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Non-Invasive Study of the Pigments of a Painting on Copper with the Inscription "*Boceto di Pablo Veronese*" on the Back

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Abstract: The palette used on a small painting on copper support, with the inscription "*Boceto di Pablo Veronese*" on the back, was characterized. Non-invasive techniques such as X-ray diffraction (XRD) and hand-held X-ray fluorescence (XRF) were proven to be highly effective for this. The objectives of the proposed work were twofold. On the one hand, the objective was the study, in situ, of the pigments of a painting on a copper support. On the other hand, it was to enrich the literature related to the study of paintings on metal supports, since few related studies are available despite the relatively large number of such 16th and 17th century paintings from Italy and Northern Europe. The results of the analysis showed a copper support with a base layer of gypsum mixed with ochre earths. Atop this layer is a sketch with lead white in the lighter areas and bone black in the darker shadow areas, suggesting that the artist performed a preliminary study of the luminosity of the scene. Finally, the upper or pictorial layer consists of a mix of pigments with some lead white to lower saturation and increase lightness, particularly evident in the flesh tones. The resulting palette thus includes lead white, vermilion, bone black, Naples yellow, and lazurite pigments. These results are compared to Veronese's other paintings, as well as to those of certain contemporary artists, and the use of the resulting pigments in 16th and 17th century Italian painting techniques is discussed.

Keywords: painting on copper support; pigments; non-invasive techniques; XRF; XRD

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Citation: Blanc, R.; Manzano, E.; López-Montes, A.; Domínguez-Gasca, N.; Vílchez, J.L. Non-Invasive Study of the Pigments of a Painting on Copper with the Inscription "*Boceto di Pablo Veronese*" on the Back. *Heritage* **2023**, *6*, 4787–4801. https://doi.org/10.3390/heritage6060254

Received: 24 March 2023
Revised: 18 May 2023
Accepted: 8 June 2023
Published: 14 June 2023

1. Introduction

In the last few decades, the study of the artist's palette has become a focus of analytical interest, not only for the analyses of painting techniques but also for dating purposes. It is well known that the presence of anachronistic pigments, the use of which is only possible after their introduction into the market, may help to authenticate the authorship of a painting [1,2]. A thorough investigation requires the use of advanced and combined techniques to extract the greatest amount of information from paintings' complex multi-layers. In situ techniques have emerged in recent years, rapidly becoming indispensable for the non-invasive analysis of objects of artistic and historical value. X-ray-based techniques are a key focus of this study [3–5], particularly X-ray fluorescence (XRF) and X-ray diffraction (XRD). These have proven to be powerful tools for the non-invasive study of pigments in historical paintings, with a minimal impact on the artwork [4–9]. XRF can yield qualitative information on elements present in pigments through their key elements, and can suggest the possible provenance of materials based on their trace element patterns. However, the basic information it provides is often insufficient, and further investigation on how the elements are combined to form molecules and crystals is required. XRD is therefore the most reliable method for crystalline material identification, able to distinguish between two or more substances containing the same elements. The combination of XRD and XRF techniques is widely used given that they are complementary methods, either using hand-held XRF instrumentation for in situ measurements [10,11], for instance with a portable powder diffractometer [12,13], or, more recently, combining several techniques in a single instrument [6]. In addition, chemical molecular and elemental mapping can be obtained, offering conclusions on the areal distribution of pigments in any kind of pictorial artwork [14–16]. Most of the literature focuses on the spectroscopic technique's application on canvas support, but fewer cases have been documented on other media such as copper or brass sheet metal [17–25].

This study characterizes the preserved pigments on a small oval-shaped painting on a copper support. This study represents the first phase of a broad investigation being conducted by our multidisciplinary team, which focuses on the material, historical-artistic study, and restoration of the painting, with the aim of connecting the painting to a historical period, a geographical region, a pictorial school, and, if at all possible, its authorship and attribution. Both the inscription referencing Veronese on the back and the use of a copper support lead us to compare the results of our preliminary study with the pigments and materials used by Veronese and other contemporary painters of 16th and 17th century Italy, especially in paintings created on metallic supports. In the present study, therefore, the objectives of the proposed work are twofold: on the one hand, through the combined use of non-invasive hand-held X-ray fluorescence (XRF) and X-ray diffraction (XRD) techniques we aim to establish the palette used by the artist; on the other hand, we aim to contribute to the literature on paintings on metal supports, since relatively few studies are available, despite the technique's prevalence in 16th and 17th century Europe.

Painting on Copper Support

The use of copper as a support for oil paintings was most prevalent in the 16th and 17th centuries, first in Italy and then in the Netherlands [17,19]. Copper was similarly priced to wood panels, so it was an economic and readily-available option. Compared to panel painting, the preparation of copper was faster and needed less material, thus saving resources and time in an era of growing demand in the art market. In addition, the strength of the copper sheets made it possible to simplify the preparatory procedures of the supports (smoothing steps, and elimination of pores and irregularities typical of wood) and allowed them to work with glazes with drying oils, producing light and subtle shadows in transitions, as well as atmospheric depth [19]. Copper aged well and avoided biological attacks. However, according to some authors, these supports were quite difficult to paint, presenting serious issues with the adhesion of pigments. For this reason, it was essential to carry out correct preparation of the support [17,22,26]. Contemporary treatises mentioned in their texts that the use of aqueous substances in the preparations was discouraged to avoid the corrosion of the metal. Instead, they proposed the application of layers with oil and lead white applied with the fingers instead of a brush to leave an irregular surface. Other treatises mentioned an initial rubbing of garlic to facilitate the adhesion of the oil layer. In addition, other pigments could be added to the preparation (red earths or black pigments) to modify the hue and leave a final smoothing with the help of a brush [26]. To a lesser extent, oil and plaster were used in the preparation [23], although discouraged because of the reaction of the copper with calcium sulfate, creating copper sulfate. This component would affect the adhesion of the preparation layer [24].

2. Materials and Methods

2.1. The Painting on Copper Support Investigated

The painting is on a copper support in the shape of an oval with two axes of symmetry (major axis: 17.5 cm; minor axis: 13.5 cm), and the thickness of the painting (copper support and pictorial layers) is between 0.70 and 0.78 mm (Figure 1a). The theme of the painting is religious, representing the Sacred Family. The Virgin carries the Baby Jesus in her arms while removing a veil, observed from behind by a figure identified as Saint Joseph. The background is dark, and no architectural or botanical elements can be observed.

An inscription is preserved on the back. The original text is shown in Figure 1b and the highlighted text of the inscription in Figure 1c. This text may refer to the authorship (by P. Veronese), or to a copy of Paolo Veronese, or to a work by his followers from his workshop or school.

Figure 1. (**a**) Frontal photographs of the painting on copper support; (**b**) back of the painting with inscription; (**c**) back of the painting with the highlighted text of the inscription.

The paint/copper interface formed between the lower layers of paint involves chemical, physical, and mechanical processes that are influenced by the environment. The copper support was affected by pitting degradation, which is a localized corrosion that produces small pits or holes in the metal [24]. In the areas where this corrosion had occurred, the preparation layer and the pictorial layer had disappeared. The surface of the paint layer displayed a darkened appearance due to the blackening of the protective varnish. At the perimeter of the painting, in the area covered by the frame, there had been a lightening effect of the varnish. The lack of saturation and brightness and the lack of varnish are due to its aged state. Although the painting must be varnished before it is framed, it must be re-varnished afterwards without being disassembled. It would be careless to re-varnish it solely to create a "paint refresher effect", which increases color tonality while providing a smoother and brighter surface. The painting also presented scratches, small flaws, and micro-cracking, possibly created by the manipulation of the piece or by the natural drying process of the pictorial layer.

