with North Italian influence, who mostly worked between Seville and Cordoba. He marked an entire era of Sevillian painting of the transition to the full Renaissance and had many followers.

The attribution is supported in comparison with another painting of the city hall of Seville known as *Tríptico del Maestro de la mendicidad* (1520), which is speculated to be made by an outstanding disciple of Alejo Fernández [3]. Both paintings show great similarity in the volume of the clothes, the modelling of the Virgin's face, and the colours, among others.

Figure 1. Anonymous: *The Virgin and Child*, 16th century.

The second painting, shown in Figure 2, is titled *Joseph sold to the Medianite merchants* [1,2]. It is a Flemish style canvas painting characteristic of the 17th century. The conservation state was very deficient, with a darkening of the superficial layers. The analysis was carried out after the first step of the restoration process which consisted of removing the layer of varnish and retouches. The experts of the Archbishop's Palace attribute this painting to Pieter Van Lint [4], a Flemish Baroque painter of the 17th century. He was well known for his history paintings, genre scenes, and portraits, although, mostly in his later works, he presented mostly religious iconography. For several years, he worked for the pope in Rome, where he studied Italian contemporary and antique roman artworks, which had an important impact on his later works. There are four paintings in the Archbishop's Palace that are attributed to him.

Figure 2. Anonymous: *Joseph sold to the Medianite merchants*, 17th century. The dots indicate where the samples were taken for SEM-EDX analysis.

The painting represents three different scenes from the life of Joseph. The first, located on the left side of the canvas, shows Joseph being thrown into the well by his brothers. In the second and principal one, represented in the foreground, Joseph is interpreting his dreams with one hand pointing to the sky and the other to the earth in front of his brothers who do not recognise him. The last scene on the right-hand side shows Joseph asleep. This one was discovered only after the cleaning process. Furthermore, the sky gets dark on the right side of the painting, which contrasts with the clear blue sky on the left. Therefore, the restorers of the Archbishop's Palace are doubtful if the dark sky was painted by the author, or it was later darkened.

The attribution is a very complicated process which requires information from an art historical point of view, detailed material analysis, and comparison with other related paintings by the alleged painter. The aim of this work is to show the systematic analytical procedure established in the palace for the material study and conservation of the paintings as a first step in the search for attribution. Different techniques were used to locate interventions, discover preparation drawings, and identify original and later pigments applied. All this information provides support in the restoration process and allows the obtention of valuable inferences about the applied materials (supports and pigments), which will be useful in comparing them, in the future, with other related works when available for analysis.

2. Materials and Methods

The equipment developed at "Centro Nacional de Aceleradores" in Seville is portable, so the analysis could be performed in situ in the restoration workshop of the palace. The study procedure consists of three non-destructive techniques applied in the following order. First, paintings are observed under ultraviolet (UV) light [5–9]. This technique locates later interventions based on the different fluorescences that new and aged materials produce after exposure to UV light, so XRF material analysis can focus on the original pigments and compare them with those likely used in conservation/restoration interventions. The UV images were taken with a Nikon D3X camera at 400 ISO and 20 s of exposure time after homogeneously lighting the painting with four Wood lamps.

Next, infrared reflectography (IRR) was applied [7–12]. Infrared radiation can penetrate and interact with deeper layers of the painting and reveal a preparatory drawing or possible changes in the composition (*pentimenti*). The camera used for the IRR was a Xenics Xeva-XS 512 with an InGaAs detector, while two halogen SDI-800 W light reflectors illuminated the artwork. For precise scanning of the painting surface, the camera was mounted on a XY robotic platform by Optimind at 32 cm from the painting.

Finally, material analysis was performed with X-ray fluorescence (XRF) [8,13–16]. This analytical technique identifies pigments based on their specific chemical elements with atomic numbers above 14, so organic material cannot be detected. Another limitation of this technique is the inability to distinguish pigments identified with the same chemical element. Nevertheless, it is possible to obtain a preliminary analysis of the pigments used by the artist and how these pigments are mixed to produce different colours and tonalities, as well as to identify the presence of preparatory and priming layers. The XRF equipment consisted of a 35 kV X-ray generator RX38 from EIS S.L. with a W anode and a 1 mm Al filter coupled to the X-ray tube exit to suppress the W characteristic peaks, and a silicon drift detector (SDD) with an energy resolution of 140 eV at Mn-Kα line. The measuring distance was always fixed by the intersection of two lasers coupled to the tube. Furthermore, for direct comparison of the results at different analysed points, the generator always operated under the same conditions: 33.4 kV and 80 μA for an acquisition time of 200 s. The presence of each element could be estimated by the XRF peaks areas in counts per second (cps). This information gave us the relative quantity of one element in the analysed point. Therefore, a comparison of the cps of one element in different areas may suggest a higher or lower presence of a certain pigment. Nevertheless, the density/weight of the elements must also be taken into consideration. The areas were measured with the PyMca programme in order to perform a semi-quantitative analysis. These data were used to perform a PCA analysis, which allowed us to observe which chemical elements were more correlated for each analysed point. In this way, we could relate different areas of the painting, but if there was a great variety of tonalities, these relationships became less evident.

