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Combining Multispectral Imaging and XRF Analysis to Examine *San Patroba predica ai fedeli di Pozzuoli* by Massimo Stanzione

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Abstract: A diagnostic analysis of the painting depicting *San Patroba che predica ai fedeli di Pozzuoli* by Massimo Stanzione was carried out. The painting was completed in 1635–1637 to decorate the choir of the Cathedral of Saint Procolo in Pozzuoli (Naples, Italy). The technique of X-ray fluorescence (XRF) and multispectral imaging were applied on site to learn about the executive technique, the palette of the painting, and the restoration works, as well as understand the influence of the other painters active in Naples in that period. The results of the research are presented and discussed to draw general aspects and peculiarities of the pigments and the pictorial technique used by this important painter, as well as the restorations.

Keywords: M. Stanzione; painting; XRF; multispectral imaging; 17th century; Naples

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1. Introduction

The analyzed painting is the artwork of Massimo Stanzione, an artist whom Bernardo De Dominici described as an excellent painter and drawer [1]. It depicts Saint Patroba preaching to the people of Pozzuoli and was painted to decorate the choir of the Cathedral of Saint Procolo in Pozzuoli (Figure 1).

This commission was completed in the fourth decade of the seventeenth century, a turning point in the evolution of Massimo Stanzione's style. The artist was engaged from 1630 in many public worksites in the city of Naples and the creation of *historia* paintings and devotional subjects for private patrons. His success can be attributed to the definition of an expressive formula characterized by a delicate naturalism, articulated within simple and clear compositional schemes and a narrative with calm tones.

After the beginnings linked to the local tradition of late Mannerist Counter-Reformationism, typical of painters such as Fabrizio Santafede, Belisario Corenzio, Giovan Bernardino Azzolino, and Giovan Vincenzo Forlì, Stanzione's painting changed and matured toward solutions aimed at combining Caravaggio's naturalism with the classical ideal [2–4]. In achieving this new equilibrium, the fundamental experience was the direct comparison with the works by Caravaggio and his "reformed" interpreters such as Orazio, Artemisia Gentileschi, and above all, Simon Vouet, as well as with the painters by the Roman–Bolognese school, mainly Annibale Carracci and Guido Reni [5,6]. An opportunity delineated during his two sojourns in the city of Rome (1617–1618 and the 1620s) and matured in Stanzione's painting with the arrival in Naples in the 1630s of eminent exponents of Roman–Bolognese classicism: Domenichino and Giovanni Lanfranco. Domenichino was hired for the decoration of the Chapel of the Treasure of Saint Gennaro; Giovanni Lanfranco arrived in Naples in 1634 to fresco the dome of the Gesù Nuovo church, the prelude to a series of prestigious Neapolitan assignments, including participation in the construction site of the

Cathedral in Pozzuoli alongside Stanzione and the other painters involved in the decorative project [7–9]. From these comparisons, Stanzione drew the useful elements for a new aulic and sophisticated language and was provided with an incisive communicative force. Through a clear narrative, the artist focuses on a pure chromatic rendering, contained within precise contours, rather than on virtuosic epidermal and textural effects. During this successful period of his artistic career (in the 1630s), appreciated by his contemporaries, Stanzione was commissioned by Bishop of Pozzuoli Martín de León y Cárdenas for the painting titled *San Patroba predica ai fedeli di Pozzuoli.*

In the acts of the Saint Apostolic Visit of 1632, the bishop described the cathedral church of Pozzuoli as inculta, denudata, and angusta proximeque ruinae. Therefore, he renovated the sacred building, which involved the architects Cosimo Fanzago and Bartolomeo Picchiatti and some of the best artists active in Naples: Artemisia Gentileschi, Giovanni Lanfranco, Cesare and Francesco Fracanzano, Jusepe de Ribera, Paolo Finoglio, Agostino Beltrano, and Massimo Stanzione. The bishop created a close cordial relationship with the Viceroy of Naples Don Manuel de Acevedo Zúñiga y Fonseca, Count of Monterrey, who financed part of the work on the cathedral and probably identified the painters, who worked for the viceregal court and the King of Spain Philip IV [10–13]. In this regard, it is significant to mention Massimo Stanzione's involvement in the decorations of the Buen Retiro Palace in Madrid and the King's Oratory. In Spain, this work also involved Paolo Finoglio and Artemisia Gentileschi, at the probable request of Stanzione himself, who was having difficulty completing the deadline set [14,15].

The subject commissioned to Massimo Stanzione for the Cathedral of San Procolo in Pozzuoli was part of an iconographic program designed by the bishop and centered on three themes: episodes from the life of Christ (*The Birth of Jesus, The Adoration of the Magi, Jesus in the Garden of Olives*); episodes narrating the origins of the Christian community of Pozzuoli (*The Landing of St. Paul in Pozzuoli; St. Paul writing to Philemon; St. Patroba preaching to the people of Pozzuoli; St. Peter consecrates St. Celsus bishop of Pozzuoli*); and testimonies of faith of the saints who experienced martyrdom in the territory of Pozzuoli (*The Martyrdom of St. Artema; The Martyrdom of Sts. Onesimus, Alphius, Philadelphus, and Cyrinus; St. Gennaro and companions in the amphitheater tame the beasts; St. Proculus and St. Nicea*).

