

Article

Non-Invasive and Micro-Invasive Characterization of the Tempera Painting Cristo in Trono (Amalfi, SA, Italy) by Domenico Morelli and Paolo Vetri: A Multivariate Statistic Approach Applied to Spectroscopic Data

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Abstract

Non-destructive diagnostic approaches play a crucial role in cultural heritage studies by enabling the assessment of artworks' conservation conditions without causing damage. This work presents the case study of the tempera painting Cristo in Trono, by Domenico Morelli and Paolo Vetri, located in Amalfi (SA, Italy). A multi-analytical approach combining portable and non-invasive techniques was employed. Hygrometric tomography revealed anomalous surface moisture values (up to 23 units) along the edges and wooden joints, identifying areas requiring particular attention during conservation. Infrared reflectography (IR-R) detected preparatory drawings, compositional changes, and evidence of previous restoration interventions. X-ray fluorescence spectroscopy (XRF) identified the elemental composition of the pigments, indicating the use of *cinnabar* (or *vermilion*), *ultramarine* (or *lapis lazuli*), *ochres*, *lead white* (*Biacca*), and *brass* (*Orone*) for the golden background. Multivariate statistical analysis of the XRF data (PCA and HCA) revealed compositional heterogeneity and chemically distinct areas within apparently similar chromatic regions. Micro-invasive analyses complemented these results by providing information on the stratigraphy and material composition. Fourier-transform infrared (FT-IR) spectroscopy identified polyvinyl acetate (PVA), attributed to previous restoration treatments and associated with the yellowing of *lead white*, together with protein-based binders. Microscopic observations revealed the woven structure of the support, pigment-layer cracking, and degradation features, while the interaction of the brass with atmospheric agents and marine chlorides was found to be responsible for the alteration of the original golden background to a greenish-gold hue. The lower part of the canvas exhibited the most severe deterioration, resulting from higher moisture levels, unsuitable past restoration treatments, and prolonged exposure to humidity, atmospheric pollutants, and marine aerosols, highlighting the importance of integrated diagnostic investigations for planning effective conservation and restoration strategies.



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1. Introduction and Historical Background

Non-invasive diagnostic methodologies play a key role in the study and conservation of cultural heritage objects, as they provide valuable information about the condition of artworks without compromising their integrity [1–6]. The characterization of constituent materials and artistic techniques is essential for understanding manufacturing processes, planning conservation measures, and selecting appropriate restoration treatments. Such information also contributes to the development of preventive conservation strategies aimed at ensuring the long-term preservation of cultural assets [7]. Since artworks are often fragile and susceptible to further deterioration, analytical approaches that minimize or eliminate physical intervention are generally preferred in the cultural heritage field [8–10]. In recent decades, significant advances have been made in the development of portable spectroscopic instruments, enabling researchers to perform investigations directly on site [11]. These technologies allow artworks to be examined in situ, reducing the need for sample collection and avoiding the risks associated with destructive laboratory procedures. Portable analytical techniques are particularly useful for identifying original materials, detecting degradation phenomena, and locating areas that may require more detailed investigation through targeted micro-sampling [12].

Infrared Reflectography (IR-R) is a well-established non-destructive diagnostic technique applied in the examination of ancient paintings: it enables the visualization of features beneath the pictorial layer by exploiting the transparency of many paint materials to infrared radiation and is useful to assess the state of conservation of materials [13]. Surface moisture is a parameter that needs to be monitored to assess the preservation condition of artworks that are particularly susceptible to humidity (e.g., wall painting and wooden structures) [14–17]. Among molecular techniques for the characterization of cultural heritage materials, infrared (IR) spectroscopy is widely applied in several modes, including Transmission and Attenuated Total Reflectance (ATR) mode, whereas Raman spectroscopy has become one of the most extensively used methods because of its ability to identify both inorganic and organic compounds with high specificity [18]. Concerning techniques for elemental characterization, Energy Dispersive X-ray Fluorescence (ED-XRF) remains the most widely used due to its portability, rapid analysis, and non-invasive nature, while complementary techniques such as Energy Dispersive Spectroscopy (EDS) coupled with Scanning Electron Microscopy (SEM), and Laser Ablation ICP-MS are employed for more specialized applications [10].

The increasing complexity and volume of spectroscopic data have made chemometric methods indispensable for data interpretation. Statistical tools such as correlation analysis, Principal Component Analysis (PCA), and Partial Least Squares (PLS) are routinely employed to classify samples [19], identify pigments and binders [20,21], determine provenance, and integrate datasets acquired from multiple analytical techniques. PCA, in particular, has become the most widely adopted approach because it effectively reveals similarities, differences, and hidden patterns within complex datasets [22]. A major application of these integrated analytical approaches is the study of material deterioration [23]. Cultural heritage objects are continuously exposed to environmental conditions, including atmospheric pollutants, humidity, radiation, microorganisms, and soluble salts, all of which contribute to chemical and physical degradation. Since no single analytical technique can provide a complete understanding of these processes, multi-analytical strategies combin-

ing molecular and elemental characterization with chemometric analysis have become essential [10]. The resulting information supports accurate diagnosis of deterioration mechanisms and provides the scientific basis for designing effective conservation, restoration, and long-term preservation strategies for cultural heritage materials.

Within this framework, the present research focuses on the examination of the painting *Cristo in Trono*, located in *Palazzo San Benedetto*, the seat of the Municipality of Amalfi (SA, Italy). This painting is a tempera on canvas dating from 1885 and is attributed to Domenico Morelli and Paolo Vetri. Both artists were involved in restoration activities carried out at the Amalfi Cathedral. Domenico Morelli was one of the most important Neapolitan artists of the nineteenth century, as one of the protagonists of the renewal of the arts in Naples and in Italy. He was among the great exponents of southern society who dedicated themselves to the safeguard of the civil and cultural items, after the Italian Unification. Primo Levi's famous manuscript (1906) reports his historical and psychological biography [24], describing him as an artist in contrast with his time and the surrounding society, never managing to fully express his talent in his works. The decoration of the pediment of Amalfi Cathedral with "golden and colored mosaic tiles" was one of his main goals, to "remove the crust of coarse plaster from the facade and possibly restore the ancient design", taking his inspiration from works-of-art as the Monreale Cathedral mosaic (Palermo, Sicily, Italy): thus he was commissioned to paint a preparatory canvas for the mosaic on the pediment. As from the Apocalypse scene, Morelli has represented a glorious Christ on an ivory Throne, wearing a green tunic with golden highlights, a blue mantle, and he is surrounded by a celestial arc that "resembles an emerald". In front of him, there is a baptismal font with seven golden lamps, and on either side of the throne are mystical creatures with seeing wings (*The Four Evangelists*), the first (from the left) resembling a winged lion which represents *Marco*, the second a winged calf which represents *Luca*, the third winged angel which represents *Matteo*, and the fourth resembling a flying eagle which represents *Giovanni*. At the back, the seats of the twenty-four Elders, who, on either side of the throne, prostrate, dressed in white, removing their crowns from their heads to adore him. The scene, included in a triangular area, symbol of the Trinity, was "all a brilliance of gold and white". Figure 1 shows the mosaic decoration reference of the Amalfi Cathedral (upper part) and the preparatory canvas, i.e., the *Cristo in Trono* painting (lower part), as obtained by photogrammetric technique after the survey and images acquisition conducted during the diagnostic investigations.

