



Article Material and Technical Analysis of La Inmaculada by Francisco Pacheco

Anabelle Kriznar ¹, Javier Moreno-Soto ^{2,3}, Antonio Gamero-Osuna ⁴, Agustín Martín-de-Soto ⁴, Francisco José Ager ^{3,5} and Miguel Ángel Respaldiza ^{3,6,*}

- ¹ Departmento de Escultura e Historia de las Artes Plásticas, Facultad de Bellas Artes, Universidad de Sevilla, C/Laraña 3, 41003 Seville, Spain
- ² Departamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería Informática, Universidad de Sevilla, Avda. Reina Mercedes s/n, 41012 Seville, Spain
- ³ Centro Nacional de Aceleradores (US), Avda. Thomas A. Edison 7, 41092 Seville, Spain; fjager@us.es
- ⁴ Conservation-Restoration Workshop, Archbishop's Palace, Plaza Virgen de los Reyes, 41001 Seville, Spain
- ⁵ Departamento de Física Aplicada I, Escuela Politécnica Superior, Universidad de Sevilla, C/Virgen de África 7, 41011 Seville, Spain
- ⁶ Departmento de Física Atómica, Molecular y Nuclear, Facultad de Física, Universidad de Sevilla, Avda. Reina Mercedes s/n, 41012 Seville, Spain
- * Correspondence: respaldiza@us.es

Abstract: Francisco Pacheco (1564–1644) was one of the most important Spanish painters, the author of the famous treatise Art of Painting, and a founder of Seville art school. His painting La Inmaculada (1610) forms part of the important art collection in the Archbishop's Palace in Seville and represents the first realization of a new iconography, established by Pacheco. Later, he carried out several paintings with the same subject which are today in different collections. As part of a larger project, La Inmaculada was recently restored and analysed. The characterization of materials and painting procedures was carried out applying noninvasive in situ analysis by ultraviolet fluorescence (UVF), infrared reflectography (IRR), and X-ray fluorescence spectrometry (XRF). Results revealed many retouches, probably from different periods, as well as some pentimenti in the composition. Chemical analysis indicates a preparation made of Seville clay, lead white and some calcite on an animal glue layer, according to Pacheco's own treatise, and a corresponding pigment palette for the 17th century: lead white, yellow and red earths, lead–tin yellow, vermilion, azurite, smalt, a copper-based green, umber, and bone black. Furthermore, modern pigments such as titanium and zinc whites, chrome green, and cadmium yellow were also identified as results of later interventions.

Keywords: Francisco Pacheco; La Inmaculada; supports; pigments; preparatory drawing; noninvasive analysis; UVF; IRR; XRF

1. Introduction

Francisco Pacheco (1564–1644) was already a renowned artist during his life and is still considered one of the most important Spanish painters of the Mannerist style [1,2]. He is well known for his art, as a teacher of Diego Velazquez and Alonso Cano, as well as for his treatise Art of Painting (Arte de la Pintura; [3]), published posthumously in 1649. It is an important source for studying the 17th century painting technique in Spain and a guide for many contemporary and later artists, since it precisely describes the materials (supports, preparation, pigments, binders) and the manner of painting in order to achieve desired results. In Seville, he founded an art school, where he emphasized the academically correct representation of religious iconography. One of his works represents the Virgin Mary, La Inmaculada (Figure 1), painted on canvas in oil technique around 1610–1615. It forms part of the art collections held at the Archbishop's Palace in Seville, one of the most prominent painting compendiums in Spain. It is considered the earliest and the simplest 17th century



Citation: Kriznar, A.; Moreno-Soto, J.; Gamero-Osuna, A.; Martín-de-Soto, A.; Ager, F.J.; Respaldiza, M.Á. Material and Technical Analysis of La Inmaculada by Francisco Pacheco. *Minerals* 2023, *13*, 541. https:// doi.org/10.3390/min13040541