The original decorative system underwent numerous changes over the centuries due to the movement and replacement of the paintings; moreover, in 1964, there was a disastrous fire that devastated the nave and the chapels of the cathedral, causing the loss of part of the paintings. Nowadays, the painting depicting St. Paul writing to Philemon originally in the choir is placed in the Diocesan Museum of Pozzuoli, adjacent to the cathedral, while the paintings depicting the Martyrdom of St. Alexander and the Jesuit Saints Ignatius of Loyola and Francis Xavier, originally related to the decoration of the Chapel of the Blessed Sacrament, are placed in the choir [16–18].

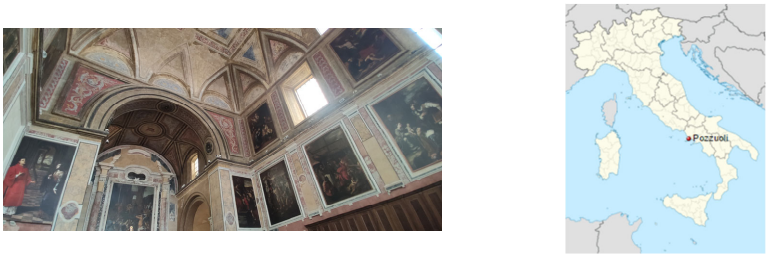
The conservation and study of these paintings are assigned to the Diocese of Pozzuoli through the Puteoli Sacra Project supported by the Regina Pacis Foundation.

A painting is generally a layered object due to its intrinsic structure and the overlapping of chronologically successive interventions, which may consist either of stylistic changes by the same author (so-called *pentimenti*) or by later authors, or of a maintenance type. Non-destructive investigation techniques provide a way to examine the stratigraphy [19] of a painting. Such investigation techniques are mainly based on the use of radiation falling within multiple regions of the electromagnetic spectrum. Therefore, different layers can be investigated using electromagnetic waves of different wavelengths. For example, the use of ultraviolet light gives information about varnish and retouching, pigments (even *pentimenti* in some cases) located under the varnish that cannot be detected visually, while infrared light permits investigation of the intermediate layers between the support and the surface of the painting, highlighting underdrawings and characteristics related to the pictorial layer. Depending on stratigraphic thickness and wavelength chosen for investigation, materials respond in the infrared range in terms of transparency: traces of drawing are more visible if carbon-based and on a light background (in contrast with dark stroke).

Multispectral imaging is a noninvasive imaging technique that can identify features imperceptible to the naked eye by acquiring images of an object illuminated with ultraviolet and infrared light [20]. This method allows for the identification of different pigments that exhibit peculiar behaviors in the range of the electromagnetic spectrum easily observed with a modified IR-VIS-UV digital camera (360–1100 nm). The advantage of this approach is the ability to conduct surveys of large areas quickly and inexpensively [21].

To identify pigments with an acceptable degree of certainty, it is necessary, as a complement to the imaging, to use at least one other material-specific technique, such as X-ray fluorescence (XRF) [22,23]. This method is a multi-elemental analysis that achieves a non-destructive, noninvasive, and fast detection of nonorganic elements. Due to these characteristics, it is mainly used in the field of cultural heritage [24,25] where preservation and integrity of an artwork are the main requirements. Knowledge of the elemental composition of a sample is useful in discerning original from restored regions and in supporting decisions on intervention treatments [26].

Non-destructive diagnostic studies were performed on the painting *San Patroba predica ai fedeli di Pozzuoli* (Figure 2) by Massimo Stanzione. Multispectral imaging and XRF analyses were carried out directly inside the church due to the large size of the painting. The goal of the present work is the characterization of the color palette and the knowledge of Stanzione's painting technique. Preliminary results were presented in an oral presentation during the AIAr conference 2023 (XII National Congress AIAr—Italian Association of Archaeometry).



(**a**) (**b**)

Figure 1. (**a**) Photos of the inside of the cathedral; (**b**) map of Italy marked with the city of Pozzuoli.

Figure 2. The painting *San Patroba predica ai fedeli di Pozzuoli* and XRF points acquired at 50 kV, 80 μA, 90 s, in air.

2. Materials and Methods

2.1. San Patroba predica al popolo di Pozzuoli

The painting is an oil on canvas with dimensions of 320 × 200 cm^2 (Figure 2) depicting Saint Patroba, who was a disciple of St. Paul and the first bishop of the Christian community of Pozzuoli.

The dating of the painting can be deduced from the sources of the work in progress in the Cathedral of Pozzuoli started in 1632 [27].