The canvas remains directly subject to the environmental microclimatic fluctuations of the exhibition room due to the absence of any protective barrier. Preliminary documentation suggests that a restoration campaign was carried out roughly two decades ago. Evidence of structural discontinuities is visible at the base of the support, where several cracks and fractures can be identified.

The present study combines non-invasive and micro-invasive analytical approaches to obtain a comprehensive understanding of the artwork's materials and conservation state. Among the non-invasive methods employed are X-ray fluorescence spectroscopy (XRF), infrared reflectography (IR-R) and Hygrometric investigations by using portable instrumentation that made it possible to carry out multiple measurements across the painting directly at its location, ensuring rapid data acquisition while preserving the physical integrity of the artwork [16]. Furthermore, these portable techniques have made it possible to identify points at which to take micro-samples for laboratory analysis, such as FT-IR spectroscopy and microscopic examination, in order to gain further insight into the nature and state of deterioration of the canvas and the materials used by the artists.



Figure 1. Upper part: mosaic decoration reference of the Amalfi Cathedral; lower part: the *Cristo in Trono* painting, as obtained by photogrammetric technique after the survey and images acquisition conducted during the diagnostic investigations.

2. Materials and Methods

2.1. Non-Invasive Analyses

Hygrometric investigations were carried out with an MO257 moisture meter from EXTECH Instruments (Boston, MA, USA), which detects relative humidity in contact with the surface by means of a spherical probe avoiding surface damage. The measuring points identified on the surface of the tempera painting *Cristo in Trono* are arranged along a point grid of 0.5 m × 0.5 m, along the entire dimension of the canvas. The values measured with the hygrometer were then processed with the Surfer software, from Golden Software (Golden, CO, USA), which made it possible to obtain a humidity distribution map of the surface (hygrometric tomography).

Infrared Reflectography (IR-R) analysis was performed using an IRIS Digital Basic camera system produced by Bresciani s.r.l. (Milano, Italy). The device operates in the near-infrared region and can record reflected radiation up to a wavelength of 1100 nm. To investigate the possible presence of underdrawings or restoration retouches not visible to the naked eye, a series of interchangeable pass-band filter lenses at 715 nm, 850 nm, and 1000 nm was employed. The acquired reflectographic images were subsequently processed and examined using IC Capture 2.4 software (Imaging Source Europe GmbH, Bremen, Germany).

The elemental composition of selected pigments (30 points as indicated with yellow dots in Figure 2) was investigated through X-Ray Fluorescence (XRF) spectroscopy. Measurements were carried out with a portable Hitachi X-MET8000 Expert GEO spectrometer, provided by TQ Technologies for Quality (Genova, Italy), featuring an X-ray tube with a rhodium (Rh) anode. This non-destructive analytical technique enabled the identification of the principal chemical elements present in the painted layers. The acquisition parameters were set as 8–15 kV for the detection of light elements (MiningLE-FP method) and 15–45 kV for the detection of heavy elements (Mining-FP method). The measurements were performed by pointing the RX source with a spot size of 3 mm, and each measurement was acquired in 30 s.

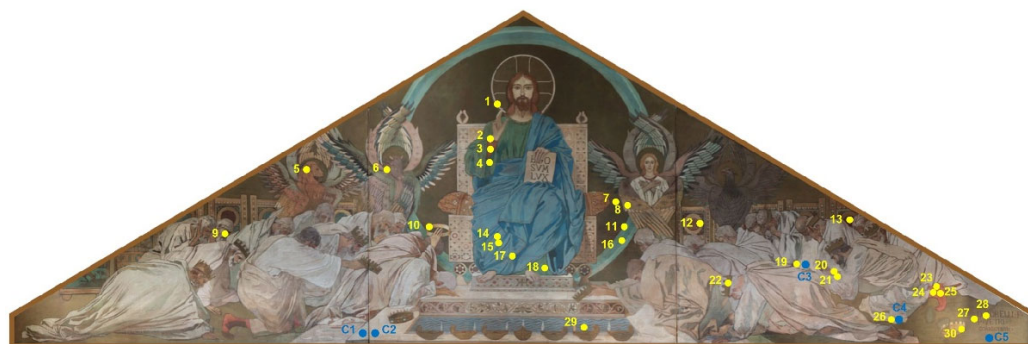


Figure 2. Yellow dots indicate the measuring points of XRF analysis. Blue dots indicate the sampling points for stereomicroscopic, microscopic and FT-IR analysis.

2.2. Micro-Invasive Analyses

Micro-samples (blue dots in Figure 2) collected from the surface of the canvas were preliminarily analyzed by stereomicroscopic observation by using a EOS 760D camera from Canon (Tokyo, Japan), in order to define the morphological characteristics of each fragment. Fourier Transform Infrared (FT-IR) spectroscopy analyses in attenuated total reflectance (ATR) mode were performed on the same micro-samples collected from the surface in order to detect the material constituents (both inorganic and organic compounds), check the nature of the binder used for the realization of the painting, as well as any organic compounds used in restoration interventions. The analysis was carried out with a Spectrum Two FT-IR spectrometer from Perkin Elmer (Shelton, CT, USA), and spectra (reported as wavelength cm^{-1} versus absorbance a.u.) were collected at a resolution of 4.0 cm^{-1} and a total of 32 scans were signal-averaged to reduce the noise.

Subsequently, each sample ($<5 \times 5 \text{ mm}$) was embedded in a bicomponent epoxy resin (Hardrock 554), then prepared in polished cross-sections for Optical Microscopy Stratigraphic (OMS) observations. The exam was performed in reflected light, in both VIS and UV mode, by using a Axioscope 5 microscope from Zeiss (Oberkochen, Germany) equipped with an Axiocam 208 color camera for the images acquisition. By means of microscopy observations of the polished sections, characteristics on the texture, the binder and the presence or absence of the preparation layer of the samples were identified, as well as any alteration phenomena (if present).

2.3. Multivariate Statistical Analysis—Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA)

Multivariate statistical analyses were performed on the XRF elemental dataset using RStudio software version 2026.01.2. Data handling and preprocessing were carried out using the dplyr, tibble, and stringr packages. PCA plots were generated using ggplot2 and ggrepel, whereas HCA heatmaps were produced using pheatmap and grid.

For the statistical treatment, the XRF dataset was divided into two separate data subsets, referred to as LE-FP and FP, according to the structure of the XRF output and the different elemental information provided by the two acquisition conditions. The two subsets were processed separately because they included different elemental variables and analytical responses. Therefore, PCA and HCA were not performed on a single merged matrix, but separately on the LE-FP and FP datasets.