Academic Editors: Marco Benvenuti, Silvana Fais and Giuseppe Casula

Received: 9 February 2023 Revised: 16 March 2023 Accepted: 1 April 2023 Published: 12 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). representation of a new iconography of the Immaculate Conception, depicted for the first time in this manner precisely by Pacheco. La Inmaculada Concepción de la Virgen (Immaculate Conception of the Virgin Mary) is one of the most repeated iconographies in the Spanish art since the 15th century and is very popular especially in Spanish Baroque art. The iconography is based on the Catholic dogma stating that the Virgin Mary's conception is free of the original sin. She is shown as a young woman, dressed in white tunic and blue coat, with symbols of purity and eternity, crowned by a nimbus of twelve stars, standing on top of a half-moon, sometimes with a snake at her feet (not in this Pacheco version), symbolizing her domain over the sin. Under her feet, a landscape with trees, buildings, sea, and a boat can be depicted, indicating the Virgin's role as the intermediary between the Earthly world and God. In this Pacheco version, the landscape shows contemporary Seville with its Torre del Oro. In later variants, the Virgin is usually accompanied by angels. Traditionally, the Virgin Mary is dressed in a red (not white) tunic which can symbolize her royalty or the Passion of Christ and can be still found in later Inmaculadas; however, the new white-and-blue vestment was painted for the first time in the Inmaculada studied in this research. This iconographic representation influenced many other Spanish painters such as Velázquez, Herrera, El Greco, Zurbarán, Ribera, Valdés Leal, and Murillo, while it also served as inspiration for Virgin's imagery in the holy processions in Seville [3–5].



Figure 1. Francisco Pacheco: La Inmaculada, 1610, Archbishop's Palace, Seville.

Later on, Pacheco carried out other Inmaculadas, several of which are still in Seville. Surprisingly, the artist decided to use the traditional red–blue vestment iconography. Among these are La Inmaculada con Miguel Cid (1619) in the Cathedral of Seville, La Inmaculada con Vázquez de Leca (1621) in a private collection of Marqués de la Reunion de Nueva España, and La Inmaculada from the church of San Lorenzo in Seville (1624). None of them have been studied from a materials point of view, but this is one of the research goals in the future, in order to compare them to the panel presented in this work.

During the last couple of years, the Archbishop's Palace patrimony has been systematically studied, restored, and conserved as a principal aim of a larger project. The present painting was one of the selected ones to be restored and studied; therefore, a concise material and technical research was carried out. The analytical study of this canvas was a once-in-a-lifetime opportunity, since it is part of the Archbishop's personal collection, where it was returned after its restoration. All available noninvasive analytical techniques at the time were used. Considering other Pacheco paintings with the same iconography, this study is a perfect start for any future analysis and technical–material comparison among them.

The painting went through an analytical process, in order to identify the support, original pigments, later interventions, possible preparatory drawings, and the painting technique in general. Obtained data offer a deeper insight into the understanding of Pacheco's way of painting and a more thorough comparison to other known works attributed to the artist, especially to other existent Inmaculadas. One of the most important objectives was to use this material analysis as support in the conservation–restoration process.

2. Materials and Methods

As it was not possible to extract samples, only noninvasive techniques available at that time were used: ultraviolet fluorescence photography, infrared reflectography (IRR), and X-ray fluorescence spectrometry (XRF). They were all applied in situ in the conservation–restoration workshop of the palace (Figure 2).



Figure 2. XRF in situ analysis of La Inmaculada.

2.1. Ultraviolet Fluorescence (UVF)

This technique [6–10] is generally used to identify later interventions, which greatly helps in the cleansing process of the painting surface. It is also a very useful tool for selecting original areas for the following chemical analysis. UVF images were taken with a Nikon D3X camera (Nikon, Tokyo, Japan), at 400 ISO and 20 s of exposure time, with the painting being homogeneously illuminated with four wood lamps, two on each side of the canvas, using the UVGL-55 model with double band wavelength (254 nm/365 nm), in a completely darkened room.

2.2. Infrared Reflectography (IRR)

IRR [6,7,11–13] can reveal possible underdrawings and *pentimenti*, changes in the composition. It can help with the authentication of a painting, generally revealing the proper handstroke of the artist. For this technique, a small 5 cm³ XenICs (Leuven, Belgium) near-IR camera Xeva-XS 512 with InGaAs detector and Pentax lens of 16 mm, F/1.4 (320 × 256 pixel resolution) in the range of 900–1700 nm was used. The painting surface was illuminated with two 800 W halogen SDI lamps. The camera was mounted on a 2D robotic Optimind platform at 32 cm from the painting to obtain high movement precision along the studied surface.

2.3. X-ray Fluorescence Spectrometry (XRF)

XRF [6,7,14–17] can identify inorganic materials used in the artwork: preparation and priming, as well as original pigments and those applied in later interventions. It allows an elemental analysis, followed by the characterization of materials applied in the selected area, based on their characteristic chemical elements. Our XRF equipment was composed of a RX38 X-ray generator from EIS S.L. with W anode, 1 mm Al filter to suppress W peaks, and a Si drift detector (SDD). The measuring distance was fixed to 1 cm from the painting surface by the intersection of two lasers. The generator was always operating under the same conditions: 33.4 kV and 80 μ A with 200 s acquisition time. The appearance of Zr peaks in every spectrum is due to its presence in the collimator of the detector. The areas of the XRF peaks observed in the spectra were used to perform a semiquantitative analysis of the colors and estimate whether a particular element belongs to the surface layer or to an inner layer of the painting.