The first interventions, directed by the architect Bartolomeo Picchiatti, are accurately described in the *ad limina* report of Bishop Martín de León y Cárdenas of 16 May 1635 (the printed originals are preserved at the Vatican Historical Archives, and microfilmed copies are at the Diocesan Historical Archives of Pozzuoli). In 1636, a second phase began for the reorganization of the presbytery area to which Cosimo Fanzago wished to give more scope (annexation of the sacristy creating a large area added to the choir and designated for the episcopal chair and a new polychrome marble high altar), and the bishop commissioned new paintings. The *ad limina* report of 1640 disclosed the placement in the choir of the cathedral of paintings commissioned to the knight Giovanni Lanfranco and other famous and talented artists. The depicted subjects are minutely mentioned by the bishop while the painters are not; among the works, there is a canvas depicting St. Patroba. It is also mentioned in a bishop's letter to the Cistercian historian Ferdinando Ughelli dated March 23, 1640, which specifies its location in the right wing of the choir: "*nella man destra della chiesa si era posto il quadro o tabula di S[an] Patroba p[rim]o vesc[ov]o di questa città discepolo di Gesù Christo Gesù nostro Signore [. . .]*" [28]. Based on these sources, the dates of 1636 and 1640 can be considered the two temporal extremes where the realization of the painting by Massimo Stanzione can be placed.

The setting of the painting is solemn; Saint Patroba appears on a flight of steps leading to a basin decorated with festoons; the crosier at his feet and the hat (*mitra*) identify him as a bishop. A crowd of listening onlookers surrounds him while he is depicted in the act of pointing to the crucifix. On the lower right, a man painted from behind acts as a *repoussoir* introducing the scene, while a man unusually dressed in contemporary Spanish clothing is depicted on the left: a doublet with decorative slits on the sleeves and back, stiff white ruff, broad cloak, and feathered cap. An open green curtain offers the viewer a glimpse of a significant moment in the religious history of Pozzuoli.

The painting testifies to a community that boasts its origins far back in time and above all, includes a disciple of the apostle Paul as its first bishop.

Stanzione resumed the same model for the realization of the fresco decoration in the chapel of San Giacomo della Marca (Church of S. Maria la Nova, Naples), a cycle datable to the years 1644–1646. Here, in one of the central medallions of the vault, the same compositional can be recognized. Similarities between the two works are the ruined architecture in the background, the man acting as a *repoussoir*, and the shot of the female figure, who in the Pozzuoli painting wears a yellow earth dress and has her head covered by an impalpable veil.

The first documented restoration of the Stanzione canvas dates to 1929 [29] and was ordered by Bishop Giuseppe Petrone, who provided for the aesthetic restoration (cleaning, pictorial retouching, and painting) of the entire pictorial series in the cathedral. Later, in 1964, a devastating fire broke out inside the nave, destroying many works and causing extensive damage to the canvases in the choir. This made it necessary to transport the paintings to the deposits of the Conservation Laboratory of the Capodimonte Museum for a major conservative and aesthetic restoration by Volpin, completed in 1968 [30]. Finally, in 2010 [31], a final restoration was carried out for the reopening of the cathedral to the public in 2014.

2.2. Multispectral Imaging

Multispectral imaging was performed to reveal details about the painting surface (varnish, pigments, and presence of underdrawings) [32–34]. The system used was a Sam-

sung NX500 Digital Camera 28 MPX (APS-CMOS BSI) designed by Madatec Srl to acquire images from different light sources. The UV-IR cut filter (390–700 nm) was employed for visible (VIS) images. Spotlights with 365 nm UV wavelengths in combination with the UV-IR cut filter (390–700 nm) were applied for induced fluorescence (UVF). Three HP infrared filters at 760, 850, and 950 nm, one interference filter at 1070 nm, and two infrared lamps at 275 W were used to acquire IR images. A 98% reflectance white chalk standard was placed near the painting during the acquisition of all images.

Infrared False-Color (IRFC) reflectography is an imaging technique used for the examination and identification of pigments by the superimposition of multiple acquisitions of the same image acquired in the VIS and NIR regions [35]. After the acquisition of the two images acquired in the VIS and the IR, the IRFC image is obtained from the RGB channels in the visible by substituting the green channel for the red channel and the blue channel for the green. The red channel has been replaced by the infrared image. Since the resulting image contains information that comes from the infrared region, the pictorial layers, chromatically similar in the visible but made with pigments of different chemical nature and different behavior in the infrared, appear in the image in differentiated by the false color.

Adobe Photoshop and Adobe Lightroom were used for image processing, as they provide fast reading and writing of RAW files.

2.3. XRF Analysis

Measurements were performed using the Elio system, a compact portable X-ray fluorescence spectrometer produced by XGLab (Bruker). It weighs about 2 kg and is mounted on a tripod with the ability to move on a motorized XY stage. The system consists of a 50 kV maximum Rh X-ray tube with a 0.2 mA maximum working current and a 1 mm collimator. A silicon drift detector (25 mm^2 active area and energy resolution < 140 eV at 5.9 keV) operates with a measuring spot of 1.2 mm. The working distance between the painting surface and the detector is 14 mm.