The painting is located in Spain and belongs to a private collection.

2.2. Analytical Techniques

2.2.1. Hand-Held X-ray Fluorescence (XRF)

X-ray fluorescence spectroscopy analysis was performed with a hand-held NITON XL3t GOLDD+ (Thermo Fisher Scientific, Waltham, MA, USA) with a silver anode (50 kV, 200 μA). The analyzer was fitted with a camera and with a suitably equipped Small Spot analyzer, with which the analysis could be restricted to a small area of the camera angle (3 mm). Before using the analyzer, we waited five minutes, allowing the instrument's electronics to stabilize and run a system check to calibrate the detector and verify that it was operating according to the specifications. Spectra were collected using the measuring mode "test all geo". The analyzer is equipped with four excitation filters (main, high, low, and light) that optimize the analyzer's sensitivity for the various elements. Measurements of 30 s for each filter were set, which means that each spot analysis took about 120 s to complete. NITON Data Transfer (NDT©) software 6.1 was used to control the instrument and for data management and transfer.

2.2.2. X-ray Diffraction (XRD)

The X-ray diffraction powder method was used for the identification and semi-quantification of crystalline materials, in this case of paint pigments. The diffraction records were acquired directly from the painting's surface using a BRUKER D8 DISCOVER diffractometer equipped with an air-cooled IμS Cu microfocus sealed tube (1 mA, 50 kV, Cu Kα line at λ = 1.5406 Å) and a PILATUS3R 100K-A detector. The results were analyzed using EVA v4.3 software.

The maps of the different pigments were obtained using the program SmART_scan, which statistically combines the color (RGB) from the visible image of the paint, the chemical information obtained via XRD, and the relative positions of the analyzed and unknown points of the paint, subsequently generating false-color maps that show the surface distribution of the pigments. The minimization of the Euclidean distance between the analyzed and unknown points in the multidimensional space throughout the whole painting allows for the creation of the maps [16].

3. Results

For the proposed analysis, some type of sampling was required, and we used in situ XRF and XRD analysis of thirty-four points from the front of the painting and three from the back in order to obtain information about the palette. Due to the penetrating nature of X-rays and the thinness of the pictorial and preparation (ground) layers on the copper support, the results of the analysis made from the recto of the painting (pictorial layer) also included data on ground layer elements, as well as the support, not just the outer layers. Thus, it was necessary to interpret whether the identified elements belonged to the support, to the composition of the ground layer, or to the pictorial layer.

Figure 2 shows the analyzed zones highlighted by points, on the front and on the back of the painting on copper support. One XRF spectrum representative of each color area has been selected, and is shown in Figure 3. For the sake of clarity, elements attributed to the support are not cited in the table, but the detected elements associated with the preparation layers and pictorial layer are collected in Table 1, following a color-based division by area, so that the corresponding number codes and the detected elements can distinguish between major, minor, and trace elements. The elements are listed from those detected in the internal layers through to those in the outer pictorial layer. Similarly, Table 2 shows the results of the semiquantitative mineral analysis of each spot, having removed the copper, and having normalized the calculated percentages to 100. Figure 4 includes five selected diffractograms, one for each of the grayish, flesh tone, blue, red, and dark areas.

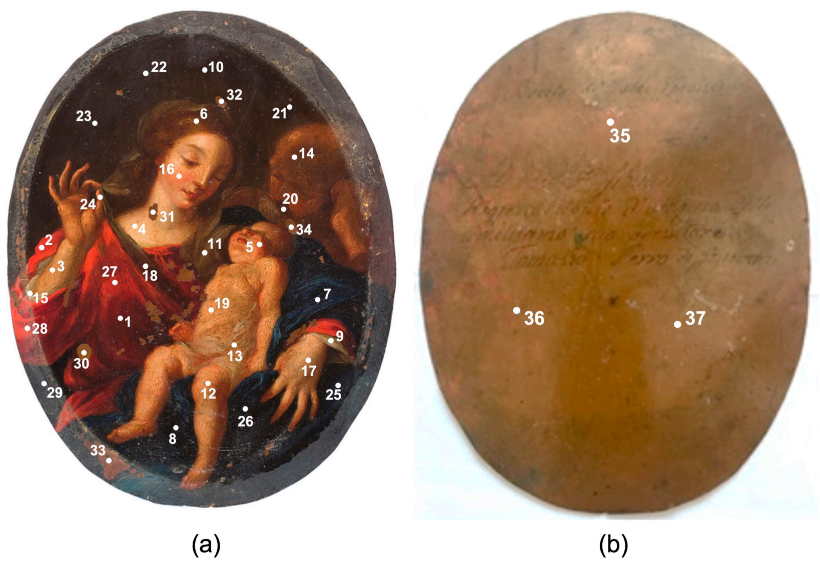

Figure 2. (**a**) Front and (**b**) back of the copper painting showing the points analyzed using both hand-held XRF and XRD techniques.

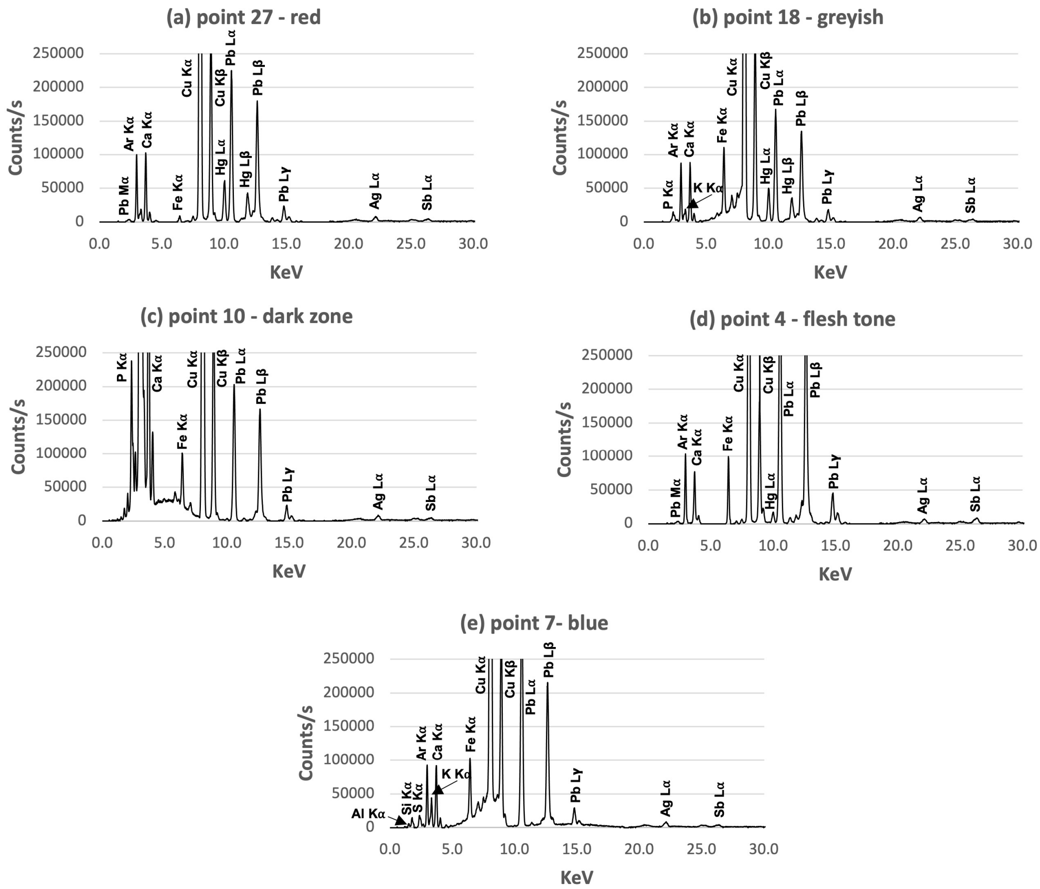

Figure 3. XRF spectra corresponding to the following areas: (**a**) Point 27—red (Virgin's blouse over right breast, light area); (**b**) Point 18—greyish (Virgin's lock of hair over right breast); (**c**) Point 10—dark zone (shadow area above Virgin's head); (**d**) Point 4—flesh tone (Virgin's right shoulder blade); (**e**) Point 7—blue (Virgin's right arm sleeve).