Before multivariate analysis, uncertainty columns associated with each elemental measurement were excluded, and only elemental values were retained. When duplicated measurements corresponded to the same XRF point, acquisition subset, and analyzed area, the mean value was used. Non-detected or zero values were replaced by half of the minimum positive value detected for each element, in order to allow logarithmic

transformation and reduce the influence of missing values. To evaluate the possible influence of this replacement strategy on the multivariate results, a sensitivity analysis was performed. PCA and HCA were repeated using alternative replacement values for non-detected or zero values, namely one tenth of the minimum positive value and the minimum positive value detected for each element. The results were compared with those obtained using the half-minimum replacement approach, while keeping all other preprocessing and modelling steps unchanged, including log10 transformation, autoscaling, Euclidean distance, and Ward's agglomeration method. The resulting data matrices were then log10-transformed and autoscaled prior to PCA and HCA.

Principal Component Analysis (PCA) was performed using the `prcomp` function in R as an exploratory chemometric approach to evaluate compositional relationships among the analyzed areas and to identify the elements mainly responsible for sample separation. For the general PCA models, only elements detected in at least 70% of the analysed points were retained. In addition, targeted PCA models were built using selected elements of pigmentological and material interest. For the LE-FP dataset, the selected variables included Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Sr, Ba, Hg, and Pb. For the FP dataset, the selected variables included S, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Sr, Sn, Sb, Ba, Hg, and Pb. PCA score plots and biplots were used to investigate the distribution of the analyzed points and the contribution of the elemental variables.

Hierarchical Clustering Analysis (HCA) was performed on targeted XRF datasets to further evaluate compositional similarities among the analyzed areas. For the HCA heatmaps, a reduced set of elements was selected to improve the interpretability of the results and to focus on the main pigmentological and material markers. The LE-FP HCA matrix included Al, Si, S, Ca, Fe, Cu, Zn, Sr, Ba, Hg, Pb, Ti, and Cr, whereas the FP HCA matrix included S, Ca, Fe, Cu, Zn, Sr, Ba, Hg, Pb, Ti, Cr, Sn, Sb, and As. HCA was carried out using Euclidean distance and Ward's agglomeration method (`ward.D2`). Heatmaps were generated from log10-transformed and autoscaled data, with rows corresponding to XRF measurement points and columns corresponding to elemental variables. Row annotations were used to indicate the chromatic area analysed, allowing comparison between the visible features of the painting and the elemental composition.

3. Results

3.1. Hygrometric Tomography

Hygrometric measurements were carried out along the entire dimension of the canvas, allowing to obtain a moisture distribution false-color map of the surface (hygrometric tomography) (Figure 3).

As can be seen from Figure 3, the investigated fresco is affected by a widespread phenomenon of moisture anomalies expressed in arbitrary units (a.u.) in a range of 0.0–100.0. Values widely detected on the canvas surface are close to 2–5 units (highlighted by the colors turning yellow), while higher values were detected in correspondence of the wood joints which separate the three panels, with measured moisture close to 23 units. The phenomenon is especially visible in the center-right upper area of the canvas (highlighted by the colors turning to blue–violet), as well as in the center-left lower area, underlining a state of evident anomalies in the superficial water content. Although the values seem to be rather low, it is clearly visible that the wettest areas correspond to the wood joints, indicating that these areas should be considered priority zones for future environmental monitoring and the assessment of the state of conservation, paying particular attention in cases of restoring interventions practices.



Figure 3. Hygrometric tomography generated for *Cristo in Trono* painting. The color scale on the right shows the moisture content detected with the instrument placed in contact with the canvas surface.

3.2. IR-Reflectography

In order to identify hidden details such as restoration interventions, preparatory drawings, compositional changes (*pentimenti*), and possible degradation phenomena, different IR-R analyses were carried out on the entire canvas of the *Cristo in Trono* painting. Figure 4 shows the images acquired using different filters (Visible, 715 nm and 1000 nm) revealing the presence of numerous preparatory drawings and restoration interventions in several areas of the painting, observable at both 715 nm and 1000 nm (Figure 4c–g). The restoration work mainly concerns the lower part of the painting, suggesting that the artwork may have deteriorated significantly.

Figure 4c shows the kneeling elders positioned on the left side of Christ. The IR-R investigation highlights some features that are not visible in the VIS image. The face of the elder in the background appears partially obscured in visible light by a brownish shadow that covers his eyes. As the wavelength increases, the infrared radiation penetrates more deeply into the painting stratigraphy, and the 1000 nm image reveals the face of the elderly more clearly than the 715 nm images (red arrows). Additional details are visible on the mantle of one of the elder, the IR-R images reveal different contours of the painted shadow of the drapery (blue arrows) suggesting either adjustments made during the painting process or the presence of underdrawing lines subsequently concealed by the final paint layers.

Figure 4d shows the winged calf representing S. Luca. The IR-R images reveal numerous hidden details associated with the preparatory phase of the composition. In IR-R images is visible the preparatory drawing of the celestial arc (blue arrows) extending underneath the calf's wing and indicating the original position of the figure. The infrared images also reveal the evidence of a *pentimento*, showing that the calf's head was initially positioned slightly higher than in the final version. The earlier location of the horns (green arrows) can still be detected beneath the paint layers, indicating a compositional adjustment made by the artist during execution. In addition, the IR-R images show the traces of a previous position of the halo, visible below its current placement (red arrows).

Figure 4e shows three of the seven golden lamps on the baptismal font. The IR-R images highlight the preparatory drawing of the flames (red arrow) which are not perceptible in the VIS image. The underdrawing shows that the flames were originally larger and elongated than those visible in the result that we can see in visible light.

Figure 4f shows the angel representing S. Matteo. The IR-R images reveal a substantial difference between the preparatory drawing and the final painted composition. The images reveal the preparatory drawing of the wings that were probably positioned in front of the angel's body (red arrows) partially overlapping the torso and arms or maybe the original idea was to realize all the angel's body with feathers. Traces of the initial design remain visible in both infrared wavelengths, providing direct evidence of compositional revisions

undertaken by the artist. There are also visible traces of underdrawing on the angel's left wing used by the artist to give the shading and *chiaro-scuro* effect.

Figure 4g shows the feet of the kneeling elders positioned on the right side of Cristo. The IR-R images reveal variations in the contours of the drapery (red arrow), indicating modifications in the arrangement of the folds and of the shadows during the painting process. Behind the foot of the elder, in the IR-R images, is visible the greenish-gold background (green arrow). Furthermore, the 1000 nm image highlights the presence of some dark stains (blue arrows), due to reintegration of the *lacune* during the restoration.