3. Results

Results obtained by all selected analytical methods are presented and compared with available information found about Francisco Pacheco and materials he used to apply.

3.1. UVF and IRR Examination

The ultraviolet fluorescence revealed many smaller and larger retouches spread around the surface (Figure 3). They must have been carried out at different times, showing varied tonalities of material fluorescence. The largest interventions can be found on the left margin, next to the Virgin's right hip and left foot, revealing more important damages suffered by the painting. IRR confirmed several retouches and the use of different pigments as well; however, at first sight, no preparatory drawing can be appreciated (Figure 4). At a closer look, an underdrawing can be observed on the half-moon and on the boat (Figure 5a,b), while there is a small pentimento, a slight change in the composition of the architecture in the left bottom corner; the painter shortened some of its walls, painted with a reddishbrown color, obtained by mixing earths (Fe), a copper-based green pigment (Cu), lead white (Pb), and a small amount of umber (Mn, Fe) and vermilion (Hg), as studied later by XRF. An interesting observation is that the trees in the lower right corner almost disappear on the IRR image.



Figure 3. UVF image of La Inmaculada, showing many retouched areas, the largest one located next to the Virgin's left foot.



Figure 4. IRR image of La Inmaculada, confirming several retouched areas, the use of different pigments, underdrawing on the half-moon, and the change in the form of the architecture on the right.

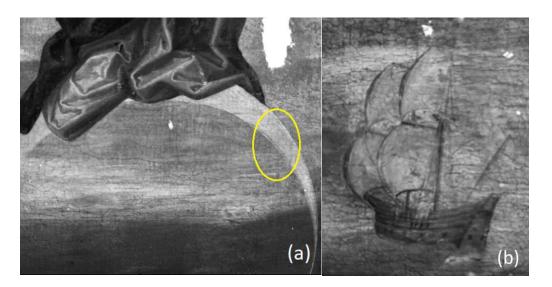


Figure 5. Detail of the IRR image, showing the underdrawing (**a**) on the half-moon and (**b**) for the design of the boat.

3.2. XRF Analysis of Materials Applied

Altogether, 38 points of different colors and tonalities were selected, in order to obtain knowledge not only on preparation and pigments, but also on their mixture and the construction of lights and shades. XRF is a great tool for the identification of most preparations and pigments; however, there are some withdrawals that call for the implementation of other complementary analytical techniques, which was not possible in this study. In this regard, pigments characterized by the same chemical element, such as copper or lead-based pigments, cannot be differentiated except by their visual color. On the other hand, organic materials such as lakes or binders that are composed of light elements cannot be identified by XRF, since it generally detects only elements heavier than Z < 14 (Si) [14,15,17].

3.2.1. Original Materials

Materials present in the painting were characterized: preparation, priming, and pigments. The summary is presented in Table 1. The presence of calcium (Ca) in all analysed areas suggests the use of calcium-based preparation, chalk, or gypsum. Nevertheless, from Pacheco's famous treatise Art of Painting [3] and some studies carried out on Andalusian contemporary painters [18–21], we know that Pacheco did not use gypsum for preparation layers (aparejo, as he calls it), finding it unstable as a painting support; the experience showed him that it moistens and rots with time, also affecting the canvas and color layers. Instead, he preferred well-grounded special Seville clay, tempered with linseed oil, to which he could also add lead white, as he describes in his text [3,20,22]. This explains the presence of Fe and Pb in all analysed areas, although both elements also identify related pigments applied as color layers, while lead compounds can be used as siccative, as well. From Pacheco's treatise we can also learn that before this earth-based preparation [preparación], he used to apply several layers of animal glue ("la cola de guantes flaca") over the entire surface of the prepared canvas to seal it. On the other hand, in other contemporary preparation layers, earths and clays could be combined with some pulverized calcium carbonate or some other pigments, as in the case of Murillo's primers [18,19,21]. Therefore, some chalk was probably also added to the La Inmaculada primer, which can explain the presence of Ca in all analysed points. This hypothesis can be supported by some studies carried out in the Museo de Bellas Artes de Sevilla on two Pacheco's paintings (St. Francis with the Cross and The Mystical Nuptials of St. Agnes), which confirm the reddish preparation made of earths and calcite, while in the case of St. Francis, also includes minium [20].