A compositional analysis was carried out on the surface layer in point mode by setting the tube with a voltage of 50 kV and a current of 80 μA. An acquisition time of 90 s was chosen for each point (twenty-seven points, Figure 2). Elio's software allowed us to see each chosen point through an integrated microscopic camera. XRF data were processed with Elio's software and the open-source PyMca software [36]. As a result of the measurement, the software's qualitative analysis packages were used to identify the chemical elements in the spectrum and, in particular, PyMca software was used for the best comparison of spectra and for calculating net area counts (deconvolution of the characteristic fluorescence peaks). The interpretation of the data was supported using MATLAB_R2019a software with specific statistical methods such as principal component analysis (PCA) [37–39], hierarchical clustering analysis (HCA) [40,41], and k-means clustering [42–44].

3. Results

3.1. Multispectral Imaging

The first phase of the work concerned the analysis of the VIS to highlight the colors and their different hues. Then, UV analysis was performed to evaluate the state of conservation and previous interventions of the painting, and IR reflectography was used to obtain information on the underlying drawing and the pictorial sketch.

As shown in the detailed images, ultraviolet-induced fluorescence revealed some hues of material. St. Patroba's tunic (Figure 3) and the kneeling woman's skirt (Figure 2) have a brighter red hue than those of the other two characters in the visible who wear red clothes; yellow parts turn to red depending on their hue in the visible while architectural elements and people in the background maintain a dark hue similar to visible images (the same results were found for characters with dark clothing). Retouches, which appear as darker areas in the UV images, are made with imitation technique by successive glazing.

Figure 3. Multispectral images of Saint Patroba: (**a**) VIS; (**b**) IR using the IR filter at 1070 nm; (**c**) UV light with the UV-IR cut filter; (**d**) IRFC using the IR image with a filter at 950 nm.

Unlike the visible images, the IR examination shows some interesting details. The left edge of the round arch placed in the background of the scene is outlined, and a change in the composition of the head of the man standing on the left edge of the painting is present. The portion of the sky between the round arch and the head of St. Patroba is made of materials that are very transparent to the IR, taking on an intense white hue.

The response of some materials to the different multispectral techniques applied is examined through the analysis of some details, such as the portion of the painting in which St. Patroba is depicted (Figure 3).

B&W infrared images do not clearly show signs of the underlying drawing. This may be due to the poor infrared transparency of the pictorial layer and the weak contrast between the drawing and the preparatory layer (e.g., dark drawing on dark preparation) or even the use of drawing materials, such as red earths or lakes, which are transparent to IR radiation.

The UV image shows the age of the surface layers of the artifact, as the fluorescence of these materials generally increases in intensity with aging. It was possible to recognize chronologically inconsistent interventions and the use of vermillion (in pink), Naples yellow (in red), and lead white (in white), as studied later by XRF. The dark area surrounding the saint appears to be made with a bituminous pigment, as evidenced by the comparison of the UV image with the IRFC image and by what was reported in [45]. It might have been added during a restoration to obtain brightness.

The IRFC image is configured with artificial (false) chromes, as these do not correspond to the "original color," but are able to express the material characteristics of the pigments. Figure 3 shows, in yellow, the presence of vermilion, which is used to paint the tunic and the flesh tones; in light yellow, the Naples yellow is used for the hems of the tunic, and, in white, the lead white is used for the sleeve. Naples yellow [45] is supposed to be white but because it was applied over vermilion, it turns out to be a light-yellow color.

Some perplexity is aroused by the signature (Figure 4a), which is different from the monogram usually used by Stanzione (Figure 4c). It is often represented by the twine of the letters in Roman square capital M A X preceded by EQ (Eques), while a twine formed by the letters M A S with a slight slant and the absence of the *Eques* title is visible in the Pozzuoli painting. This is an unusual choice found in few other paintings by Stanzione. They include the *Madonna delle Anime del Purgatorio*, intended to decorate the high altar of the Church of St. Mary of the Souls in Purgatory, the *Santa Agnese* of the Pio Monte della Misericordia, and the *Annunciazione* of the Church of St. Mary Regina Coeli; but, in these paintings, the twine of the letters EQ is also used. Another unusual variant is based on the

twine of the letters M S preceded by the title EQ; this abbreviation can be identified in the canvases depicting the Morte di Orfeo in the Banca Manusardi and C., the *Madonna con Bambino* in a private collection in Genoa, and the *Santa Dorotea* in a private collection in Buenos Aires.

Figure 4. Detail of Stanzione's signature. (**a**) VIS image; (**b**) IR image at 850 nm; (**c**) B&W image of the signature normally used by the artist.

The *Eques* title is absent in the painting of St. Patroba, perhaps due to a loss over time as a result of the inadequate conservation of the painting and not by choice. In 1938, Ortolani cited the painting as a signed work [46], while Schütze S. specified that the signature referred to by Ortolani was no longer legible in 1992 [5]. Between these two citations, the 1964 fire and subsequent restoration occurred, so the absence of the title could be due to deep cleaning or restoration (see retouches in that area, Figure 4b).

In this painting, the signature is followed by "neap f", which denotes *Neapolis Fecit*, i.e., made in Naples, the place of realization.