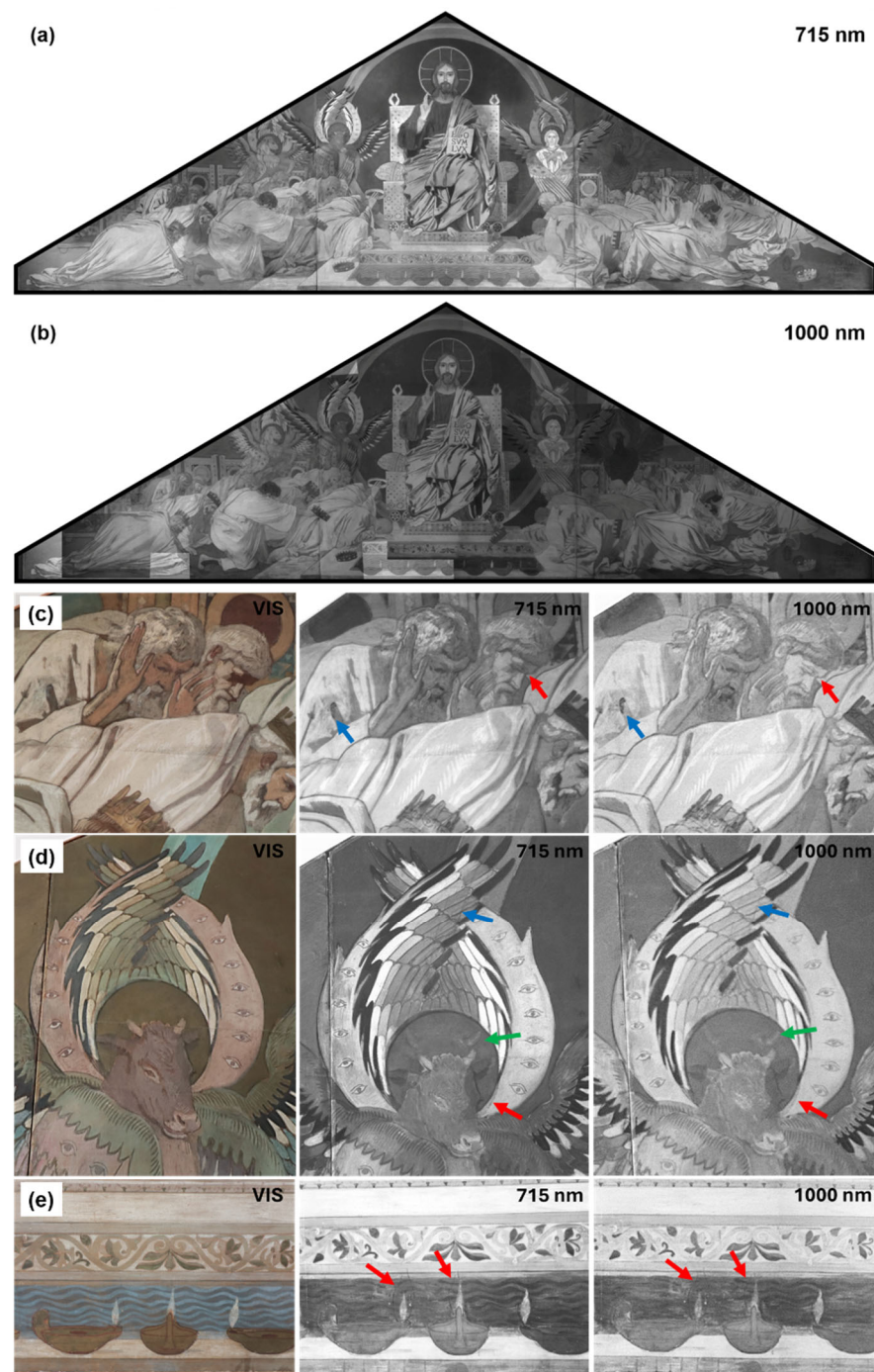


Figure 4. Cont.

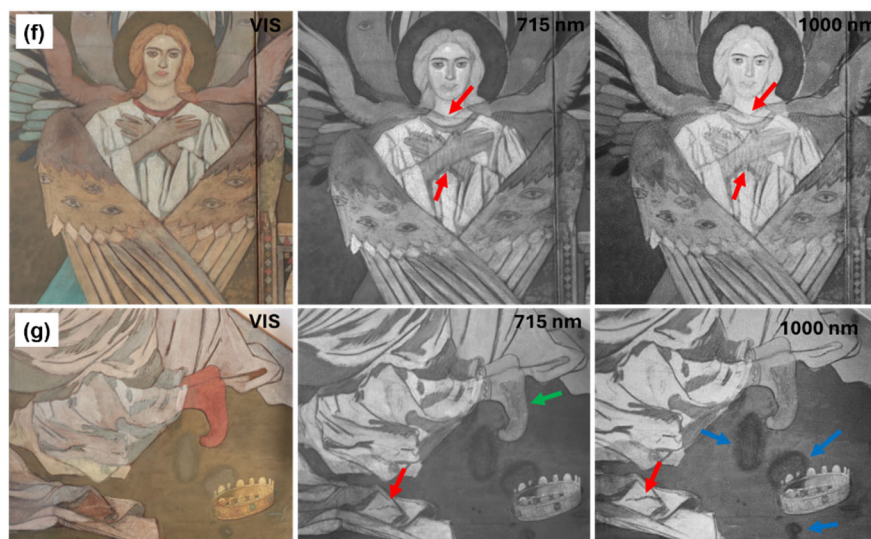


Figure 4. IR-R image of *Cristo in Trono* painting: overall picture at 715 nm (a) and at 1000 nm (b); Magnifications of areas of the canvas (c–g) where differences can be seen between images captured at different wavelengths (from left to right: in the visible, at 715 nm and at 1000 nm). Arrows indicate specific points.

3.3. XRF Analysis

In order to investigate the nature of the pigments used by the artists in the painting *Cristo in Trono*, an XRF elemental analysis was carried out on 30 points of the canvas, as indicated in Figure 2 and in Table S1 (see Supplementary Materials), where the complete list of the XRF measurement points is reported, together with the magnification images of the point analyses.

The results of XRF analyses on the most relevant points analyzed were reported in Figure 5, grouping the spectra (displayed as an overlay of the spectra recorded at 8, 15 and 45 kV) according to the type of color and similarities/differences in elemental composition. In all spectra, calcium and sulfur signals attributed to the underlying gypsum-based preparatory layer can be observed.