Preparation, Pigments	Chemical Formula/Elements	Principal Use
	ORIGINAL MATERIALS	
Animal glue	Ca	Sealing layers
Seville clay + lead compounds	Fe, Pb	Preparation/priming
Lead white	2PbCO ₃ ·Pb(OH) ₂	Flesh tones, highlights, clouds, sky, aureola, moon
Yellow earth	Fe(OH) ₂	Aureole, crown, hair, clouds, town, landscape
Lead-tin yellow	Pb_2SnO_4	Highlights—crown, trees, clouds
Red earth	Fe ₂ O ₃	Addition to other pigments
Vermilion	HgS	Flesh tones, lips, red and pink flowers
Red lake	Unidentified, Ca substrate	Pink flowers
Smalt	Diverse chemical compounds, containing Co , Ni , As , Ni, Si, K, Bi.	Sky, clouds, see, town, landscape
Azurite	2CuCO·Cu(OH) ₂	Virgin's coat; in green hues?
Green—questionable use	A Cu-based compound	Landscape, flesh-tones?
Umber	$ \begin{array}{c} \textbf{Fe}_2\textbf{O}_3 + \textbf{Mn}\textbf{O}_2 + \textbf{n}\textbf{H}_2\textbf{O} + \textbf{Si} + \\ \textbf{Al}_2\textbf{O}_3 \end{array} $	Virgin's hair, ground, fountain, architecture, shades
Bone black	$Ca_3(PO_4)_2 + CaCO_3 + C$	Shades, darkest hues
	INTERVENTIONS	
Chalk or gypsum	$CaCO_3$ or $CaSO_4$	Filler
Titanium white	TiO ₂	- Retouches
Zinc white	ZnO	
Cadmium yellow	CdS	
Chrome green	Cr ₂ O ₃	

Table 1. Systematic representation of original and modern materials identified in La Inmaculada by XRF, with characteristic chemical elements for each material in bold.

Regarding the original pigments that compose Pacheco's palette, they are all common for the 17th century [3,18,23–25]: lead white (Pb), yellow and red earths (Fe), lead–tin yellow (Pb, Sn), vermilion (Hg), smalt (K, Co, Ni, As), and azurite (Cu). A copper-based green pigment (Cu), umber (Mn, Fe), bone black (Ca), and an organic red lake on the calcium substrate are also probable. Lead white, identified by intense Pb peaks, was used for all white areas, such as the half-moon, white aura around the Virgin, for her white tunic, and was largely added for lighting other colors. It was also used as a principal pigment for flesh tones, mixed with other pigments such as earths (Fe), vermilion (Hg), and azurite or a green copper-based green pigment (Cu), depending on the lighter or darker flesh tonality that Pacheco wished to obtain. Vermilion is highly present in reddish areas such as the Virgins' cheeks and decreases in lightest flesh tones, where lead white predominates. Shades were carried out with higher presence of a copper-based pigment, some umber (Mg, Fe), and bone black (Ca), while in light tones they almost disappear (Figure 6).

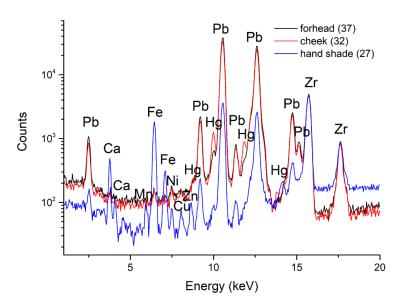


Figure 6. Comparison of XRF spectra of different flesh tones: light forehead (black line) with predominant presence of lead white (Pb), reddish cheek (red line) with higher amount of vermilion (Hg), and dark hand shade (blue line) with umber (Mn, Fe) and bone black (Ca).

The principal yellow pigment used was yellow ochre (Fe) that was applied for the Virgin's aureole, for her crown, and her hair. In low amounts it was added to other colors such as the sky, the landscape, or the sea below. However, for the highlights, Pacheco choose lead–tin yellow (Pb, Sn), which was identified on the crown (Figure 7), some trees, and a yellowish cloud. The principal red pigment was vermilion (Hg), used in flesh tones as well as, in high concentration, for the Virgin's lips and the red flower on her crown. Pink flowers were made with lead white and very little of vermilion; probably, a red lake was also used. Since the latter one is an organic colorant, it cannot be detected by XRF, but high Ca peaks in this area suggest a possible calcium substrate for the liquid lake. A small amount of vermilion was added to the brownish color of the architecture underneath and even for the shades of the blue coat and the tunic. Red earth (Fe) was probably used as addition to other pigments, as well.