To overcome the limitations of XRF, we were allowed to take a total of 12 samples of different areas of the Flemish painting marked in Figure 2, while from the Spanish one this procedure was not possible. The samples were studied in the laboratory of the Instituto Andaluz del Patrimonio Histórico de Sevilla (IAPH). They were prepared as stratigraphic sections and coated with a thin gold layer for improved imaging by avoiding charging of the sample during SEM-EDX analyses. They were studied by optical microscopy (OM) using a LeicaDM4000M optical microscope, and by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), whose equipment for the SEM imaging was developed by JEOL 5600 LV and for the EDX analysis by Oxford, Inca X-sight. These techniques allowed us to study the sequence and thickness of the colour layers, their composition, and the granulometry of the pigment [16–18].

3. UV and IRR Examination

For both paintings in this study, UV images were taken. The painting *Joseph sold to the Medianite merchants* did not offer any information on retouches because, as mentioned previously, the analysis was possible only after the cleaning conservation process. On the other hand, *The Virgin and Child* revealed several interventions observed as dark areas on the surface (Figure 3). The largest intervention vertically crosses the centre of the painting due to a fracture in the panel produced by the natural dilation process of the wood. The other important areas were mainly located on the head of the Child and the halo and tunic of the Virgin.

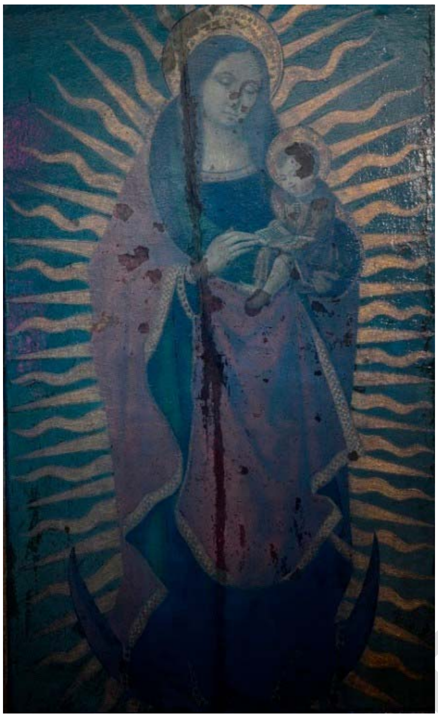

Figure 3. UV image of the painting *The Virgin and Child*.

The IRR image of *The Virgin and Child* reveals a complete preparatory drawing by the painter. It was carried out with a material with great absorption of IR radiation, probably carbon black. Figure 4 shows some interesting areas of the IRR image in which we can observe the artist's brushstrokes to trace the Virgin's hair and drapery shades. Additionally, Virgin's right hand presents a slightly different modelling in the final execution, revealing the artist's *pentimenti*.

Figure 4. IRR images of some areas of the painting of *The Virgin and Child*.

In the IRR image of *Joseph sold to the Medianite merchants*, no preparatory drawing could be detected. However, an interesting discovery was observed in the tunic of one of the brothers, presented in Figure 5. In visible light, the tunic appears completely flat, while in IRR, some textures and volumes can be appreciated. Furthermore, the light tonality of the bottom area of the coat in IRR is inconsistent with the dark colour of the visible image. The restorers removed a small area of the surface layer, finding a slightly lighter colour underneath. Therefore, we can confirm that the current flat dark colour is a later repainting, in which the tunic of this brother was darkened.

Figure 5. Comparison between IRR and visible images of the clothes of one of the brothers in the painting of *Joseph sold to the Medianite merchants*.

4. Material Study

Different colours, tonalities, shades, and highlights were analysed with XRF to determine the pigments applied and their mixtures. We analysed not only the original pigments but also those used in the interventions located by UV light. The presence of each element depends on the pigment used and the relative quantity at the radiated point. This allows us to characterise most of the artists' palette, but in specific areas, sampling was needed to complement the information of inconclusive results by XRF; as it is an elemental technique, several pigments can be characterised by the same chemical element. However, this was possible only for the Flemish painting, as previously explained, while for the Spanish painting, this difficulty of relating pigments with certain chemical elements exists. Table 1 summarises the preparations and pigments found in both paintings, indicating the colour of the pigment and the chemical formula to support the understanding of the results.