When interpreting the spectroscopic data obtained, it must be borne in mind that the canvas under examination was originally commissioned from the artists as a preparatory drawing for the mosaic in Amalfi Cathedral. As can be seen from Figure 1, the background of the mosaic is gold in color, a feature not observable when viewing the canvas under investigation, which was originally intended to reproduce all the colors of the mosaic. The measurement performed on the greenish-gold pigment of the background (point 27 in Table S1, spectra in Figure 5d) shows high quantities of Copper (Cu) and Zinc (Zn) attributable to the presence of brass (*Orone*). Brass powder was widely used as a cost-effective substitute for gold in both historical and modern artwork. To apply it, artists typically dispersed finely ground brass or bronze powders into organic binders such as drying oils, natural resins, gum Arabic, or synthetic mediums to ensure proper adhesion to the canvas [25]. In the present case study, brass powder was probably applied with a binder on the canvas surface to reproduce the effect of a golden pigment: the deterioration of the copper, caused by the lack of physical protection for the canvas against the atmospheric elements, has resulted in a change in color from gold to the gold-green hue, currently visible. The same pigment was used for the gold gilding on the edges of some elements and for the other elements originally colored gold. Furthermore, traces of copper and zinc were detected in most of the areas analyzed for other pigments, probably due to the presence of a layer of brass evenly distributed beneath the entire design. Titanium and vanadium were also detected in trace amounts: the presence of titanium may be due either to impurities of

this element in earth/ochre pigments, or to the use of pigments such as titanium white in restoration treatments; on the contrary, the vanadium detection, at amount not attributable to impurities in the pigments used by the artists or to restoration work, is more prone to instrumental errors, such as overlap with spectral lines of titanium which prevent its accurate quantification.

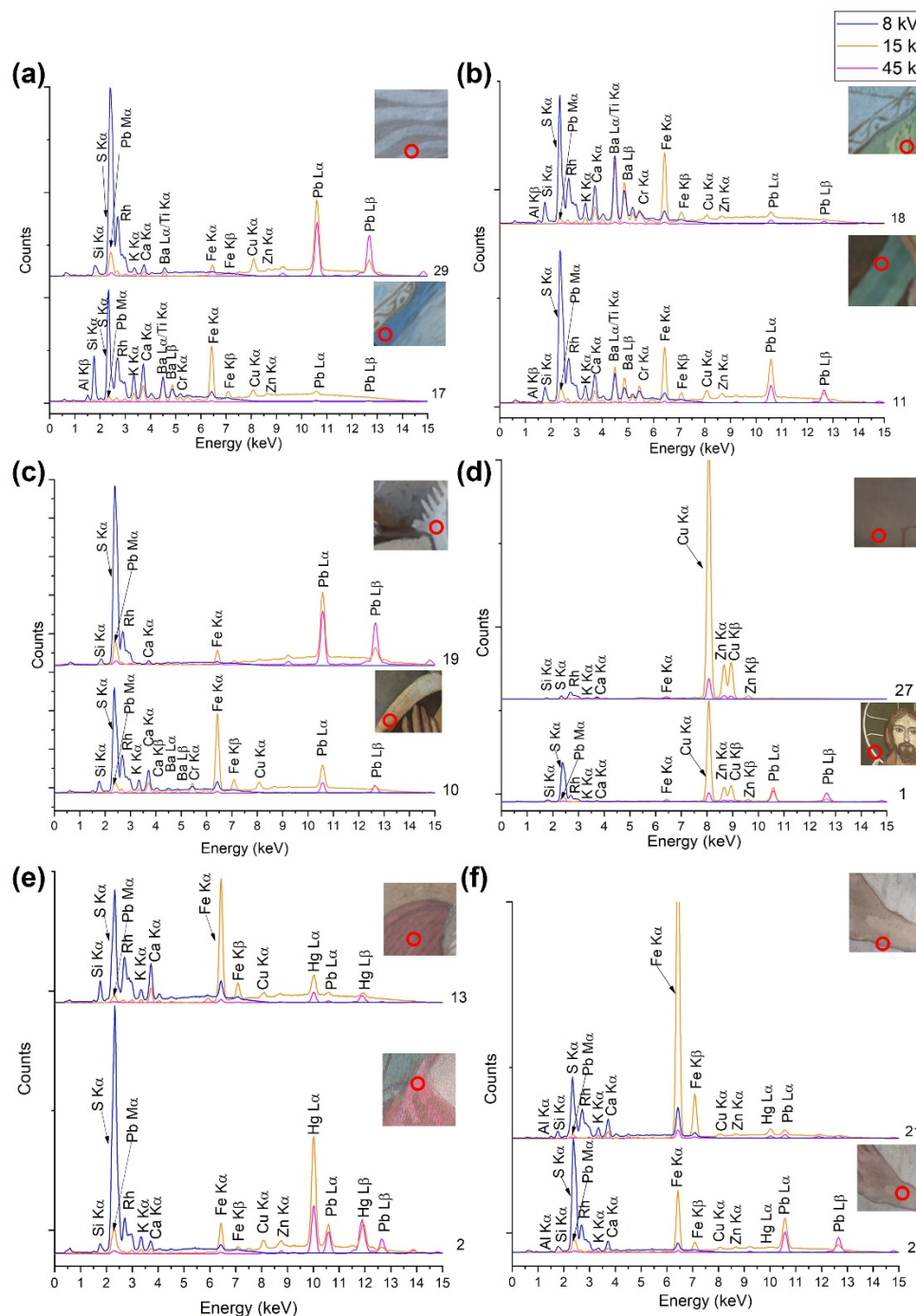


Figure 5. XRF spectra of the most relevant points analyzed, grouped according to the type of color observed and similarities/differences in elemental composition: blue (a); green (b); mainly white-yellow (c); mainly greenish-gold (d); red-brown (e,f). The label for each point is shown to the right of the spectrum, displayed as an overlay of the spectra obtained at the three selected voltages: 8 kV (blue line)—15 kV (orange line)—45 kV (magenta line). The assignment of the principal peaks is also shown (the Rh signal caused by the X-ray source is also indicated). At the top right of each spectrum the image of the measurement point is also reported, with red circles that indicate the exact point of measurement.

XRF analyses performed on white pigments (Figure 5c,d) show a similar elemental composition: lead (Pb) is widely present as the main component of the lead white pigment (basic lead carbonate, i.e., *Biacca*), as shown for white pigment no. 1 and 19, reaching an amount close to 65%. Yellow pigments are similar in composition, where the smallest amount of lead is mixed together with discrete amounts of iron (Fe), and some trace elements such as calcium (Ca), potassium (K), as typical composition of earth-based and ochre pigments, confirming the use of the *Yellow ochre*. Sulfur (S) was also detected in discrete amounts, which was related to sulphation phenomena which lead to the degradation of the pigments, as well as the presence of copper and zinc, belonging to the greenish-gold *Orone* background.

The analyses on blue pigments (Figure 5a) show similar elemental composition: a predominance of S, silicon (Si), aluminum (Al), and Ca, and the absence of cobalt (Co) and Cu in significant amounts supports the attribution of the blue pigments to *ultramarine*. Moreover, the detection of K (2–3%) and Fe (0.6–3%) suggests that this pigment is most likely natural *ultramarine* derived from *lapis lazuli*. However, further characterization techniques (Raman Spectroscopy, FTIR Spectroscopy and X-ray Diffraction) would be required to confirm the hypothesis of a natural origin. Elevated Pb levels were also observed, which may indicate the addition of lead white (*Biacca*) to the pigment mixture, likely to enhance opacity or modify the hue. Nevertheless, the possibility that part of the lead signal originates from later restoration treatments should also be considered. Chromium (Cr) was likewise detected in the analyzed area. Its presence may suggest the use of chromium-containing yellow pigments, such as *chrome yellow* or *Naples yellow*, potentially employed for tonal adjustment. However, considering the historical introduction of these materials, their occurrence is more likely related to conservation or retouching interventions carried out after the original execution of the artwork rather than to the artist's initial palette. Point 29 shows the use of a modified lead pigment, probably a chlorinated chrome yellow, mixed with mineral binders, to achieve a cool, opaque blue hue, with additional components (Sb, Cu, V, Ti) suggesting complex industrial pigments. It is possible that this section was retouched at a later date (19th–20th century) using industrial pigments or painted with a hybrid pigment introduced towards the end of the 19th century.