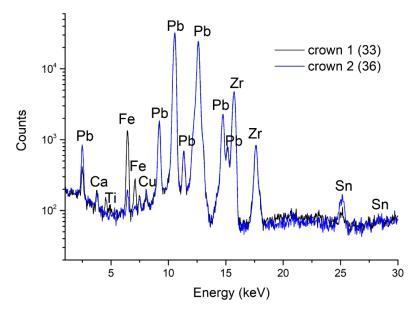


Figure 7. Comparison of XRF spectra of the crown. The basic yellow pigment applied is yellow earth (Fe) observed with black line, while highlights are carried out with lead–tin yellow (Pb, Sn) shown with blue line.

Large blue and greenish areas, such as the sky, the sea, the town on the horizon, and the landscape, were carried out with blue smalt (Figure 8), which in some areas lost its blue intensity due to chemical changes in the pigment, probably caused by the reaction with the oil binder or the instability of potassium glass [25,26].

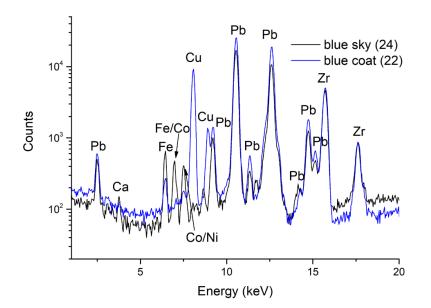


Figure 8. Comparison of two XRF spectra from blue areas reveal the use of azurite (Cu) for the Virgin's coat (blue line), and smalt (K, Co, Ni, As) for most of the background (black line).

Smalt is identified by common peaks of K, Ni, Co, and As; the high amount of Ni is surprising, its peak intensity being almost as high as that of Co, which was not detected in any of our previous painting studies. It must be a smalt compound due to a specific pigment preparation. On the other hand, a copper-based blue, probably azurite (Cu), an expensive pigment obtained from the semiprecious mineral, was selected for the Virgin's blue coat (Figure 8). This pigment is generally used for vestments of the most important sacred figures in a composition, revealing their celestial meaning. The blue coat of the Virgin symbolizes the eternity, as explained in the Introduction [4,5]. Azurite was also applied for the Virgin's blue eyes. Perhaps some azurite was added to smalt for the color of the sea; however, it could also be obtained as a mixture of smalt and a copper-based green pigment, Cu being the characteristic element in this bluish-greenish area. With XRF it is not possible to identify the green pigment precisely, but there exist several copper-based ones in the 17th century, such as malachite, verdigris, or copper resinate [14,18,24–26]. We can exclude verdigris, as Pacheco's own testimony in his treatise reveals that he did not use verdigris: "Keep away from verdigris like the plague, because it's your worst enemy" [3,22]. In La Inmaculada, a green color can be found in the landscape, mixed with a small amount of smalt. Darker tones and shades were modeled with umber (Mn, Fe), identified in the Virgin's hair basic color, the ground, the fountain, the architecture in the right corner, and on dark tones of the drapery and flesh tones. In the darkest areas and shades, high Ca peaks are observed, indicating a probable use of bone black.

3.2.2. Interventions

Following the UVF and IRR images, different retouches were confirmed by XRF as well, carried out by modern pigments such as zinc (Zn) and titanium (Ti) whites, chrome green (Cr), and cadmium yellow (Cd). In most cases, the white areas of zinc and titanium do not concur, indicating at least two different interventions, bearing in mind that the first pigment was in use since the second half of the 19th century, while the second one entered only in the 1920s [23–26]. The largest intervention is located in the lower part of the aureole, next to the Virgin's left leg (Figure 9). It is made on a calcium-based filler (gypsum or chalk),

with both modern whites and a low amount of cadmium yellow (Cd) and chrome green (Cr), which was also located in the Virgin's left eye.

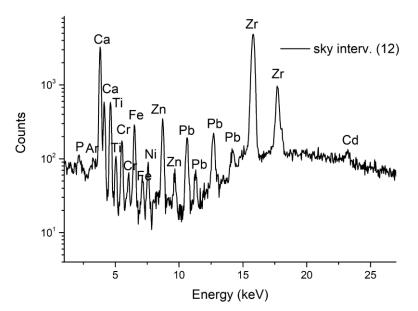


Figure 9. XRF spectrum of a retouched area in the sky, revealing the use of a calcium-based filler (probably gypsum), overpainted with modern pigments, zinc (Zn) and titanium (Ti) whites, chrome green (Cr), and cadmium yellow (Cd).