Table 1. Summary of the preparations and pigments found in both paintings. The colour of the pigment and the chemical formula with the characteristic elements detected by XRF, highlighted in bold, are also indicated.

Preparation/Colour	Pigment	Chemical Formula
Preparation	Gypsum	$\mathbf{Ca}SO_4$
	Chalk	$\mathbf{Ca}CO_3$
White	Lead white	$2\mathbf{Pb}CO_3 \cdot Pb(OH)_2$
	Titanium white	$\mathbf{Ti}O_2$
	Zinc white	$\mathbf{Zn}O$
Green	Malachite	$\mathbf{Cu}CO_3 \cdot Cu(OH)_2$
	Verdigris	$\mathbf{Cu}(CH_3COO)_2 \cdot 2H_2O$
	Copper resinate	$\mathbf{Cu}(C_{19}H_{29}COO)_2$
	Chrome green	$\mathbf{Cr}_2H_4O_5$
Yellow	Lead-tin yellow	$\mathbf{Pb}_2\mathbf{Sn}O_4$
	Yellow earth/ochre	$\mathbf{Fe}(OH)_2$
	Yellow lake	unidentified, **Ca** substr
Red	Red earth/ochre	$\mathbf{Fe}_2O_3$
	Vermilion	$\mathbf{Hg}S$
	Minium red	$\mathbf{Pb}_3O_4$
	Red lake	unidentified, **Ca** substr
	Cadmium red	**CdSe**
Blue	Azurite	$2\mathbf{Cu}CO \cdot \mathbf{Cu}(OH)_2$
	Smalt	not a definite chemical compound, containing **Co**, Si, K, As (Ni, Bi . . .)
	Prussian blue	$C_{18}\mathbf{Fe}_7N_{18}$
Brown	Umber	$\mathbf{Fe}_2O_3 + \mathbf{Mn}O_2 + nH_2O + Si + Al_2O_3$
Black	Bone black	$\mathbf{Ca}_3(PO_4)_2 + CaCO_3 + C$

4.1. *Preparation and Priming*

The presence of Ca was observed in all analysed points indicating that this element must form part of the entire painting. For the painting of *The Virgin and Child*, the presence of Ca would reveal a preparation made of calcium carbonate (chalk) or calcium sulphate (gypsum). The latter was more commonly used in the Iberian Peninsula, therefore, we suggested gypsum as preparation [19]. Similar XRF results indicating a Ca based preparation were obtained for *Joseph sold to the Medianite merchant*; considering the Flemish origin of the painting, the use of calcium carbonate (chalk) was more likely [19]. The gypsum could be identified with the additional presence of S. However, we could not confirm its presence, as the signal was highly attenuated by air and was found in a region of the spectrum affected by electronic noise and Pb M-peaks. Moreover, the variation in the area of the Ca peak was of the order of a few thousand counts between the analysed points, so part of Ca must have come from the pigments used in the paint layers.

Furthermore, the presence of Fe and Pb in all areas analysed in the Flemish painting suggested the existence of a priming layer composed of earths (Fe) and lead white or other lead-based pigments (Pb). At this point, the OM and SEM-EDX analyses were of great help in identifying a preparation layer made of chalk and some red earths, having a thickness of up to 260 µm. There was no pigment-based primer, but we could observe a thin organic layer on top of the preparation moisturising it and preparing the surface for the overlaid colour layers. The high presence of Pb mentioned above may have resulted from the use of lead pigments in (a) preparation layers, (b) as pigments in colour layers, and (c) as siccative. While (a) and (b) can be determined by SEM-EDX, its use as siccative can only be hypothesised. The highest Pb intensity is found in carnations, and the lowest one, in the dark sky colour. The Pb intensity depends, of course, on the lighter or darker colour that is being analysed. Most of the signal comes from the lead pigment(s) in the colour layers; however, we cannot discern how much of it corresponds to the preparation or, if given the case, from the siccative. Regarding the binder, it is more likely to be oil, but with SEM-EDX we were unable to characterise the organic material.

4.2. Pigments

4.2.1. The Virgin and Child

The painting of *The Virgin and Child* presents a small colour palette in which red and green predominate. The chemical elements detected in the points analysed showed that the artist used pigments that were common in the 16th century [20,21].