A special case emerged from the UV analysis. The woman's eye turns out to have no pupil and iris in the VIS (Figure 5a) and IR (Figure 5b) images. It was probably made by the artist in the shade. More definition appears in the UV image (Figure 5c) where the eye seems to be drawn. The visible result could be an effect of a restoration. Probably, the heat of the fire caused the color to fall off, the treatment was performed without a reference, and the eye was summarily recovered.

Figure 5. Details of the featured woman. (**a**) VIS image; (**b**) IR at 760 nm; (**c**) UV image; (**d**) IRFC at 850 nm.

In this case, the IRFC (Figure 5d) suggests how the smalt, copper-based pigment, and vermilion are distributed. Smalt-rich parts and vermillion-rich parts appear colored red and yellow, respectively, while the copper pigment remains the same as in the visible.

The area investigated in Figure 6a also showed particular interest.

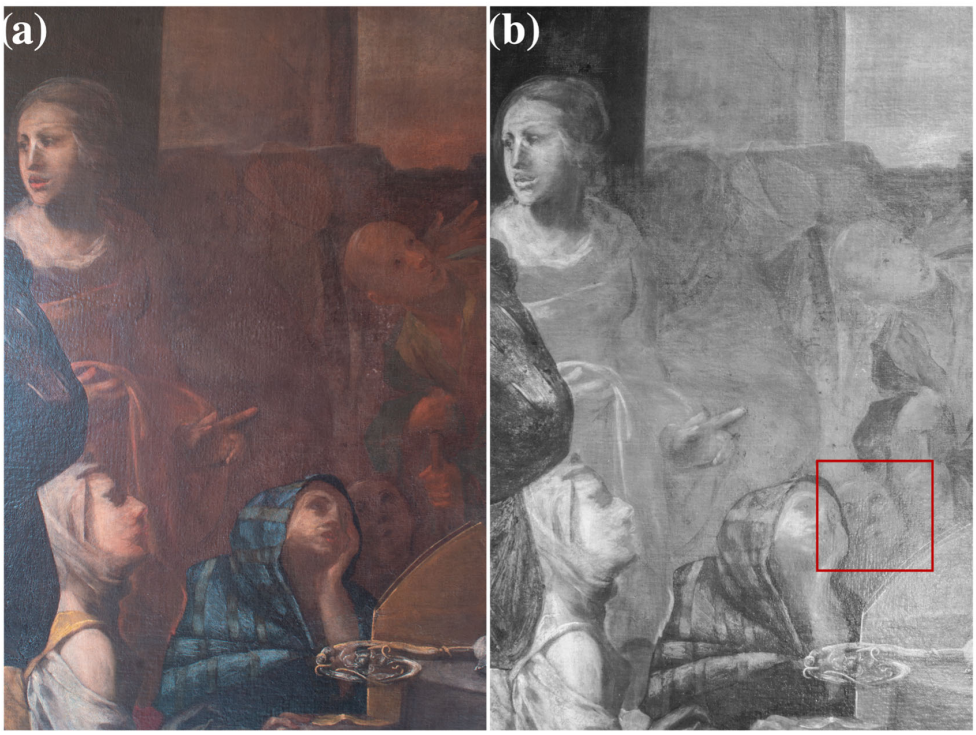


Figure 6. Central detail of the painting: (**a**) VIS image and (**b**) IR image at 850 nm: the red box highlights an interesting area.

The people are hairless, poorly detailed, and have a fast pictorial stroke. This choice could be due to the size and location of the painting at a height of more than 5 m from the floor (current location). Surely, they were drawn and/or painted before the foreground elements, such as the woman with the blue cloak. In fact, in the IR (Figure 6b, red box), the face of the figure in the background was partially covered by the foreground figure.

3.2. XRF Analysis

Considering these previous results, twenty-seven points were selected for XRF analysis (Figure 2).

The HCA method was applied to raw XRF spectra. It was performed at all measurement points, considering the correlation matrix of the spectra (27 × 27). Figure 7 shows the dendrogram using the complete method and the Chebyshev distance metric.

This method allows us to consider pigments in three main groups: (i) the green cluster is related to the restoration areas; (ii) the red cluster groups blue pigments in which copper is present; and (iii) the blue cluster represents all other lead-rich colors. This pre-screening eliminates any recovery points from follow-up analyses.

In addition, a more in-depth analysis of the spectra was made, considering the peaks of the characteristic elements and their net area counts (Table S1, Supplementary Materials). The k-means method was used for cluster analysis. The normalized matrix of net counts of the main X-ray characteristic line, excluding restoration points, wwas considered. In the partition, each cluster was defined by its member objects and centroid (Figure 8).