4. Discussion

The results obtained by these noninvasive analyses correspond to what it is known so far about Pacheco's painting technique from his treatise and from the analysis of his artworks performed in other institutions [3,18–21]. Even if the artist preferred to use wooden panels, especially oak when possible, this painting was made on canvas. According to Pacheco's treatise and our results, the canvas was probably first covered with several layers of animal glue, on top of which one or more preparation layers (*preparación* as he calls it; [3,20]) made with Seville's clay ("barro que se usa en Sevilla") and lead white (albayalde) or minium (azarcón) were extended. He also mentions priming (emprimación or emprimadura) referring to a colored priming that could be overlaid on top of the preparation [22]. The existence of the latter cannot be confirmed by XRF alone. This kind of preparation offers already toned painting support that helps in quicker and easier modeling.

The pigment palette known from Pacheco's treatise and other material studies corresponds to our results; nevertheless, the broad use of smalt found in La Inmaculada is not common in his paintings. According to his treatise, he preferred to use "the blue of Santo Domingo" (azul de Santo Domingo), which most studies recognizes as azurite, however it has not been identified conclusively. It could refer to a naturally occurring copper blue from the Spanish Indies, as suggested by Zahira Véliz in her English translation of a part of the Third Book of Pacheco's treatise [22]. He instructs to work on the blue intensity by grounding the pigment more thoroughly for lighter blue tones and leaving larger particles for a darker color [3,20,22]. In some parts he also refers to the "fine ash blues" (azules de cenizas finas), which might be the same pigment, but it is not clear. The blue pigment was generally also chosen to create green hues, which he did not obtain by a simple green pigment, although he suggests including in a painter's palette (verde de montaña y tierras sutiles), which can correspond to malachite and green earth. To obtain a green color, he suggests mixing the blue pigment with a yellow one, often yellow ochre ("buenos ocres") or a yellow lake (amarillo de ancorca, as Pacheco calls the dark yellow tincture of plant origin on a calcium substrate), especially for dark greens. According to his treatise, he also used dark indigo (añil) or purple archil (orchilla) to darken blues [3,20,22]. Archil was obtained from the composite organism lichen, one of the main historic products exported from the

Canary Islands. In this research, we can confirm the use of azurite (or a copper-based blue of Santo Domingo) in the Virgin's blue coat, but cannot identify either the yellow lake or indigo, both being organic. The presence of Cu in the green tones might characterize blue azurite or a copper-based green pigment (perhaps malachite), which could be clarified only by a stratigraphic section.

Pacheco considered flesh tones to be one of the most important parts of a painting and wrote largely about how to achieve a certain tonality: for young women he suggests light flesh tones, obtained by high amount of lead white ("lindo albayalde Venecia"), mixed with some vermilion ("bermellón famoso") and red lake (he mentions carmín), the latter not possible to detect with certainty by XRF in La Inmaculada. Furthermore, he added a small amount of yellow ochre and some azurite, but not a copper-based green pigment, as it was common in Europe for the flesh tones of living people; azurite was used frequently for corpses [3,20,22]. This mixture was confirmed by our study, as seen in Figure 6. Yellow ochre was one of his most used pigments, which he applied generously in flesh tones and in backgrounds; therefore, in this painting we also identified important Fe presence in the background (Figure 8, black line). However, he considered lead-tin yellow (probably identified with genuli in his text; [22]) as the best yellow pigment, creating bright colors; nevertheless, in the present artwork it was rarely found (Figure 7). We also did not find orpiment in this painting, although he mentions it as jalde in his treatise [3,22]. As explained above, organic materials cannot be detected by XRF, but due to high Ca intensity in some pink, red, and dark areas, we proposed a possible use of red lake, yellow lake, and bone black. Red lake was suggested for pink flowers on the lower part of the scene and the Virgin's flesh tones. Pacheco's texts about the achievement of a pink color confirm it, instructing to sketch first with vermilion, overlaying it with lead white and carmine [3,20,22]. As a black pigment, he preferred the use of carbon black; nevertheless, we still suggest the use of bone black in very dark tones, as the shade of the Virgin's hands (Figure 6, blue line). For shades he often used also umber ("sombra de Italia"). His palette corresponds to other great painters of the Golden Area of Spanish painting [18–21], and the pigments found on La Inmaculada uphold it. With our study it was not possible to analyse binders, but from his treatise and previous studies, it is known that he preferred to use linseed oil (aceite de linaza), adding as siccative a vitreous pigment (probably smalt) or litharge (side product of burning lead pigments) and rarely minium (lead red), which could correspond to the presence of Co or Pb in the wide painted surface of the artwork.