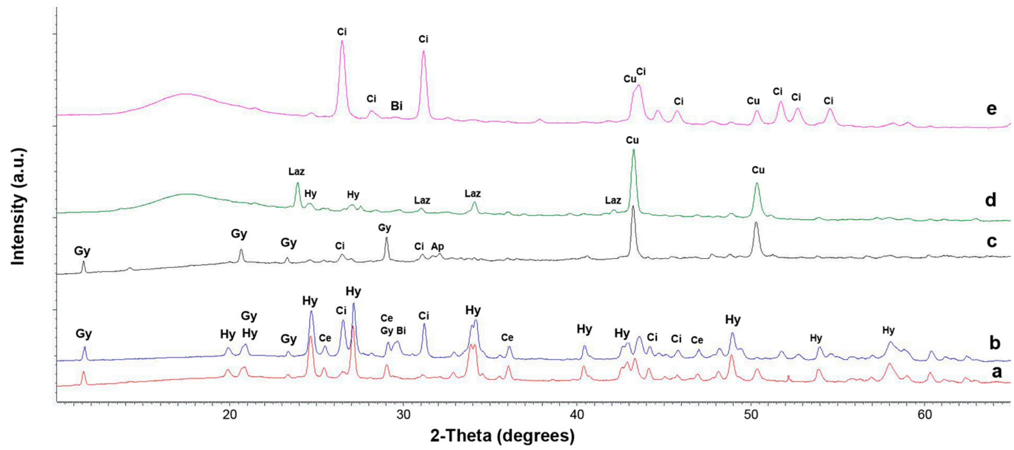

Figure 4. XRD diffractograms corresponding to the following areas: (**a**) Point 11 (Virgin's scarf over left shoulder); (**b**) Point 12 (Virgin's right cheek); (**c**) Point 10 (Above the Virgin's head); (**d**) Point 26 (Virgin's mantle next to Baby Jesus's left leg); (**e**) Point 27 (Virgin's breast, light area). [Gy = gypsum, Hy = Hydrocerussite, Ap = Hydroxyapatite, Ci = Cinnabar, Ce = Cerussite, Bi = Bindheimite, Laz = Lazurite, Cu = Copper].

As for the results of the XRD and XRF analyses, first the chemical nature of the support will be discussed, followed by the analysis of the chemical and mineral nature of the materials present on the ground, and finally the pigments present in the red, flesh tone, blue, grayish, whitish, dark, and brown areas. Since it was paramount to avoid damaging the painting, no samples were taken, and all the results were obtained solely from the use of non-invasive techniques.

Table 1. Elements identified via XRF associated with the ground and pictorial layers of the painting on copper support. (M) major, (m) minor, and (tr) trace elements.

Color	No.	Elements Detected										
		Ca	**S**	**Fe**	**Mn**	**Pb**	**P**	**Hg**	**Sb**	**Si**	**Al**	**K**
Red	1	m	M	m	tr	m	M	M	tr	tr	tr	tr
	2	m	M	M	tr	M	-	M	tr	-	-	-
	27	m	M	m	tr	m	-	M	tr	tr	-	tr
	28	m	M	m	tr	m	-	M	tr	tr	-	tr
Flesh tone	3	m	M	M	tr	M	-	M	tr	-	-	-
	4	m	M	M	tr	M	-	m	tr	-	-	-
	5	m	M	M	tr	M	-	m	tr	tr	-	tr
	12	m	M	M	tr	M	-	m	tr	tr	tr	tr
	14	M	M	M	tr	M	M	m	tr	tr	-	tr
	16	m	M	M	tr	M	-	m	tr	tr	-	-
	17	m	M	M	tr	M	M	m	tr	tr	tr	tr
	19	m	M	M	tr	M	-	m	tr	-	-	-
	24	m	M	M	tr	M	M	m	tr	-	-	-
Blue	7	m	M	m	tr	M	-	tr	tr	tr	tr	tr
	8	m	M	m	tr	M	-	m	tr	tr	tr	
	25	m	M	m	tr	M	-	tr	tr	-	tr	tr
	26	m	M	m	tr	M	M	m	tr	tr	tr	
Grayish	11	M	M	M	tr	M	M	m	tr	tr	tr	tr
	18	m	M	m	tr	m	M	M	tr	tr	tr	tr
Whitish	9	m	M	m	tr	M	-	m	tr	tr	tr	tr
	13	m	M	M	tr	M	-	m	tr	-	-	-
	15	m	M	m	tr	M	-	M	tr	tr	tr	tr
Dark zone	10	M	M	M	tr	m	M	tr	tr	-	-	-
	21	M	M	M	tr	m	M	tr	tr	-	-	-
	22	M	M	M	tr	m	M	tr	tr	-	-	-
	23	M	M	M	tr	m	M	tr	tr	-	-	-
	29	m	M	m	tr	m	-	M	tr	tr	tr	
Brown	6	M	M	M	tr	m	M	tr	tr	-	-	-
	20	M	M	M	tr	M	M	m	tr	tr	-	tr

3.1. Support

The XRF analysis of the support material was made on three random areas of the back of the plate (points 35, 36, and 37), showing the following elements: Cu as the major element, and traces of Sn, Pb, Ni, Fe, and Cl as minor components. These impurities were also detected in other studied paintings on copper supports [21]. XRD spectral data confirmed high-purity copper as the support and ruled out brass or other alloys. The Ag L lines originated from the scatter of the primary X-ray lines from the silver tube source, and the Ar K lines were associated with atmospheric XRF measurements. The chlorine signal in the spectra from the front and back of the painting could be attributed, as in many other similar artworks, to sheet copper corrosion typical of chloride-rich environments [27].

Table 2. Percentage calculated of mineral phases in all the points analyzed, removing copper.