Green was selected to paint the background and the inner area of the Virgin's coat. In all the points analysed, the pigment was characterised by high Cu peaks. However, several green pigments based on Cu were used in that century (malachite, verdigris, and copper resinate, among others), so we cannot specify the pigment by XRF. The background presents different tonalities produced by an inhomogeneous amount of copper-based green pigment whose count rates range from (179.5 ± 1.4) to (376.9 ± 0.9) cps. In addition, this pigment was mixed with earths and lead white. Similarly, the green area of the Virgin's coat was made with the same pigments but with the addition of lead-tin yellow (Pb and Sn). The shades of the green coat revealed an increase in copper-based green [neutral: (359.6 ± 1.4) cps; shade: (480.2 ± 1.6) cps] and earths [neutral: (3.7 ± 0.2) cps; shade: (7.6 ± 0.3) cps]. The earths can be red or yellow, iron oxides or alumosilicates, but we cannot distinguish them because both are identified by XRF only on the basis of Fe. Therefore, we can rely only on the analysed colour to deduce which one was used, but—in mixed colours—it is not always possible. On the other hand, the Virgin's dark tunic showed the highest Cu peaks in the painting with a count rate of (2414 ± 3) cps. It was obviously carried out with azurite, which according to the iconography, represents eternity. The dark/black colour was achieved with a high amount of this expensive blue pigment on a dark underlayer, as can be already observed with the naked eye. For the dark underlayer, an organic black must have been used, but regarding the low Ca peaks in all analysed areas of the blue tunic, it was not a bone black, whereas other black pigments, mostly organic, cannot be detected by XRF. Perhaps a copper-based green pigment was also added for the shades, bearing in mind that greens were generally used for deep shades, creating volume since plain black looks flat. The mixture of blue and green copper-based pigments would support the high Cu peaks in the tunic. In these dark areas, we can also observe a decrease in lead white amount, from (2563 ± 5) cps in lighter areas to (576 ± 3) cps for dark/black areas, on average.

The main red pigment was vermilion (Hg), which was found in large amounts in the Virgin's red coat with a count rate of up to (483.2 ± 1.6) cps. This red pigment was mixed with earths, a lead-based pigment, which can be lead white or minium red, and a small amount of copper-based green to achieve the different tonalities. For shades, the concentration of vermilion decreased to (111.8 ± 0.8) cps, while ochre increased from (7.3 ± 0.2) cps in neutral tones to (26.8 ± 0.4) cps in shades. In addition, the greater amount of Ca compared to the green areas would indicate the possible use of a red lake due to the application of the liquid colourant on the $CaCO_3$ substrate. On the other hand, the hair of both figures was made using the same mixture of pigments as in the red coat, but more ochre was applied to obtain a brownish tonality. However, the Virgin's hair, which is darker, presented more ochre and vermilion than the Child's hair.

The principal component analysis (PCA) considering the colours mentioned above is shown in Figure 6. In this way, we can see that black coloured areas are mainly characterised by the presence of Cu, while the green coloured areas are mainly correlated with Sn or

Pb. On the other hand, the red and brown coloured areas are identified by Hg and higher amounts of Fe and Ca, on average.

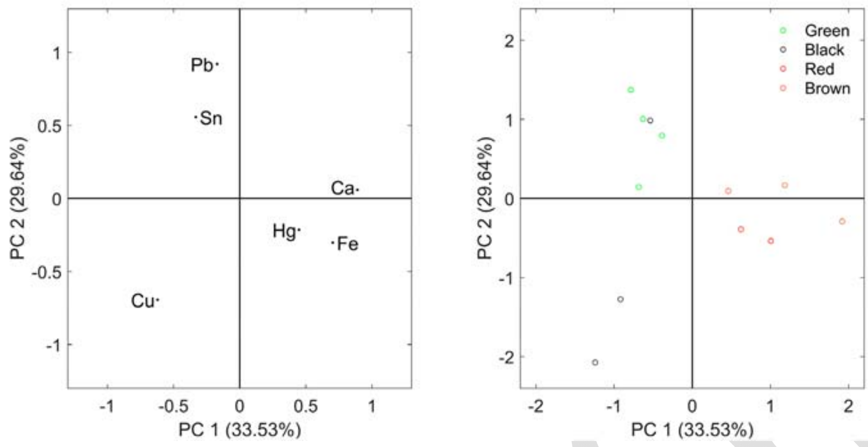

Figure 6. PCA scores (**left**) and results of the PCA analysis applied to different colours (**right**).

The skin tones were made mainly of lead white and vermilion, to which different amounts of earths and a copper-based green were added to create different tonalities. The shades showed an increase in these two last pigments in a similar way to what was found in the clothing.