The centroid of a cluster is the mean of the points in that cluster. Squared Euclidean distance was chosen. To get an idea of how well-separated the resulting clusters are, a silhouette plot (Figure 8b) was made using the cluster indices output from k-means. The

silhouette plot displays a measure of the proximity of each point in a cluster from the points in neighboring clusters. This measure ranges from −1 to + 1. The value of +1 indicates points that are far away from neighboring clusters, 0 indicates points that are not distinctly in one cluster or another, and −1 indicates points that are probably assigned to the wrong cluster. In our case, the best choice is the result of partitioning the points into four clusters representing the color of the main pigments. The average value of the silhouette is 0.46. Cluster 1 (blue) corresponds to the colors containing copper (blue/green pigment); cluster 2 (green) corresponds to the colors containing mercury (red/flesh pigments); cluster 3 (pink) corresponds to the colors containing antimony (yellow pigment); and cluster 4 (yellow) corresponds to the Pb colors. Spectra 5 and 6 are between clusters 1 and 4 due to the overlapping of the red vermilion (HgS) and Naples yellow pigments ($Pb_3(SbO_4)_2$). In particular, the spectra related to the two points, 5 and 7, which present yellow colors, are compared in Figure 9.

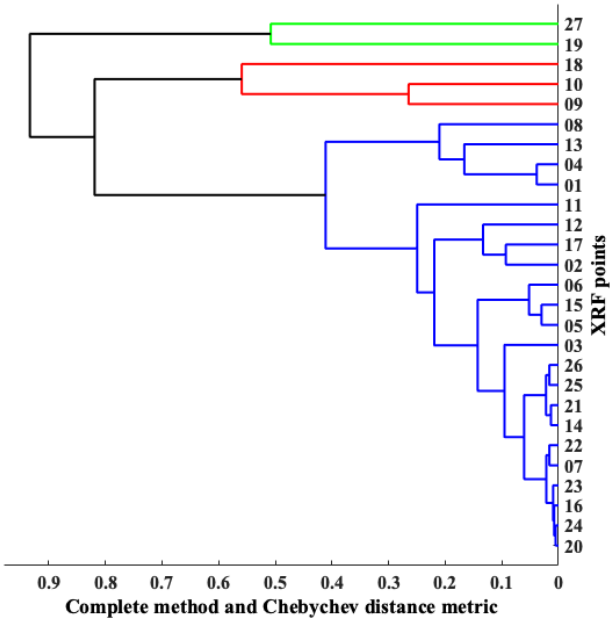
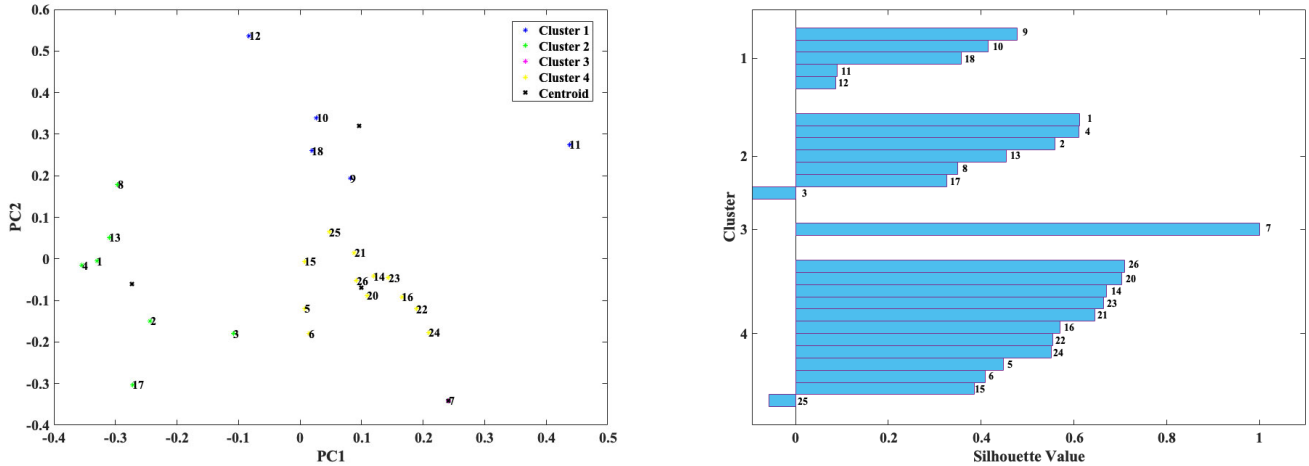


Figure 7. Dendrogram of all spectra detected using the complete method and Chebyshev distance metric.



(**a**) (**b**)

Figure 8. (**a**) A k-means plot using the two first components of PCA and (**b**) a silhouette plot.

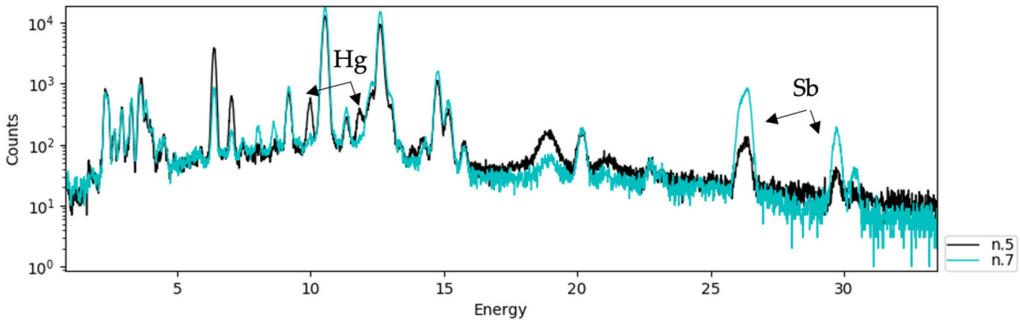


Figure 9. Comparison of the XRF spectra of the yellow pigments detected in points 5 and 7. The graph is obtained using PyMca.