Colour	No.	Minerals Detected *										
		Gy	Hy	Ce	Ci	Laz	A	Ap	Bi	Si	H	Ca
Red	1	32.0	21.0	4.6	12.8	-	13.6	-	1.6	14.4	-	-
	2	19.5	9.5	4.9	65.2	-	-	-	1.0	-	-	-
	27	25.7	-	7.2	90.4	-	-	-	2.4	-	-	-
	28	31.4	-	4.9	63.7	-	-	-	-	-	-	-
Flesh tone	3	41.0	44.0	7.0	2.0	-	-	-	6.0	-	-	-
	4	36.8	38.4	7.7	2.2	-	-	-	1.9	5.7	7.4	-
	5	44.0	34.0	11.0	6.0	-	-	-	5.0	-	-	-
	12	29.6	49.3	10.4	4.5	-	-	-	6.0	-	-	-
	14	86.1	3.2	2.2	6.5	-	-	-	2.1	-	-	-
	16	41.2	33.2	10.1	11.0	-	-	-	4.4	-	-	-
	17	47.9	69.8	22.8	4.4	-	-	-	3.0	-	-	-
	19	51.3	26.9	12.8	3.9	-	-	-	5.0	-	-	-
	24	33.3	35.9	17.1	9.0	-	-	-	4.7	-	-	-
Blue	7	23.0	-	-	-	61.6	-	-	-	15.4	-	-
	8	15.6	-	-	-	62.7	-	-	-	37.3	-	-
	25	1.6	-	2.9	-	82.8	-	-	-	12.8	-	-
	26	18.3	9.0	4.0	-	67.0	-	-	-	19.9	-	-
Grayish	11	29.8	22.2	10.7	1.7	15.3	-	6.2	-	14.0	-	
	18	29.6	13.5	5.5	2.9	15.2	-	13.5	-	19.8	-	-
Whitish	9	23.5	62.3	8.3	-	-	-	-	-	-	-	5.9
	13	39.0	41.0	12.5	3.0	-	-	-	4.5	-	-	-
	15	26.0	38.1	12.2	-	-	16.0	-	-	-	-	7.7
Dark zone	10	54.0	-	3.0	2.5	-	-	25.5	-	15.0	-	-
	21	48.6	23.1	7.6	-	51.2	-	-	-	18.0	-	-
	22	50.0	13.0	5.0	2.0	-	-	30.0	-	-	-	-
	23	53.0	9.9	6.4	2.1	-	-	28.6	-	-	-	-
	29	10.6	5.0	2.0	1.1	60.0	-	-	-	21.3	-	-
Brown.	6	68.0	10.0	5.0	3.0	-	12.6	-	1.4	-	-	-
	20	59.1	7.4	-	3.6	-	-	27.7	2.0	-	-	-

* Semiquantitative analysis; Gy = gypsum ($CaSO_4 \cdot 2H_2O$), Hy = Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), Ce = Cerussite ($PbCO_3$), Ci = Cinnabar (HgS), Laz = Lazurite ($(Na,Ca)_8(Al_6Si_6O_{24})(SiO_4, S, Cl)_2$), A = Apatite ($Ca_5(PO_4)_3(OH, F, Cl)$), Ap = Hidroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), Bi = Bindheimite ($Pb_2Sb_2O_6O$), Si = Silicates (Phlogopite ($K(Mg,Fe,Mn)_3Si_3AlO_{10}(F, OH)_2$), Feldspar ($KAlSi_3O_8$), Muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), H = Hematite ($Fe_2O_3$), Ca = Calcite ($CaCO_3$).

3.2. Ground Layer

In addition to the elements attributed to the support (Cu and traces of impurities not listed in Table 1), there was another group of elements that appeared in all the analyses carried out on the pictorial layer (points 1 to 34) that could be reasonably attributed to the composition of the ground layer, such as S, Ca, Pb, Fe, and Mn, the latter at trace level. Calcium and sulfur were related to the calcium sulfate used in this preparatory layer.

Although the S-Kα line was too close to the L-lines of Hg and also to the Pb-M-lines, the identification of gypsum ($CaSO_4 \cdot 2H_2O$) by X-ray diffraction in all the areas confirms its presence in the ground layer.

Some conclusions can be drawn from the histograms (Figure 5), considering only net areas greater than three times the statistical propagated deviation. All histograms presented the statistical propagated deviation bars, based on the repeatability study performed. This has drawn a line for the background signals of Mn, Fe, Pb, P, Ca, Sb, and Hg to differentiate between the elements present in all the analyzed areas and those that correspond to the pictorial layer. This signal helps to interpret the distribution of the materials identified in the present painting.

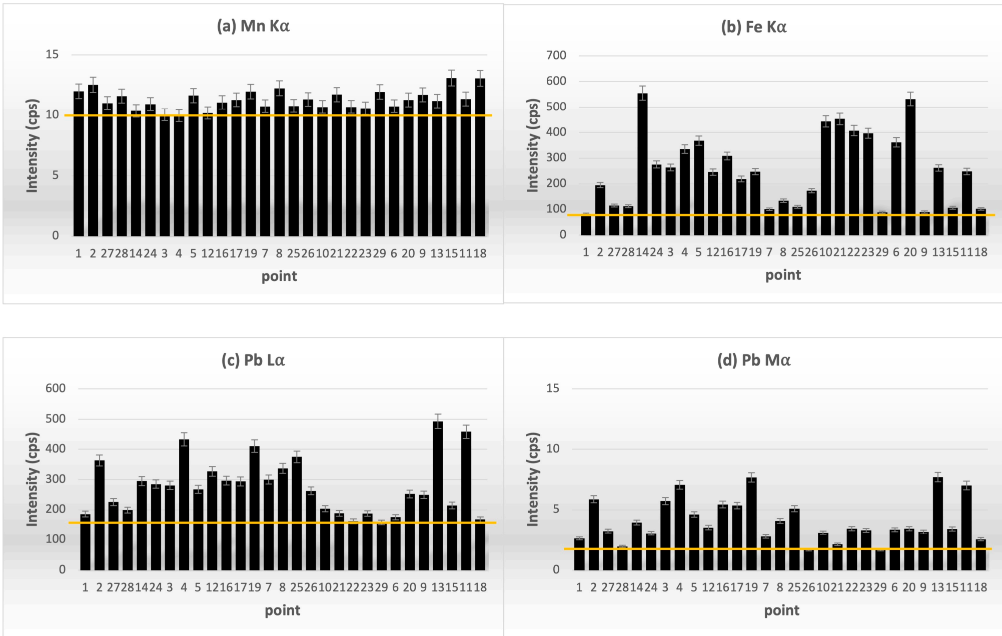

Figure 5. Line count rates histogram showing the net area for each analyzed point, determined via XRF.

Besides gypsum, brown ochre (Fe and Mn) was unevenly dispersed. This conclusion can be drawn from the histogram (Figure 5a) showing a low and uniform manganese content in all areas, confirming its use in the ground layer. It should be added that traces of pyrolusite (MnO_2) in the dark blue zone (point 7) are confirmed. Iron was detected as a major component, present throughout the painting (Figure 5b). Although the Fe signal from the brown ochre was indistinguishable from iron oxides due to the red pigment from the pictorial layer, the higher intensity of the Fe Kα line, particularly on the flesh tones and dark areas, could have confirmed its additional use in these areas.

Regarding the Pb X-ray fluorescence, a prominent line in all spots was observed, suggesting lead white pigment resulting from cerussite and hydrocerussite. Both mineral forms were confirmed in practically all areas of the figures of the scene, with the percentage of lead white being greater in the lighter areas than the darker ones. This correlates with the results obtained from the hydrocerussite map distribution shown in Figure 6c, providing a clearer image of the flesh tone areas. This observation is also fully consistent with the histograms showing the line count rates for each XRF analysis point (Figure 5). In Figure 5c,d in particular, corresponding to the intensity of Pb-Lα and Pb-Mα lines, higher intensity values of Pb-Lα can be appreciated compared to the lowest intensity Pb-Mα line. The Pb Lα/Pb Mα ratio shows values higher than those obtained in reference samples of lead white, previously made by our team for this purpose. This indicates, as per published research [28,29], that lead white is more abundant in the inner than in the upper layer. We can therefore conclude that the artist performs a preliminary study of the luminosity of the scene with the use of this white pigment. Nevertheless, in the flesh tone areas, the

Pb Lα/ Pb Mα ratio is lower, suggesting that the artist uses a more abundant lead white pigment on the pictorial layer. XRD mapping (Figure 6c) confirms the hypothesis of the artist's intention of lowering the color saturation of the pigments and increasing their lightness in the flesh tones.