Finally, the use of gold (Au) on top of bole (Fe) or mixtion (Ca, Fe, Pb) was confirmed in the halos of the Virgin and the Child, in the rays around the Virgin, in the Child's tunic and in the pearl on the neck of the Virgin's tunic. The moon presented silver peaks (Ag), as seen in Figure 7, characterised by the presence of As that could indicate its origin. However, the brown colour of the moon does not correspond to the maximum amount of silver analysed [(22.6 ± 0.5) cps], which may be in a lower layer or may have been detached from the moon in the past. The intense Ca peaks observed in this area may be due to the use of animal glue in mixtion instead of bole as the base for the metal foil application. Additionally, Zr peaks come from the collimator of the detector with a stable area in all the measurements, while Sr peaks generally appear together with a high Ca presence, indicating a calcium-based preparation impurity; the intensity varies according to the intensity of Ca peaks. Studies show that a high Sr content often occurs in gypsum preparations such as $SrSO_4$ [22,23].

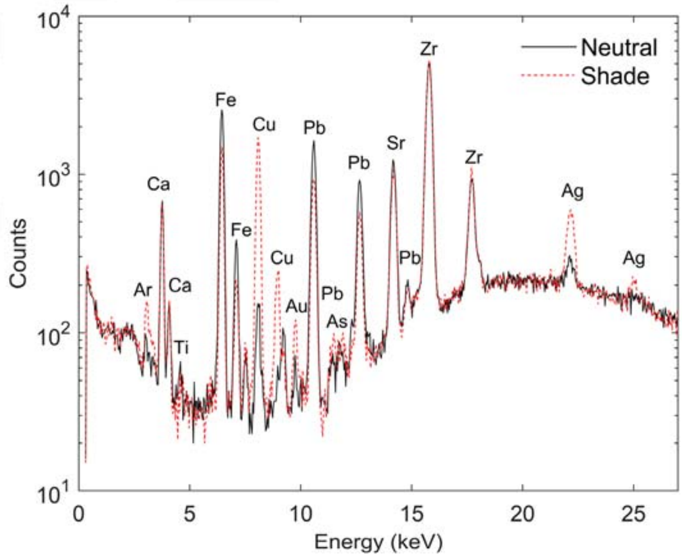

Figure 7. XRF spectra of the moon.

4.2.2. Joseph Sold to the Medianite Merchants

For the painting of *Joseph sold to the Medianite merchants*, the artist applied a broader pigment palette, which corresponds to those used in the 17th century [20,21,24,25]. Only the clothing presents red, blue, brown, yellow, and violet colours. In this case, the PCA was not useful in studying the correlation of the colours with the chemical elements due to the wide variety of colours and tonalities present in the painting.

We found three different red pigments, red earth (Fe), vermilion (Hg), and red lake, identified by high Ca peaks in the XRF and confirmed its presence by SEM-EDX on several cross-sections of the sky and clothing. Vermilion was the main red pigment, which was used in almost all the points analysed, except in some blue, yellow, and green areas. The highest amount of this pigment appeared in red clothing with a count rate of (330.4 ± 1.3) cps, while in other areas, the amount decreased with an average concentration of (10.3 ± 0.8) cps. On the other hand, the yellow colour was obtained with lead-tin yellow and yellow earths. Furthermore, in the yellow coat of the brother to the left of Joseph, SEM-EDX showed that the pigment used was a yellow lake mixed with lead-tin yellow. This result was also found by the XRF in Figure 8 with intense Ca peaks, indicating the use of a yellow lake on a $CaCO_3$ substrate. In addition, the cross-section showed an underlayer made mainly of red earths (Figure 9, Table 2). Similarly, as in the red colour, the average amount of lead-tin yellow decreases from (7.1 ± 0.3) cps in the basic colour areas to (1.9 ± 0.2) cps in the highlighted areas where it was mixed with other pigments.

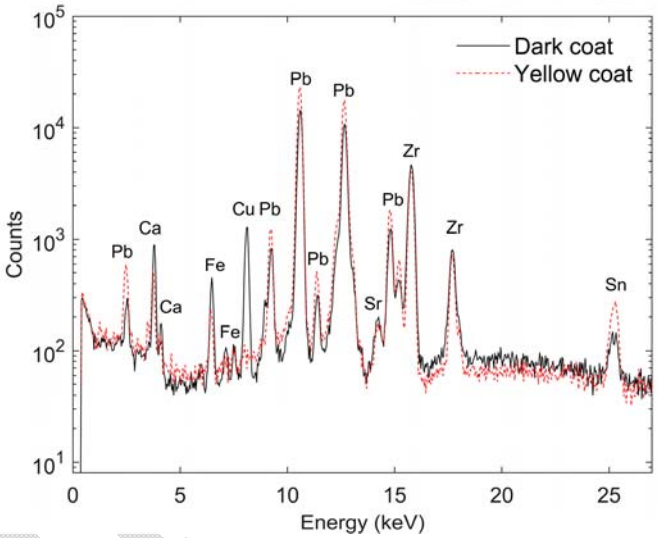

Figure 8. XRF spectra of the yellow coat and the possible repaint of the dark coat showed in the IRR image.