Another feature to keep in mind is Pacheco's preparatory drawing. For him, the drawing is the essential part of every painting: "The sure and good grace of the work is in the proper delineation of the entire figure or history because it's certain that all the difficulty of paintings consists in the contours" [22]. However, he believes that drawings of the same size as the final work are not necessary, but suggests composing images per parts, as a mosaic. His bozzettos are first drawn with black stencil, finished with precision using a pen and ink, modeling volumes and shades by different grades of ink dilution. Once the sketch was finished, it was passed on to the canvas, using charcoal or other materials [20]. Therefore, it is surprising that IRR does not reveal much, but when comparing our images with other IRR studies [11–13,20,27], it is clearly quite common. This is explained by Pacheco using dark lines on dark preparation, especially where dark colors were overlaid. With time, on lighter or more transparent areas, some lines can appear, as can be observed on La Inmaculada on the half-moon and the boat (Figure 5a,b). In other IRR studies where the underdrawing was revealed [20,27,28], very sharp black lines with white highlights made with a brush can be observed that perfectly correspond to the colored overlaid paint; this also makes the underdrawing more difficult to discern. His drawings express a very confident, precise, and high-quality artist, who prepared his works very thoroughly, which is why almost no *pentimenti* can be found. Again, La Inmaculada confirms this.

5. Conclusions

The analysis carried out on Pacheco's La Inmaculada panel painting confirms the materials used in the preparation and color layers, as known from the artist's treatise and other studies. They also correspond to the painting procedures of the 17th century "Golden Age" in Spain and especially Seville. Regarding this material characterization, the conservation–restoration process was completed accordingly, and the painting returned to the private area of the Archbishop's Palace in time. Although some questions remain open, there will be no other possibility of performing more analyses on this canvas. Nevertheless, the information gathered with UVF, IRR, and XRF offers an important knowledge that can be used by art historians, restorers, and conservation scientists in the study of Pacheco's works or as a comparison to other Inmaculadas that could be analysed in the future.

Author Contributions: Conceptualization, A.K., J.M.-S., A.G.-O., A.M.-d.-S. and M.Á.R.; methodology, A.K. and J.M.-S.; software, A.K., J.M.-S. and FJ.A.; validation, A.K., J.M.-S. and FJ.A.; formal analysis, A.K., A.G.-O. and A.M.-d.-S.; investigation, A.K., J.M.-S., A.G.-O. and A.M.-d.-S.; resources, A.G.-O. and A.M.-d.-S.; data curation, A.K., J.M.-S. and F.J.A.; writing—original draft preparation, A.K.; writing—review and editing, A.K., J.M.-S. and F.J.A., A.G.-O., A.M.-d.-S. and M.Á.R.; visualization, J.M.-S., F.J.A., A.G.-O., A.M.-d.-S. and M.Á.R.; supervision, A.G.-O. and A.M.-d.-S.; project administration, F.J.A. and M.Á.R.; funding acquisition, M.Á.R. All authors have read and agreed to the published version of the manuscript.

Funding: Work supported by the project P18-RT-1877 of Junta de Andalucía (Spain) and by the Margarita Salas contract given by the Spanish Ministry of Universities and funded by the European Union—"NextGenerationEU".