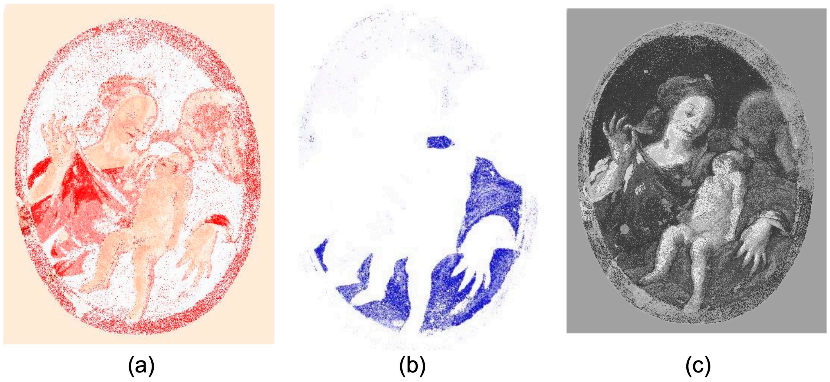

Figure 6. XRD mapping of each mineral with a color code: (**a**) cinnabar (correlated with red saturation); (**b**) lazurite (correlated with blue saturation); (**c**) hydrocerussite (correlated with white intensity).

All the results lead to the conclusion that the artist performed a preliminary study of the luminosity of the scene with the use of this white pigment. A sketch can be discerned above the ground layer, made with lead white in the highlights and some bone black in the dark or shadow areas. The use of bone black in the dark or shadow areas of the sketch, such as the Virgin's breast, scarf, hair, Saint Joseph's moustache, and the dark area (points 1, 11, 14, 18, 10, 20, 21, 22, 23, 24, 25 and 26), was confirmed by the XRF detection of P and Ca. The observation of the line count rate histogram of P-Kα and Ca-Kα for all measured spots (Figure 7a,b) clearly revealed P in the darkest areas of the painting, coinciding with a noticeable increment of Ca compared to other areas. This can be explained by assuming that, in addition to calcium sulfate in the ground layer, the excess of Ca is in the form of calcium phosphate ($Ca_3(PO_4)_2$) in the darker regions of the pictorial layer. Finally, the use of bone black (C+ ($Ca_3(PO_4)_2$) by the artist to modify the hues is confirmed by the apatite or hydroxyapatite found in these areas.

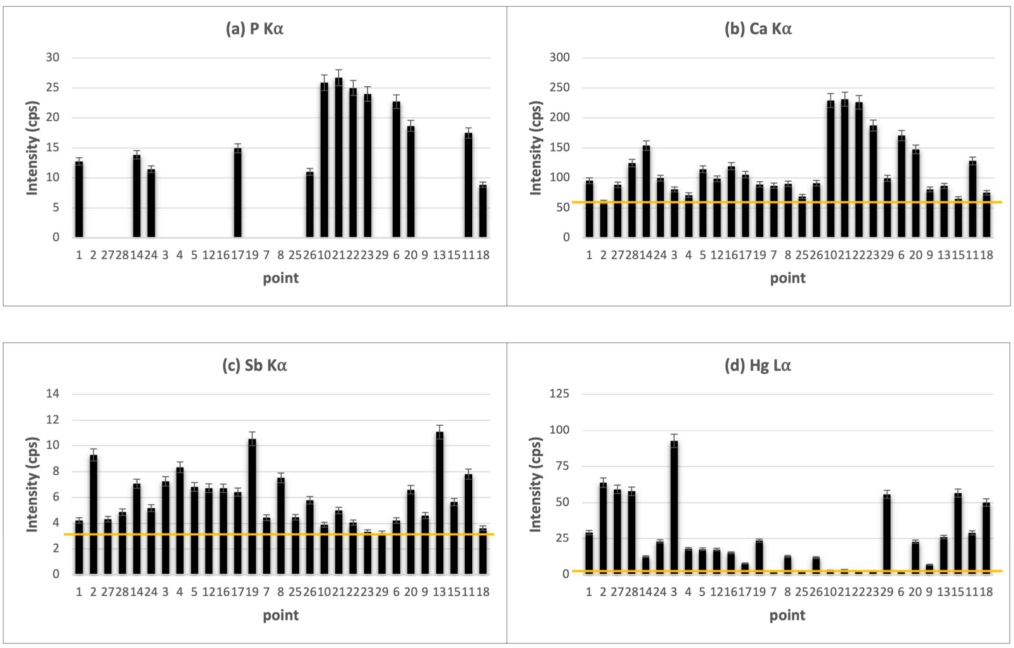

Figure 7. Line count rates histogram showing the net area for each analyzed point, determined via XRF.

3.3. Pictorial Layer

- Flesh tones

The pink tonalities of the flesh tones, as on the forearm, shoulder blade, cheeks, hand, knee, head, and belly (points 3, 4, 5, 12, 14, 16, 17, 19, and 24), were all characterized by the presence of Hg, S, and Pb, compatible with the use of lead white mixed with a low proportion of vermilion. According to the XRD results, both gypsum from the ground layer and hydrocerussite were main components in the diffractogram (removing copper), where their proportions were quite uniform in all flesh tones samples. This was not the case for point 14, measured on a darker flesh tone of Saint Joseph's head, and, therefore, with a much lower proportion of white lead (hydrocerussite) in the ground layer.

Cerussite, cinnabar, and a crystalline phase of bindheimite were found to a lesser extent in the pictorial layer. This Sb-rich Naples yellow pigment is often added to mixtures of lead white and vermilion to soften the high whiteness of the Pb pigment in the flesh tone areas. This hypothesis is supported by the Sb-Kα line (Figure 7c), showing trace levels at all points except in the dark areas of the painting. The vermilion spectrum is dominated by the Hg L-lines. The count rate histogram of Hg-Lα for all measured regions provides evidence of the use of vermilion in the reds and flesh tones. Figure 7d shows the histogram of the Hg-Lα line, with some peaks of exceptionally high Hg intensity when compared to other spectra measured in the same color. The resulting molecular distribution maps made it possible to distinguish pigments in the painting, such as vermilion, lead white, and lazurite (Figure 6).

- Red color

There was evidence of the use of vermilion mixed with lead white and some yellow Naples pigments in the reddish colors of the Virgin's breast, forearm, and sleeve (points 1, 2, 27, and 28), and peaks were found of Hg, Pb, and Sb. The cinnabar map (Figure 6a) displays firm evidence on the reds and flesh tones. It suggests the presence of iron oxides in addition to vermilion in these areas due to the major content of Fe observed via XRF. As described above, some bone black was incorporated into the mixture to provide darker and browner hues.

- Blue color

The blue areas of the Virgin's mantle (points 7, 8, 25, and 26) were interpreted via XRD, such as the lazurite mineral, the main constituent of lapis lazuli, in association with traces of silicaceous minerals such as phlogopite, muscovite, and feldspar (between 13% and 37%). The feldspar peaks can be distinguished at point 26, with difficulty due to the size of Figure 4, at 25.6°, 27.0°, and 29.7° of 2θ (not labeled in the figure).

It highlights that two areas located in the dark zone (21 and 29 points) show a notable presence of lazurite (51.2% and 60.0%, respectively) (Table 2), indicating an intentional addition of this pigment to obtain the darker tone, as discussed later.