Table 2. Results of the SEM-EDX analysis of the samples shown in Figure 9. The chemical elements detected and their composition are indicated for each layer in the stratigraphies.

	Layer	EDX	Interpretation/Composition
Sample (A)	Preparation	Mg, Al, Si, Ca, Mn	Calcite (chalk) with earth grains
	First colour layer	Al, Si, Fe, Sn, Pb	Lead white, lead-tin yellow, earths
	Second colour layer	Al, Si, Fe, Sn, Pb	Lead white, lead-tin yellow, earths
	External colour layer	Pb, Sn	Lead white, lead-tin yellow
	Partial repaint	Mg, Al, Si, Ca, Fe, Pb,	Calcite, earths, lead white.

Table 2. *Cont.*

	Layer	EDX	Interpretation/Composition
Sample (B)	Preparation	Mg, Al, Si, Ca, Mn	Calcite (chalk) with earth grains
	External colour layer	Al, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Pb	Calcite, red earths, bone black, umber, lead white, copper resinate, Prussian blue.
Sample (C)	Preparation	Mg, Al, Si, Ca, Mn	Calcite (chalk) with earth grains
	External colour layer	Mg, Al, Si, P, Cl, K, Ca, Cu, Pb	bone black, lead white, possible copper resinate

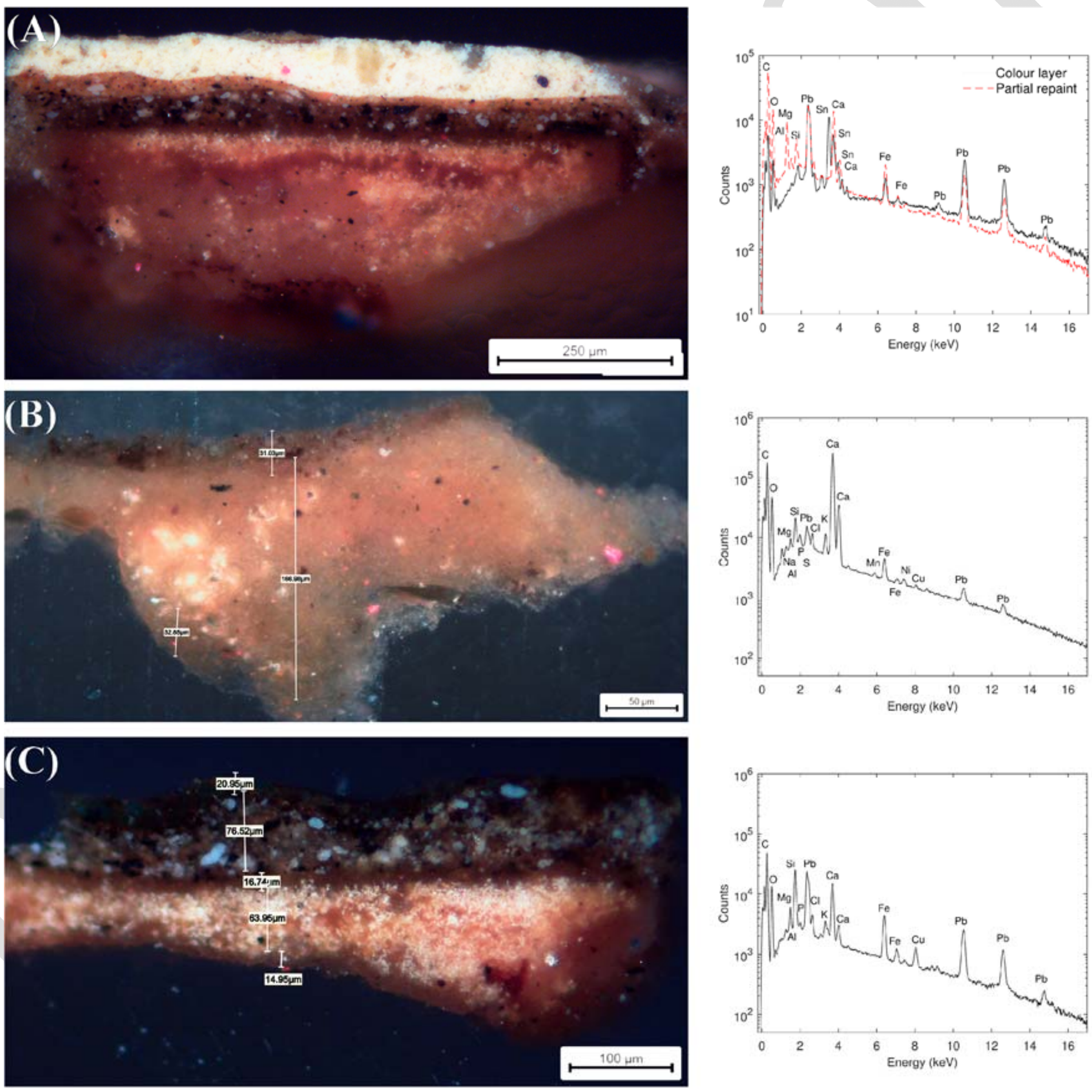

Figure 9. Samples analysed by OM and SEM-EDX. (**A**) Yellow coat, (**B**) blue pants, and (**C**) green tree. The spectra correspond to the external colour layer of each sample. Detailed results are shown in Table 2.