Similar elemental composition was observed for the green pigments (Figure 5b): Si, Al, K, and Fe as the main constituents, compatible with the use of green earth. Pb was also detected, possibly indicating the addition of lead white (*Biacca*) to the pigment mixture in order to modify its opacity and tonal properties. In addition, traces of Cr were identified, which may point to the presence of a small quantity of a chromium-based pigment employed to enhance the overall chromatic response.

Spectra obtained from the red pigments (Figure 5e,f) show well-defined mercury-related peaks, confirming HgS (*cinnabar* or *vermilion*) as the primary red pigment in points 2 (29% of Hg) and 13 (6.7% of Hg). The distinction between *cinnabar* and its synthetic counterpart (*vermilion*) is very complex since the impurities in mercury-based pigments are difficult to assess, depending also on the geographical origin of the mineral, and a correct discrimination between natural and synthetic requires specific techniques (μ -Raman and isotopic analyses). Pb was also detected, which is most plausibly associated with the presence of lead white (*Biacca*) added to the pigment mixture in order to obtain a brighter and less saturated tone. The presence of Fe in varying proportions (from 2% of point 2 to 20% of point 21) suggests that *red ochre* was used as the main component in the other red areas, mixed with HgS, which was used primarily around the edges of the figures. In addition, Si, K and Al were identified, that are typically linked to earth-based pigments and ochres.

Chlorine was also detected in some areas of analysis (the highest concentration, equal to 10%, was found at point 29). Possible sources of chlorine include marine aerosol deposition from the coastal town of Amalfi, impurities in the pigments, substrate pretreatment or cleaning interventions with chloride-based biocidal products. Such materials could have contributed to localized deterioration phenomena observed in the lower portion of the canvas, potentially aggravated by prolonged floor contact and moisture absorption.

3.4. Elaboration of XRF Analyses by Multivariate Statistical Analysis

In the present work, PCA and HCA were used as complementary chemometric tools to provide a global and comparative interpretation of the XRF elemental dataset. Their purpose was not to replace the direct interpretation of individual XRF spectra, but to evaluate all analyzed points simultaneously and to highlight compositional relationships, heterogeneity, and chemically distinct areas within the pictorial surface. This approach is particularly useful in cultural heritage studies, where visually similar chromatic regions may correspond to different pigment mixtures, stratigraphic contributions, degradation products, or restoration materials.

In detail, Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA) were applied to the elemental data in order to obtain a more integrated interpretation of the XRF dataset. These multivariate approaches were used as exploratory tools to support the direct interpretation of the XRF results, rather than as standalone methods for pigment identification. Their aim was to highlight compositional similarities and differences among the analyzed points and to identify possible chemically distinct areas within the pictorial surface. Among the processed datasets, the targeted LE-FP dataset was selected for the main discussion because it included both light elements and diagnostic elemental markers relevant to the interpretation of pictorial materials, such as Al, Si, S, Ca, Fe, Cu, Zn, Sr, Ba, Hg, Pb, Ti, and Cr.

The PCA biplot obtained from the targeted LE-FP dataset is reported in Figure 6a. The first two principal components explained 48.9% of the total variance, with PC1 accounting for 33.3% and PC2 for 15.6%. Although the first two components do not account for the entire variability of the XRF dataset, they provide a useful overview of the main compositional trends among the analyzed points. The score distribution shows that the separation of the samples is only partially related to the visible color of the investigated areas. This indicates that the elemental composition is also influenced by additional factors, including pigment mixtures, stratigraphic contributions, underlying layers, local alteration phenomena, and possible restoration materials.

Several red areas are distributed along positive PC2 and in the direction of the Hg loading. This trend supports the direct XRF evidence for the presence of Hg-bearing red materials, consistent with the use of cinnabar/vermilion in different red regions of the painting. However, the red points do not form a single compact group, indicating compositional variability among visually similar red areas. This variability may be related to differences in pigment mixtures, layer thickness, local stratigraphy, contributions from underlying red or brownish layers, or conservation/restoration effects. Therefore, the PCA does not indicate a chemically homogeneous red palette but rather supports the presence of Hg-rich red areas within a more complex compositional framework.

Blue and blue-green areas also show a heterogeneous distribution in the PCA space. Some points related to the blue mantle and the celestial arc are located in the positive PC1 region and are associated with elemental contributions such as Ca, S, K, and Sr, whereas other blue points occupy distinct positions. In particular, the point corresponding to the blue area of the baptismal font is separated from the main group of blue/light-blue areas. This suggests that visually comparable blue regions may not share the same elemental

profile. Such behavior may reflect differences in pigment mixtures, variable contributions from underlying layers, or later interventions. Thus, the PCA supports the presence of compositional heterogeneity among the blue areas, without implying direct pigment identification from the multivariate model alone. A relevant example of the added value of the multivariate treatment is represented by point 29, visually classified as a blue area of the baptismal font. Although this point belongs to a blue chromatic region by visual inspection, it does not group with the main blue/light-blue areas associated with the Christ mantle and the celestial arc. Its distinct position in the PCA space and its different clustering behavior in the HCA indicate that this visually blue area is characterized by a different elemental profile. This evidence suggests that the blue appearance of point 29 may result from a different pigment mixture, a stronger contribution from underlying layers, or a possible later restoration intervention. Therefore, PCA/HCA allowed the recognition of a chemically anomalous point within an apparently similar chromatic class, providing information that would be less evident from visual observation or from isolated point-by-point XRF interpretation alone.

Green and blue-green areas are mainly distributed toward positive PC1 and negative PC2, in the direction of elements such as Ba, Sr, Cr, V, Ti, and Pb. This distribution suggests that these areas are characterized by an elemental profile different from most red, white, and yellow/gilded regions. Nevertheless, these elements cannot be attributed to a single pigment only on the basis of PCA. Their association may reflect multiple material contributions, including pigment mixtures, fillers, preparatory or underlying layers, alteration products, or restoration-related compounds. For this reason, the PCA results should be interpreted as evidence of compositional differentiation among the analyzed areas, rather than as a direct assignment of specific pigments.

The HCA heatmap of the targeted LE-FP dataset is shown in Figure 6b. The clustering provides complementary information to the PCA by visualizing similarities among the measurement points on the basis of their overall elemental profiles. The heatmap shows that the grouping of the analyzed points is not exclusively controlled by the visible color of the areas. Some green and blue-green points show relatively similar compositional behavior, whereas red, yellow/gilded, white, brown, and background-related areas are distributed across different branches of the dendrogram. This result highlights the heterogeneous nature of the pictorial materials and indicates that visually similar regions may differ in their elemental composition.