- Grayish color

The grayish color (points 11,18) was achieved by mixing lazurite and lead white and traces of vermilion applied in a smooth layer as a glaze. This way of applying the paint, in very thin coats, reveals the tonality of the previous undercoats. In addition, hydroxyapatite was detected in the darkest zone along with Si compounds.

The grayish color was achieved by mixing lazurite, hydrocerussite, cerussite, and traces of cinnabar applied in a smooth layer as a glaze. This way of applying the paint in very thin coats impacted the tonality of the previous undercoats.

- Whitish color

Regarding the whitish color, it contained a high proportion of lead white (between 38.1% and 62.3% of hydrocerussite) and to a lesser extent calcite at the edge of the blouse and on both of the Virgin's hands (points 9, 15). Moreover, traces of bindheimite and cinnabar on the tunic of the Baby Jesus (point 13) were detected, likely due to transparency revealing the flesh tone under the robe layer.

- Brown and dark color

It should be noted that the dark areas at the top, left, and next to the lower left edge of the painting (points 10, 21, 22, 23, and 29) contained bone black (P and Ca, hydroxyapatite), lead white (hydrocerussite and traces of cerussite), vermilion, and, in points 21 and 29, a significant proportion of lazurite. Figure 6b confirms the rest of the lazurite in the dark areas at the top of painting, as well as traces of vermilion.

Regarding the brown color on Saint Joseph's moustache and the Virgin (points 6 and 20), almost negligible amounts of cinnabar, bindheimite, and hydrocerussite were observed. An analysis of P and excess Ca via XRF, and apatite and hydroxyapatite via XRD confirmed bone black in this area. No lazurite was detected in the brown area.

4. Discussion

In the present study, X-ray diffraction analysis (XRD) and hand-held X-ray fluorescence analysis (XRF) were used for the phase and elemental analysis of the pigments, respectively, on a small painting on a copper support. Its small size allowed it to fit into the XRD equipment, and the use of a hand-held XRF facilitated the in situ analysis.

The analysis showed a copper support, upon which gypsum was extended and mixed with an ochre earth pigment. Over this, a sketch using lead white and bone black suggested that the artist performed a preliminary study of the luminosity of the scene. Atop this were the pigments mixed with some lead white to lower the saturation and increase the lightness, as seen particularly in flesh tones.

Our research focused on comparing the pigments and materials used by Veronese and other contemporary painters of 16th and 17th century Italy, especially on paintings created on metallic supports. Both the inscription referencing Veronese on the back of this painting and the use of a copper support led us to explore its authorship and date.

Regarding the use of a metallic support, artists working in Venice during the Italian Renaissance period, such as Federico Barocci, Carlo Saraceni, Veronese, and other contemporaries, all did so on occasion [20,25,29,30]. Although Veronese painted predominantly on canvas and in large sizes [29,31,32], he also experimented with different types of supports and sizes, as can be seen in the Pietá and Saints [30], one of very few altarpieces anywhere painted on a copper support.

The ground layer over copper was mainly made up of gypsum, although mixed with some ochre earth pigment, providing a light coloring to this layer. This tinted ground has been found in three allegorical paintings by Veronese [32], as well as in other contemporary painting precursors of colored ground layers from the 15th to the mid-18th century [33,34]. The most common ground layer used for painting on copper support is lead white with some red earths or black pigments to modify the hue [24]. Gypsum ground layer has been found in the current painting but has only been detected in a few studies on copper supports [23]. The gypsum ground layer was more frequently used on canvases in the 16th and 17th centuries, and was less recommended on copper support because of the reaction of the metal with calcium sulfate, and the formation of copper sulfate, which affects the adhesion of the preparation layer [24].

The XRF and XRD results suggest a sketch over the ground layer that the artist created using lead white and bone black to outline the lights and shadows of the scene. It has been reported that the Italian painter Carlo Saraceni, from the beginning of the 17th century, also used dark areas without lead white to highlight the optical effect of the copper's natural tonality [25]. It is also known that Veronese made a very refined sketch, worked the chiaroscuro, deepened his study of color, and applied light impastos with innumerable transparencies.

The resulting palette contains lazurite, vermilion, brown earths, bone black, lead white, and Naples yellow pigments, mixed with some lead white to lower the color saturation value of the pigments and increase their lightness value. The identified color palette includes high-quality, high-priced pigments such as vermilion and ultramarine blue. These pigments are common in the palette used by P. Veronese and have already been identified in other studies [29–32]. These pigments are also common to painters of the Venetian school, along with lake red, lead white, lead-tin yellow (I), lead-tin yellow (II), orpiment, realgar, earth, azurite, enamel, and copper malachite resinate [33,34], although in this case study not all of these pigments are present, as it is a small painting with a reduced palette. During the 16th century, the city of Venice was a center of economic and commercial exchange and painters such as Tintoretto, Veronese, and others had access to these materials [35,36]. Lead antimonate yellow (Naples yellow) enjoyed its highest popularity in Europe from 1600 to 1800 [37] but it had not been described in the literature as a pigment used by the artists mentioned. Nevertheless, in the present painting, traces of bindheimite mineral were confirmed via XRD analysis, in addition to the absence of Sn. Consequently, no lead-tin yellow pigment was present. Synthetic variants of lead yellows were developed due to interests in glass and ceramic colors from very early times, and were later used as pigments for wall paintings, easel paintings, polychromies, and manuscript decorations. Lead, tin, and antimony yellow (known as Naples yellow) were used at the same time as other very similar lead yellows, such as lead yellow type II and tin yellow and lead antimonate yellow, in 17th century Italian paintings. The crystalline structure of Naples Yellow is similar to that of the mineral bindheimite, known and used as early as the 16th century BC. C. Cennini mentions the term “giallorino” in a generic way for all those yellows used in Italy in which there was lead, so it is difficult to identify and delimit the use and appearance of this Naples Yellow compared to other lead yellows [38,39]. By means of Raman spectrometry, it has been possible to differentiate and identify Naples Yellow in 17th century Italian paintings, specifically in works by Giovanni Battista Langetti and Luca Giordano [39].

Areas affected by copper oxidation degradation known as pitting were observed (Figure 2, points 30–34). This degradation could have been caused by the loss of preparation and the pictorial layer that exposed the copper support, later being affected by humidity and oxygen. Following analysis, the composition of the superficial faults detected by the XRF was identical to those of the support (Table 1). The lack of paint layers could be due to the adhesion problems that a ground layer with gypsum can cause [36]. Another hypothesis is that the pitting was the cause of the loss of the pictorial layers. The deformation of the support under manipulation could have caused excessive tension, causing the detachment of the paint.

5. Conclusions

The present study of a painting on copper support aims to unveil the palette used by the artist. The research carried out represents an advancement in the knowledge on paintings on metal supports, as this area is in need of more studies. Avoiding sample extraction, non-invasive techniques such as X-ray diffraction (XRD) and hand-held X-ray fluorescence (XRF) were proven to be highly effective. Moreover, it has been proposed that the stratigraphic design of the painting is more compatible with the results obtained in the XRF and XRD studies. Unfortunately, no in situ Raman signal could be obtained from any areas of painting due to the fluorescence phenomena. Although the painting had the inscription “*Boceto di Pablo Veronese*” on the back, this study has no intention of attributing this painting to the brush of Veronese, but instead simply aims to compare the materials used and the hypothesized artistic technique with other paintings of artists from the Italian Renaissance period. Veronese’s ability to innovate and experiment with format, size, pigments, and supports is well known, as is that of Veronese’s followers who participated in the innovations of the artist’s final years. As such, the precise authorship of this painting is difficult.