Unlike the first painting analysed, dark pigments were also applied. The brown pigment was umber, which is characterised by Mn and Fe, while the black pigment was bone black confirmed by SEM-EDX. We cannot confirm the presence of bone black with P originating from apatite by XRF because of the air attenuation, electronic noise, and the Pb M-peaks that affect this range of energy. However, intense Ca peaks (average intensity of 25 cps) in all dark areas indicate that this element does not belong only to the preparation (average intensity of 9,4 cps measured in areas of colour loss) but also to the colour layer, so we can also suggest the use of bone black by XRF. These two pigments were used to model the shades and were generally applied together and mixed with a great amount of earths (Fe). The cps of the earths decrease by half on average when not used in dark areas. Additionally, the vegetation and the house, which show generally muted colours with brownish tonalities, were painted mainly with a large amount of earths and umber, to which vermilion and bone black were added. However, in green areas, the amount of copper increases, indicating a greater use of copper-based green pigment. As in the first painting, we cannot identify the specific copper-based green pigment only by XRF, as different pigments were in use in the 17th century. Additionally, EDX gives us only Cu, but on the OM and SEM images of the related cross-sections, we can identify the pigment as a copper resinate due to its morphology (Figure 9, Table 2). For skin tones, lead white and vermilion were the principal pigments, while lead-tin yellow, ochre, copper-based green, umber, and bone black were added accordingly to obtain the desired tonality.

The dark coat of one of the brothers, which showed a different texture in the IRR observed in Figure 5, presented a great amount of lead-tin yellow at some points, as shown in Figure 8. However, the dark colour of the coat is inconsistent with the high use of this clear pigment, although a copper-based green and bone black were also applied, the last of which was identified by large Ca peaks. This result, together with the IRR image, indicates the existence of a dark repainting of the clothing of this brother.

Three blue pigments were identified depending on the area studied, as shown in Figure 10. For the blue areas of the clothing, the pigment applied was azurite (Cu), showing the highest amount of Cu with a count rate of (1080 ± 2) cps. On the contrary, in the blue pants of the brother with a yellow coat, the concentration of Cu decreases to (4.7 ± 0.2). The analysis of the corresponding cross-section indicates the use of Prussian blue, as confirmed by SEM-EDX (Figure 9, Table 2), and also identified by the Fe peaks by XRF. This pigment was synthesised only around 1706 [19–21], which would exclude Pieter van Lint as the painter of this painting, postponing its creation to the 18th century or later. The artist must be van Lint's follower or a copyist. The Prussian blue entered soon into the market, replacing the expensive ultramarine blue. Finally, the sky was painted with smalt (Co), although earths (Fe) was also detected, which was probably used underlaid or mixed with smalt to give more body to this vitreous pigment or to model darker areas. Moreover, lead-tin yellow was found in the yellowish area where a sunrise is represented on the left side of the painting. Additionally, in the right area of the painting, the sky appears darkened. In all points analysed in this sky area, umber was applied together with bone black, identified by an increase in the intensity of the Ca peaks compared to the left area of the sky [Ca: (2.7 ± 0.2) cps; Ca: (13.7 ± 0.3) cps] and confirmed by SEM-EDX. Furthermore, the quantity of smalt decreases [Co: (4.9 ± 0.2) cps; Co: (2.1 ± 0.2) cps], which also explains the gradual darkening of the sky. On the other hand, some points at the lower part of the sky in this right area of the painting show the use of vermilion and red lake. These pigments are usually used to represent a sunset, which confirms the iconography of the painting, explained in the Introduction. Nevertheless, the result is a very dark sky due to the large amount of umber and bone black added.