The spectrum of point 5 shows the presence of mercury and antimony (highlighted in Figure 9). This means that the artist first painted the bishop's tunic red and then painted the hems Naples yellow. For this reason, measurement point 5 is located between clusters 1 and 4. The same goes for measurement point 6.

Statistical analysis provided a preliminary analysis of the spectra, which allowed restoration points to be eliminated immediately, the pigments to be divided into four main colors, and an initial indication of the similarities and differences was established.

All XRF spectra present lead (Pb), calcium (Ca), and iron (Fe), which could indicate a background layer composed of chalk, lead white, and earths, as was typical for a 17th century painting.

Lead counts are among the highest in the white areas, confirming the use of lead white ($2PbCO_3$-$Pb(OH)_2$) in the artist's palette. In the different hues of white and gray, the predominant presence of lead white and earths was found. They were used for clothes, tunics, drapes, scales, vessels, and all areas in light.

Mercury (Hg) is the main element present in the red areas, such as the clothes and lips, and indicates the presence of vermilion (HgS) pigment [47]. However, the presence of lead could refer either to lead white, from the preparation layer or used to lighten the hue (in the flesh tones) or another lead-based pigment, probably mixed with or underlying vermilion. The iron lines indicate the presence of red earth. The good correlation between iron and manganese also suggests the use of earths, specifically umbers, for darker areas (e.g., in point 4). Stanzione used lead white to give more brightness to the flesh tones (point 14) and vermilion to obtain a brighter red hue (point 13).

Various blue/green hues were used by the artist, such as for the clothes and curtains. The blue hue of point 9 is a copper-based pigment, most likely azurite ($2CuCO_3 \bullet Cu(OH)_2$). At point 11, the blue hue is obtained with smalt (a cobalt-rich glass pigment [48]) and a copper-based pigment. Their combination [49] is a very interesting result that was also found during diagnostic investigations of paintings by Artemisia Gentileschi made in the same painting cycle (manuscript in preparation by the same authors of the present one). The use of azurite is possible [49] but other copper-based pigments have to be considered since in the 17th century, green pigments such as malachite, verdigris, or copper resinate were applied in mixtures with smalt [50]. Unfortunately, XRF is able to identify only Cu as the main characteristic of these pigments. The combination of smalt with a copper-based pigment can be related to different intentions by the artist. Shades can be carried out with a copper-based pigment [33] and smalt can be added to accelerate the drying processes of the oil [47,51]. At the upper right margin of the canvas, the green drape (point 18) has a high concentration of copper and traces of antimony (Sb). It could be a mixture of a copper-based blue pigment, such as azurite, and Naples yellow, or it could be malachite with traces of Sb [47].

In the yellow areas (points 5, 6, 7), similar to clothes and hems, lead and antimony could indicate the use of the Naples yellow (Pb3(SbO4)2) [52]. Instead, the yellow hue of point 8 (*mitra*) is due to an Fe-rich pigment, most likely a yellow earth.

Several restoration points (dark areas in the painting), such as numbers 19 and 27, are recognized by the presence of elements that are inconsistent with the historical period of the painting's making, such as titanium, chromium, zinc, and barium.

A summary of the results obtained for each color is shown in Table 1. It should be noted that some of the original pigments that make up Stanzione's palette were also used in some Spanish paintings in the 17th century [50,53].

Table 1. Summary of the results relative to the main elements detected by XRF analysis, point measurements, and the possible pigment and its principal use.

Color/Point	XRF Elements	Pigments [1]	Principal Use
All points	Pb, Fe, Ca	Chalk, lead white, earths	Ground layer
Dark/19, 27	Ba, Zn, Cr, Ti	Lithopone, titanium white, chrome green	Retouches
Red/1, 2, 4, 3, 13	Hg	Vermilion	Clothes, lips
Flesh tones/14, 15, 16, 17, 26	Pb, Hg, Fe	Lead white, vermilion, earths	Flesh tones
White/20, 22, 23	Pb	Lead white	Tunic, drape, highlights
Green/18	Cu, Pb, Sb	Copper-based blue, Naples yellow	Curtain
Gray/21, 24, 25	Pb, Fe, Mn	Lead white, umber	Vessel, scale
Yellow/5, 6, 7, 8	Pb, Sb Pb, Fe, Mn	Naples yellow Yellow earth, umber	Clothes, decoration Mitra
Blue/9, 10, 11, 12	Cu Cu, Co, As	Copper-based blue (i.e., azurite) Copper-based blue, smalt	Clothes Clothes

[1] Hypothetic identification.