This study is an initial approach to understanding the historical period and geographical area of the origin of this painting, via the study of the materials used and their distribution in the pictorial layers, without damaging it. The advanced scientific and historical-artistic studies of the painting that our multidisciplinary group (heritage restoration, art historians, mineralogy, optics, computer science and chemistry) is currently carrying out will help to formulate a hypothesis about the authorship and dating of the painting.

Author Contributions: Conceptualization, R.B., E.M. and J.L.V.; methodology, R.B., E.M.; software, R.B.; formal analysis, R.B., E.M., N.D.-G.; investigation, R.B., E.M., A.L.-M.; resources, data curation, writing, original draft preparation, writing, review and editing, supervision, R.B., E.M.; Project Administration R.B., J.L.V., R.B., E.M., A.L.-M.: The authors belongs to the research team Unit of Non-Invasive Analytical Techniques (University of Granada, Spain) funded by EQC2018-004952-P, A-HUM-164-UGR18 Projects and Research Group of Analytical Chemistry and Life Sciences, FQM-338 (University of Granada, Spain). J.L.V. is responsible for the research team Unit of Non-Invasive Analytical Techniques (University of Granada, Spain) and the IP of Research Group. R.B.: Full Professor of Analytical Chemistry at the Department of Analytical Chemistry applied Cultural Heritage of the University of Granada, Spain; E.M. (corresponding author): Professor of Analytical Chemistry applied Cultural Heritage at the Department of Analytical Chemistry of the University of Granada, Spain A.L.-M.: Professor of Restoration at the Department of Painting of the University of Granada, Spain. N.D.-G.: Centre for Scientific Instrumentation of the University of Granada (CIC). and J.L.V.: Full Professor of Analytical Chemistry at the Department of Analytical Chemistry of the University of Granada, Spain. All authors have read and agreed to the published version of the manuscript.

Funding: The present work has received financial support from the research project FEDER/Junta de Andalucía-Consejería de Economía y Conocimiento/A-HUM-164-UGR18 and the research group FQM-338. We also acknowledge the Non-Invasive Analytical Techniques Unit EQC2018-004952-P for providing the hand-held XRF instrumentation.

Data Availability Statement: The data presented in this study are available on request from the corresponding authors. The data are not publicly available as the painting is privately owned.

Acknowledgments: We thank Jose Romero Garzón for their help with the XRD study.

Conflicts of Interest: The authors declare that they have no competing interests.

References

1. López-Ramírez, M.R.; Navas, N.; Rodríguez-Simón, L.R.; Otero, J.C.; Manzano, E. Study of modern artistic materials using combined spectroscopic and chromatographic techniques. Case study: Painting with the signature "Picasso". *Anal. Method.* **2015**, *7*, 1499–1508. [CrossRef]
2. Simon, S.; Röhrs, S. Between fakes, forgeries, and illicit artifacts—Authenticity studies in a heritage science laboratory. *Arts* **2018**, *7*, 20. [CrossRef]
3. Manzano, E.; Blanc, R.; Martin-Ramos, J.D.; Chiari, G.; Sarrazin, P.; Vilchez, J.L. A combination of invasive and non-invasive techniques for the study of the palette and painting structure of a copy of Raphael's Transfiguration of Christ. *Herit. Sci.* **2021**, *9*, 150. [CrossRef]
4. Manzano, E.; Rodríguez-Simón, L.R.; Navas, N.; Capitán-Vallvey, L.F. Non-Invasive and Spectroscopic Techniques for the Study of Alonso Cano's Visitation from the Golden Age of Spain. *Stud. Conserv.* **2021**, *66*, 298–312. [CrossRef]
5. Robledo, J.I.; Leani, J.J.; Sánchez, H.J. Possibilities of spatially-resolved energy dispersive inelastic X-ray scattering (EDIXS) spectroscopy for painting characterization. *Spectrochim. Acta Part B At. Spectrosc.* **2022**, *198*, 106552. [CrossRef]
6. Van de Voorde, L.; Vekemans, B.; Verhaeven, E.; Tack, P.; De Wolf, R.; Garrevoet, J.; Vincze, L. Analytical characterization of a new mobile X-ray fluorescence and X-ray diffraction instrument combined with a pigment identification case study. *Spectrochim. Acta Part B At. Spectrosc.* **2015**, *110*, 14–19. [CrossRef]
7. Bonizzoni, L.; Caglio, S.; Galli, A.; Poldi, G. A non-invasive method to detect stratigraphy, thicknesses and pigment concentration of pictorial multilayers based on EDXRF and vis-RS: In situ applications. *Appl. Phys. A* **2008**, *92*, 203–210. [CrossRef]
8. Martin-Ramos, J.D.; Zafra-Gómez, A.; Vílchez, J.L. Non-destructive pigment characterization in the painting Little Madonna of Foligno by X-ray Powder Diffraction. *Microchem. J.* **2017**, *134*, 343–353. [CrossRef]
9. Artioli, G. Science for the cultural heritage: The contribution of X-ray diffraction. *Rend. Lincei* **2013**, *24*, 55–62. [CrossRef]
10. Andrić, V.; Gajić-Kvaščev, M.; Crkvenjakov, D.K.; Marić-Stojanović, M.; Gadžurić, S. Evaluation of pattern recognition techniques for the attribution of cultural heritage objects based on the qualitative XRF data. *Microchem. J.* **2021**, *167*, 106267. [CrossRef]
11. Pitarch, A.; Ramón, A.; Álvarez-Pérez, A.; Queralt, I. Characterization of "oil on copper" paintings by energy dispersive X-ray fluorescence spectrometry. *Anal. Bioanal. Chem.* **2012**, *402*, 1481–1492. [CrossRef] [PubMed]
12. Nakai, I.; Abe, Y. Portable X-ray powder diffractometer for the analysis of art and archaeological materials. *Appl. Phys. A* **2012**, *106*, 279–293. [CrossRef]