The HCA also helps to identify specific points with distinct compositional behavior. For example, not all blue and light-blue areas cluster together, in agreement with the PCA evidence of variability among blue regions. Similarly, yellow and gilded areas are not grouped into a single cluster, suggesting that these regions may include different material contributions or different interactions with underlying layers and restoration materials. The distribution of white and background-related points across separate branches further supports the complexity of the painted surface and the absence of a simple one-to-one relationship between visible color and elemental composition.

The sensitivity analysis showed that the main PCA results were not substantially affected by the replacement strategy adopted for non-detected or zero values. In the targeted LE-FP dataset, PC1 and PC2 explained 47.5–49.3% of the total variance across the three tested strategies, whereas in the targeted FP dataset they explained 46.9–49.9%. In addition, the correlations between PCA scores obtained using the alternative replacement strategies and those obtained with the half-minimum approach were very high, ranging from 0.990 to 0.999 for PC1 and from 0.954 to 0.994 for PC2. These results indicate that the PCA score distribution and the main compositional patterns were stable with respect to the tested preprocessing approaches.

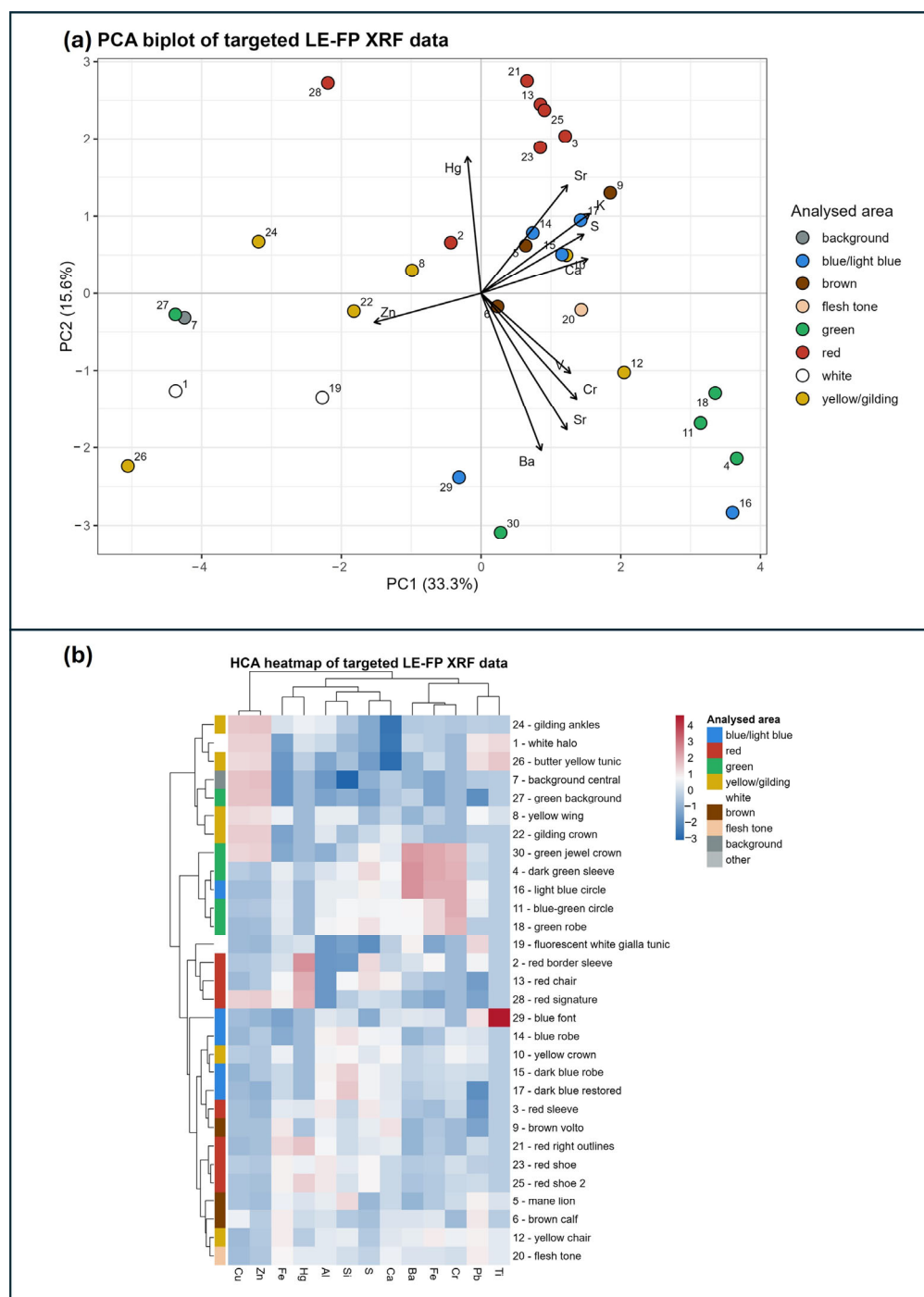


Figure 6. Multivariate statistical analysis of the targeted LE-FP XRF dataset. **(a)** PCA biplot showing the distribution of the analyzed points and the contribution of the elemental variables. Points are colored according to the chromatic area investigated. **(b)** HCA heatmap obtained from log10-transformed and auto scaled XRF data. Rows correspond to XRF measurement points, columns correspond to elemental variables, and row annotations indicate the analyzed chromatic areas.

For HCA, minor variations in dendrogram topology were observed, as expected because hierarchical clustering is more sensitive to small changes in the distance matrix. However, the cophenetic correlations between the dendrograms obtained using the alternative replacement strategies and those obtained with the half-minimum approach ranged from 0.672 to 0.909, indicating moderate-to-high similarity. Therefore, although some local differences in cluster arrangement may occur, the main HCA-based interpretation and the

overall conclusions drawn from the multivariate analysis were not substantially affected by the replacement strategy.

Overall, the combined PCA and HCA elaboration provided an additional interpretative layer to the XRF results. PCA highlighted the elemental variables mainly responsible for the separation of the analyzed areas, whereas HCA visualized compositional similarities and differences among the measurement points. Importantly, the multivariate approach showed that the relationship between visible color and elemental composition is not always one-to-one. It revealed compositional heterogeneity within visually similar red and blue areas, including the anomalous behavior of point 29, and showed that yellow/gilded and background-related regions are distributed across different compositional groups. These results support the complex conservation history of the painting but also provide additional information by identifying chemically distinct areas that are not immediately evident from visual classification alone.

3.5. Stereomicroscopic and Optical Microscopic Observations and FT-IR Analyses

Stereomicroscopic, Optical Microscopic Stratigraphic (OMS) observations and FT-IR analyses were performed on micro-samples collected as shown in Figure 2.