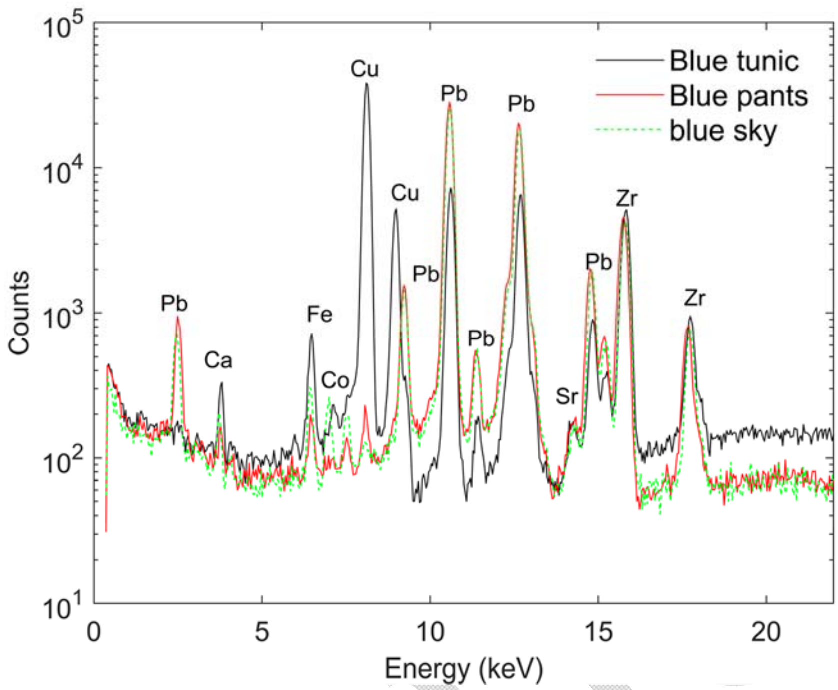

Figure 10. XRF spectra of different blue areas. Joseph's blue tunic (black), blue pants (red), and light blue sky (green).

4.3. Later Interventions

Several points were selected on the bases of the UV image of *The Virgin and Child* to identify the pigments applied for the retouches. These areas had important concentrations of Ti, Zn, and Cr. These elements confirmed the use of titanium white, zinc white, and chrome green, respectively, which are modern pigments [20,21,24,25]. Cd and Se were detected at one point, indicating the use of cadmium red, a modern pigment used only since the 1920s, as well as titanium white. Finally, the highest Ca peaks appear in all retouches, which mostly correspond to calcium-based fillings of the lacunas, while umber (Mn, Fe) was applied only in some intervention points. In the Flemish painting, the XRF analysis was carried out after the cleaning process; therefore, no modern pigments were found, as explained before.

5. Conclusions

Two paintings (16th and 17th centuries) by anonymous authors, part of the art collection of the Archbishop's Palace in Seville, were mostly analysed with non-invasive techniques presented here as a recommended basic procedure for artwork study: UV, IRR, and XRF. Only in the Flemish painting could several samples be extracted, prepared then as cross-sections, and studied by OM and SEM-EDX to clarify some doubtful XRF results. This systematic procedure allowed us to locate later retouches, discover preparatory drawings and *pentimenti*, and characterise the painting materials based on their chemical elements.

The study of materials showed the presence of a calcium-based preparation, which is probably gypsum in the Spanish painting and chalk with red earths in the Flemish one. The pigments identified in each painting correspond to those used in the 16th and 17th centuries, respectively; however, the palette of the 16th century painting is much narrower than the palette of the 17th century. The analysis showed that both artists typically used two or more pigments to achieve the desired tonality. They modelled the highlights by mixing selected pigments with a higher amount of lead white, adding lead-tin yellow for specific details. Regarding the shades, there are some differences. In the painting of *The Virgin and Child,* they were obtained with different quantities of earths and copper-based green, while in the painting of *Joseph sold to the Medianite merchants*, umber and bone black were also used. In addition, the XRF confirmed the use of gold and silver in some areas of the 16th century painting, all these materials being possible in the work of Alejo Fernández or his workshop, confirming its original attribution. On the contrary, in the Flemish painting, the Prussian blue was found by SEM-EDX, which confronts the proposed attribution to Pieter van Lint and postpones the date of the painting to the 18th century or later. Therefore, it must be the work of a Van Lint follower or copyist. The darkening of the sky of the right side on this painting must be original, corresponding to the sunset iconography, and is not a later overpainting, as thought.

The retouches were confirmed on the basis of modern pigments only in the 16th century painting, carried out by modern pigments such as titanium and zinc whites, chrome green and cadmium red, overlaid on calcium-based fillings. The Flemish painting was analysed only after the cleaning process.

All these results obtained with accessible analytical techniques represent important information that is useful in the conservation process and in the understanding of artists and their use of painting materials. They are also an important step in the search for authorship. With this objective, as soon as possible in the future, we expect to include additional non-invasive techniques to complete our analytical procedure and to study other paintings related to both artists, aiming for a precise comparison of their materials and painting procedures.

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