13. Hirayama, A.; Abe, Y.; van Loon, A.; De Keyser, N.; Noble, P.; Vanmeert, F.; Nakai, I. Development of a new portable X-ray powder diffractometer and its demonstration to on-site analysis of two selected old master paintings from the Rijksmuseum. *Microchem. J.* **2018**, *138*, 266–272. [CrossRef]
14. Hocquet, F.P.; Calvo del Castillo, H.; Cervera Xicotencatl, A.; Bourgeois, C.; Oger, C.; Marchal, A.; Strivay, D. Elemental 2D imaging of paintings with a mobile EDXRF system. *Anal. Bioanal. Chem.* **2011**, *399*, 3109–3116. [CrossRef]
15. Gonzalez, V.; Cotte, M.; Vanmeert, F.; de Nolf, W.; Janssens, K. X-ray Diffraction Mapping for Cultural Heritage Science: A Review of Experimental Configurations and Applications. *Chem.–A Eur. J.* **2020**, *26*, 1703–1719. [CrossRef]
16. Martin-Ramos, J.D.; Chiari, G. SmART_scan: A method to produce composition maps using any elemental, molecular and image data. *J. Cult. Herit.* **2019**, *39*, 260–269. [CrossRef]
17. Komanecky, M.K.; Bowron, E.P.; Bargellini, C. *Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575–1775*; The Phoenix Art Museum, Oxford University Press: Oxford, UK, 1999; ISBN 0-19-512397-2. Available online: https://www.gettextbooks.com/isbn/9780195123975/ (accessed on 20 March 2023).
18. Pitarch, A.; Ramón, A.; Álvarez-Pérez, A.; Castro, K.; Madariaga, J.M.; Queralt, I. Multispectroscopic characterization of oil on copper painting. *Spectrosc. Lett.* **2014**, *47*, 38–51. [CrossRef]
19. Bowron, E.P. A brief history of European oil paintings on copper, 1560–1775. In *Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575–1775*; The Phoenix Art Museum; Oxford University Press: Oxford, UK, 1999; pp. 9–30, ISBN 0-19-512397-2.
20. Zaccaron, S.; Grespan, C.; Ganzerla, R. Characterization of pigments on paintings on copper plate. A case study: The copy of La sepoltura di Cristo by Federico Barocci. *Sci. Ca'Foscari* **2013**, *1*, 48–56.
21. Corregidor, V.; Oliveira, A.R.; Rodrigues, P.A.; Alves, L.C. Paintings on copper by the Flemish artist Frans Francken II: PIXE characterization by external mi-crobeam. *Nucl. Instrum. Methods B* **2015**, *348*, 291–295. [CrossRef]
22. Donahue-Wallace, K. *Copper as Canvas: Two Centuries of Masterpiece Paintings on Copper, 1575–1775*; Phoenix Art Museum, Nelson-Atkins Museum of Art, The Sixteenth Century Journal; 2000; Volume 31, pp. 874–876. Available online: https://www.jstor.org/stable/2671133?origin=crossref (accessed on 20 March 2023).
23. Alvarez, M.C. La restauración: Recuperación de una memoria pictórica en una nueva instancia. In *En Lecciones barrocas: Pinturas sobre la vida de la Virgen de la Ermita de Egipto*; Departamento editorial del Banco de la República: Bogotá, Colombia, 1990; pp. 20–39.
24. Pavlopoulou, L.C.; Watkinson, D. The degradation of oil painted copper surfaces. *Stud. Conserv.* **2006**, *51* (Suppl. S1), 55–65. [CrossRef]
25. Rodriguez, S.H.; Appoloni, C.R.; Campos, P.H.O.V.; Gonçalves, B.; Kajiya, E.A.M.; Molari, R.; Winter, C. Non-Destructive and portable analyses helping the study and conservation of a Saraceni copper plate painting in the São Paulo museum of art. *Microchem. J.* **2020**, *155*, 104787–104799. [CrossRef]
26. Vega, D.; Pombo Cardoso, I.; Carlyle, L. Pintura sobre cobre: Investigación sobre materiales y técnicas de aplicación de la capa de preparación a través de los tratados tradicionales y estudio analítico de dos obras atribuidas a las escuelas portuguesa y flamenca. *Conserv. Patrim.* **2018**, *27*, 23–35. [CrossRef]
27. Spring, M.; Grout, R. The blackening of vermilion: An analytical study of the process in paintings. *Natl. Gallery Tech. Bull.* **2002**, *23*, 50–61. Available online: https://www.jstor.org/stable/42616159 (accessed on 20 March 2023).
28. Ruberto, C.; Mazzinghi, A.; Massi, M.; Castelli, L.; Czelusniak, C.; Palla, L.; Raffaelli, M. Imaging study of Raffaello's "La Muta" by a portable XRF spectrometer. *Microchem. J.* **2016**, *126*, 63–69. [CrossRef]
29. Penny, N.; Roy, A.; Spring, M. Veronese's Paintings in the National Gallery Technique and Materials: Part II. *Natl. Gallery Tech. Bull.* **1996**, *17*, 32–55. Available online: http://www.nationalgallery.org.uk/technical-bulletin/penny_roy_spring1996 (accessed on 20 March 2023).
30. Armstrong, L. Passion in Venice: Crivelli to Tintoretto and Veronese (New York, Museum of Biblical Art [MOBIA], 11 February–12 June 2011). Passion in Venice: Crivelli to Tintoretto and Veronese, The Man of Sorrows in Venetian Art. *Renaiss. Stud.* **2012**, *26*, 441–449. Available online: https://www.jstor.org/stable/24420075 (accessed on 20 March 2023). [CrossRef]
31. Penny, N.; Spring, M. Veronese's Paintings in the National Gallery. Technique and Materials: Part I. *Natl. Gallery Tech. Bull.* **1995**, *16*, 4–29. Available online: http://www.nationalgallery.org.uk/technical-bulletin/penny_spring1995 (accessed on 20 March 2023).
32. Mahon, D.; Centeno, S.A.; Wypyski, M.T.; Salomon, X.F.; Bayer, A. Technical study of three allegorical paintings by Paolo Veronese: The choice between virtue and vice, wisdom and strength, and mars and venus united by love. In *Metropolitan Museum Studies in Art, Science, and Technology*; The Metropolitan Museum of Art: New York, NY, USA, 2010; Volume 1, ISBN 978-1-58839-365-4. Available online: https://www.researchgate.net/publication/260418022_Technical_Study_of_Three_Allegorical_Paintings_by_Paolo_Veronese_The_Choice_Between_Virtue_and_Vice_Wisdom_and_Strength_and_Venus_and_Mars_United_by_Love (accessed on 20 March 2023).
33. Zagora, J. Historical Development of Coloured Grounds in Italian Painting from the 15th to the mid-18th Century–Present Insights and Open Questions. *Portal Godišnjak Hrvat. Restaur. Zavoda* **2017**, 73–94. Available online: http://www.hrz.hr/images/portal/portal_08_zagora1.pdf (accessed on 20 March 2023). [CrossRef]

34. Komanecky, M.K.; Horovitz, I.; Eastaugh, N. *Catalogue "Painting Techniques History, Materials and Studio Practice: Contributions to the IIC Dublin Congress, 7–11 September 1998"*; International Institute for Conservation of Historic and Artistic Works: London, UK, 1998; pp. 136–139. ISBN 0950052582.
35. Uffelman, E.S.; Court, E.; Marciari, J.; Miller, A.; Cox, L. Handheld XRF Analyses of Two Veronese Paintings. In *Collaborative Endeavors in the Chemical Analysis of Art and Cultural Heritage Materials*; American Chemical Society: Washington, DC, USA, 2012; pp. 51–73. [CrossRef]
36. Osticioli, I.; Pagliai, M.; Comelli, D.; Schettino, V.; Nevin, A. Red lakes from Leonardo's Last Supper and other Old Master Paintings: Micro-Raman spectroscopy of anthraquinone pigments in paint cross-sections. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2019**, *222*, 117273. [CrossRef]
37. Sandalinas, C.; Ruiz-Moreno, S. Lead tin-antimony yellow, historical manufacture, molecular characterization and identification in seventeenth-century Italian paintings. *Stud. Conserv.* **2003**, *49*, 41–52. [CrossRef]
38. Hradil, D.; Grygar, T.; Hradilová, J.; Bezdička, P.; Grűnwaldová, V.; Fogaš, I.; Miliani, C. Microanalytical identification of Pb-Sb-Sn yellow pigment in historical European paintings and its differentiation from lead tin and Naples yellows. *J. Cult. Herit.* **2007**, *8*, 377–386. [CrossRef]
39. Ruiz-Moreno, S.; Pérez-Pueyo, R.; Gabaldón, A.; Soneira, M.J.; Sandalinas, C. Raman laser fibre optic strategy for non-destructive pigment analysis. Identification of a new yellow pigment (Pb, Sn, Sb) from the Italian XVII century painting. *J. Cult. Herit.* **2003**, *4*, 309–313. [CrossRef]