Data Availability Statement: The data presented in this study are available on request from the corresponding author. They are not publicly available due to the intern data policy.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Valdivieso, E.; Serrera, J.M. Catálogo de las Pinturas del Palacio Arzobispal de Sevilla; Editorial Sever Cuesta: Sevilla, Spain, 1979.
- 2. Valdivieso, E. *Francisco Pacheco*; Caja San Fernando: Sevilla, Spain, 1990.
- 3. Pacheco, F. Arte de la Pintura; Bassegoda i Hugas, B., Ed.; Cátedra: Madrid, Spain, 2001.
- 4. Escobar Correa, J.G. *Ave Maria Gratia Plena: Oconología e Iconografía de la Inmaculada Concepción;* Universidad Nacional de Colombia: Bogotá, Colombia, 2012.
- Parejo Delgado, M.J. La iconografía de la Inmaculada Concepción en las parroquias sevillanas. In La Inmaculada Concepción en España: Religiosidad, Historia y Arte, Symposium Proceedings, Bd. II; Campos, F.J., Ed.; Real Centro Universitario Escorial-María Cristina, Ediciones Escurialenses San Lorenzo del Escorial: Seville, Spain, 2005.
- 6. Matteini, M.; Moles, A. *Scienza e Restauro. Metodi D'indagine*; Nardini: Firenze, Italia, 1994.
- 7. Stuart, B.H. Analytical Techniques in Materials Conservation; John Wiley & Sons, Ltd.: Chichester, UK, 2007.
- 8. Rene de la Rie, E. Fluorescence of Paint and Varnish Layers, Part I–III. Stud. Conserv. 1982, 27, 1–7, 65–69, 102–108.
- 9. Hain, M.; Bartl, J.; Jacko, V. Multispectral analysis of cultural heritage artefacts. Meas. Sci. Rev. 2003, 3, 9–12.
- 10. Cosentino, A. Notas prácticas sobre a fotografía de ultravioleta para o examen de obras de arte. *Conserv. Patrim.* **2015**, *21*, 53–62. [CrossRef]
- 11. Van Asperen de Boer, J.R.J. Infrared Reflectography: A Method for the Examination of Paintings. *Appl. Opt.* **1968**, *7*, 1711–1714. [CrossRef] [PubMed]
- 12. Mairinger, F. The infrared examination of paintings. In *Radiation in Art and Archeometry*; Creagh, B.D.A., Ed.; Elsevier: Amsterdam, The Netherlands, 2000; pp. 40–55.
- Faries, M. Analytical Capabilities of Infrared Reflectography: An Art Historian's perspective. In *Scientific Examination of Art: Modern Techniques in Conservation and Analysis*; Berrie, B., René de la Rie, E., Hoffman, R., Tomlinson, J., Wiesel, T., Winter, J., Eds.; National Academies Press: Washington, DC, USA, 2005; pp. 87–104.
- 14. Seccaroni, C.; Moioli, P. Fluorescenza X: Prontuario per L'analisi XRF Portatile Applicata a Superficie Policrome; Nardini: Firenze, Italy, 2004.
- 15. Janssens, K. X-ray based methods of analysis. In *Non-Destructive Microanalysis of Cultural Heritage Materials;* Jannsens, K., Ed.; Elsevier: Amsterdam, The Netherlands, 2004; pp. 129–226.
- Glinsman, L.D. The practical application of air-path X-ray fluorescence spectrometry in the analysis of museum objects. *Stud. Conserv.* 2005, 50, 3–17. [CrossRef]
- 17. Artioli, G. Scientific Methods of Cultural Heritage; University Press: Oxford, UK, 2010.

- 18. Broquetas, R. *Técnicas y Materiales de la Pintura Española en el Siglo de Oro;* Fundación de Apoyo a la Historia del Arte Hispánico: Madrid, Spain, 2002.
- 19. Gayo, M.D.; Jover de Celis, M. Evolución de las preparaciones en la pintura de los siglos XVI y XVII en España. *Boletín Mus. Prado* 2010, *28*, 39–59.
- Muñoz Rubio, M.V. Francisco Pacheco: Teoría y práctica. In Pacheco, Teórico, Artista, Maestro; Muñoz Rubio, M.V., Cano Rivero, I., Eds.; Junta de Andalucía, Consejería de Cultura: Sevilla, Spain, 2016.
- Križnar, A.; Ager, F.J.; Caliri, C.; Romano, F.P.; Respaldiza, M.R.; Gómez-Morón, M.A.; Núñez, L.; Magdaleno, R. Study of two large-dimension Murillo's paintings by means of macro X-ray fluorescence imaging, point X-ray fluorescence analysis, and stratigraphic studies. X-ray Spectrom. 2019, 48, 482–489. [CrossRef]
- 22. Véliz, Z. Francisco Pacheco's Comments on painting in Oil. Stud. Conserv. 1982, 27, 49–57.
- 23. Mayer, R. The Artist's Handbook of Materials and Techniques, 5th ed.; Viking Penguin: New York, NY, USA, 1991.
- 24. Wehlte, K. Werkstoffe und Techniken der Malerei; Urania: Stuttgart, Germany, 2005.
- 25. Feller, R.L.; Roy, A.; West Fitzhugh, E.; Berrie, B. (Eds.) *Artists' Pigments: A Handbook of Their History and Characteristics*, 2nd ed.; Archetype Publications: London, UK, 2012.
- Cocciato, A.; Moens, L.; Vandenabeele, P. On the stability of mediaeval inorganic pigments: A literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments. *Herit. Sci.* 2017, *5*, 12. [CrossRef]
- 27. Navarette Prieto, B. Un nuevo dibujo d Francisco Pacheco para su Libro de Retratos: La efigie de Pablo de Céspedes en los Uffizi. *Arch. Español Arte* **2016**, *89*, 77–84. [CrossRef]
- 28. Navarette Prieto, B. El dibujo como fundamento del pensamiento de Francisco Pacheco: Procesos y principios. In *Pacheco, Teórico, Artista, Maestro*; Muñoz Rubio, M.V., Cano Rivero, I., Eds.; Junta de Andalucía, Consejería de Cultura: Sevilla, Spain, 2016.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.