4. Discussion

The study of this work is an important asset in the knowledge of the palette and execution technique of Stanzione since only one diagnostic study has been published on his artworks [54]. Stanzione seems to have employed a brown-toned ground layer of earths, chalk, and lead white according to other typical seventeenth-century paintings.

The dark ground and pictorial layers show considerable thickness, making the infrared legibility of the underlying drawing difficult. In addition, the setting drawing coincides with the final outlines, creating considerable ambiguity in reading the IR image [54]. Despite this, traces of a diffuse drawing and contouring of the shapes that are rather broad but irregular and, therefore, probably executed by brush, are observed. The marks are clearly visible, e.g., a contour figure in the foreground. There appears to have been no change and uncertainty in the positioning of the figures, except in the character of Christ (Figure 10) and the head of the male figure on the left.

The artist's palette turns out to be varied. The flesh tones are executed with short, full-bodied, interwoven, and overlapping brush strokes that mainly consist of lead white and vermilion.

Here, Stanzione does not use the expensive ultramarine like he did for *Immacolata Concezione in Pescocostanzo* [54] but copper-based pigments and smalt for clothes.

Two different yellows are identified: Naples yellow for the clothes and yellow earth for the bishop's hat (*mitra*). Using different colorations, the artist probably wanted to give different importance to the objects on the scenery. Instead, a mixture of pigments including Naples yellow, a copper-based pigment, and smalt was used to obtain a green coloring for the curtain drape in the upper right corner of the painting.

The use of lead white and earths/umbers as whites and browns (e.g., for clothes, vessels, scales, architecture), respectively, is confirmed in the artist's palette by the presence of Pb, Fe, and Mn. The lead-based pigment can also have been mixed as siccative. In [47], it

is used to accelerate the complex process of oil drying. As an example, Spanish paintings in the oil technique were realized by adding lead white for this property [50].

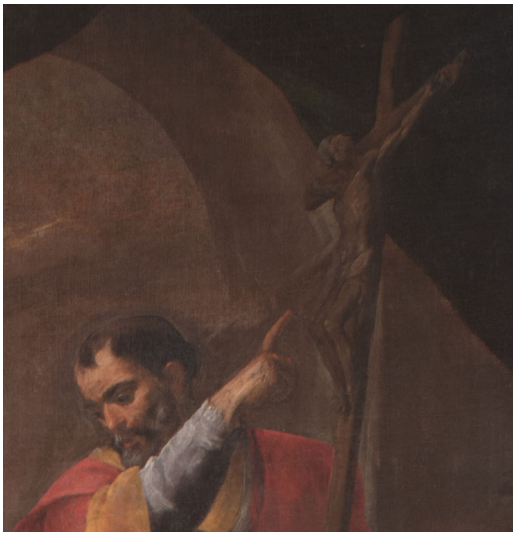


Figure 10. Detail of the crucifix.

Like *the Immacolata Concezione in Pescocostanzo* [54], Stanzione doses the concentration of some pigments differently with the presence of lead white for light tones that is based on a different chromatic background according to the areas. The light color base also performs the function of volume construction. In fact, the dense brush strokes emphasize some edges of the clothing and several inner drapes.

The high temperatures reached during the fire in the cathedral baked the color, making the already dark tones even darker, and the aging of the pigment/oil mixture caused the dark backgrounds to degrade further. This happens all the time because the brush strokes are less full-bodied and are often diluted with turpentine, as opposed to light pigments that are more resistant. It cannot be excluded that the restoration removed the final veils, but this cannot be identified as the only cause.

The background characters mixed with brown earths and a few light veils to define the details have almost vanished also because the cleaning carried out during the restoration took away the light ones. The flesh tones of the more advanced figures resisted, although they are still visible in their evanescence; this is because they were originally in a brighter light and, therefore, the color used was of a lighter tone.

The blue of the mantle in Figure 6 has not undergone any radical alteration at high temperatures. This may be due to the specificity of the pigment used, but further assessments would have to be made to explain this.

Many pigments and their distribution are identified by combining the IRFC images and the results of the XRF technique.

5. Conclusions

Multispectral imaging and XRF techniques were performed to analyze the painting *San Patroba predica ai fedeli di Pozzuoli* made by Massimo Stanzione for the Cathedral of Pozzuoli in the 17th century.

The thick pictorial layer does not allow the preparatory drawing to be revealed through the IR image. The unusual signature is different from the monogram usually used by Stanzione. In this painting, it appears that the artist has limited *pentimenti*.

The results of the XRF technique suggest the composition of the preparatory layer and the main colors used. The preparatory layer seems to be composed of lead white, gypsum, and earths. The main colors used by the artist are vermilion, lead white, copper-based blue, smalt, Naples yellow, and earths.

This work is the first step to getting to better know Stanzione and understand if the other artists, who painted coeval canvases for the cathedral, influenced each other. In the future, the other paintings will be analyzed to obtain a complete overview of the palettes of all the artists.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/qubs7040030/s1, Table S1: Counts of the X-ray characteristic lines of main elements detected by XRF analysis.

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