Samples C1 and C2 were collected near the junction of two panels of the canvas (from the left and the center panels, respectively), macroscopically showing two different grades of white pigment (*Biacca*), as identified by means of XRF analyses, while samples C3 to C5 were collected from the right panel of the canvas. Samples C3 and sample C4 consist of two different grades of white pigment, too. Lastly, sample C5, which was collected from the right panel, consists of a fragment of the brass background (*Orone*).

All the samples (C1 to C5) were preliminary observed as collected by stereomicroscopy and analyzed by FT-IR spectroscopy in ATR mode, without any preparation, for the identification of the painting materials, in terms of pigments and binders (Figure 7).

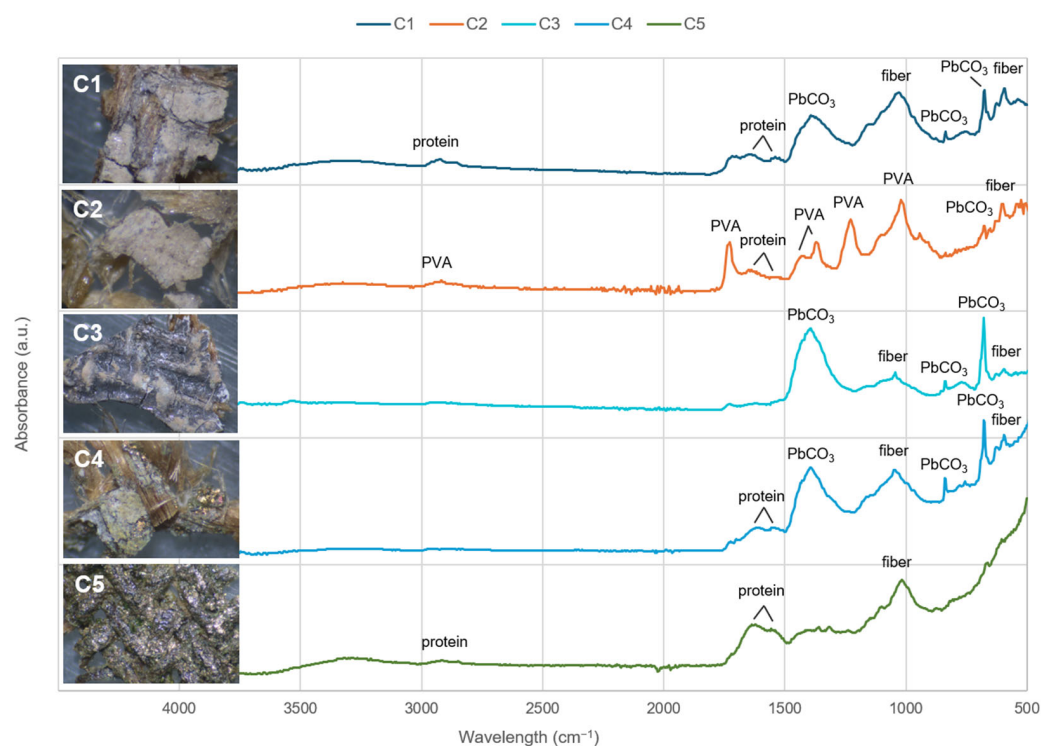


Figure 7. FT-IR spectra, acquired in the wavelength range from 500 cm^{-1} and 4000 cm^{-1} , performed on white pigment samples C1, C2, C3, C4 and C5.

FT-IR spectra provided valuable information on the pigments, the binding media and the support. Overall, all spectra exhibit a significant contribution from cellulose (named as “fiber” in Figure 7), due to the fibrous support of the canvas, as evidenced by the characteristic absorption bands around 3300 and 2900 cm^{-1} , corresponding to O–H and C–H stretching vibrations, respectively, as well as the bands in the region between 1100 cm^{-1} and 870 cm^{-1} , and by the bands located at 624 and 590 cm^{-1} . Moreover, the white pigment samples (particularly C1, C3 and C4) show very similar spectral profiles, reporting the characteristic absorption bands of lead white (i.e., *Biacca*, named as “ PbCO_3 ” in Figure 7) at approximately 1364 – 1397 cm^{-1} and 678 cm^{-1} , which are associated with carbonate group vibrations, accordingly to what was detected by XRF spectroscopy. As for the binder medium detection, vibrational bands compatible with the presence of protein-based binder were detected at 1700 cm^{-1} and 1500 cm^{-1} . In detail, the occurrence of a protein-based binder is indicated by absorption of the amide groups, typically observed in the regions around 1650 – 1540 cm^{-1} . It is worth noting that in sample C2, consisting with the same lead white pigment composition (i.e., *Biacca*), the presence of poly(vinyl acetate) (PVA in Figure 7) was detected, in addition to the characteristic bands of lead white and cellulose. Vibrational bands of PVA are clearly shown at 2919 , 1729 , 1429 , 1370 , 1228 , 1097 , 1019 , 943 , and 795 cm^{-1} . Poly(vinyl acetate) is usually used as a consolidant in art restoration: this synthetic polymer may indicate a later intervention or the use of modern conservation materials, as PVA is commonly employed as an adhesive and consolidant in restoration practices. In this case, probably the application of PVA on the central panel of the canvas has led to the color change of the white pigment [16] from a cold to a yellowish white color. It is noting that the vibrational bands located at 1050 cm^{-1} and 1400 cm^{-1} result from the contribution of the cellulose and the lead carbonate, belonging to the canvas support.

Lastly, sample C5 was collected from the greenish-gold “*Orone*” painted area, exhibiting a spectrum dominated by the characteristic absorption bands of cellulose, with major peaks located at 3290 , 2920 , 1620 , 1360 , 1317 , 1240 , 1155 , 1100 , 1016 , 820 , 624 and 590 cm^{-1} [26,27]. Further absorption bands of the amide group at 1650 and 1540 cm^{-1} indicate, even in this case, the presence of a protein-based binder, confirming the using of an organic binder for the application of the brass powder [28].

Optical Microscopy Stratigraphic (OMS) observations were performed on samples C3 and C5 by embedding them in epoxy resin and cutting them in cross sections, only after their preliminary study by stereomicroscopy and FT-IR spectroscopy. Samples C3 and C5 consist of the white pigmented and gilded areas, respectively, chosen for their preservation of all the stratigraphic layer succession. OMS observations were performed in VIS and UV reflected light mode (Figure 8). The combined use of these techniques for the study of the canvas surfaces provides a full range of parameters (as color, fluorescence response, surface morphology, layer thickness and interfaces, roughness profile, degradation phenomena such as cracks, gaps, and discontinuities in the layers) [29].

Stereomicroscopic and microscopic images of samples show the absence of a preparatory layer. The white pigment (*Biacca*) layer in sample C3 and the greenish-gold pigment (*Orone*) layer in sample C5 observed in stereomicroscopy shows the morphology of the woven fibers of the canvas. Sample C3, corresponding to the white-painted area, exhibits a compact and relatively homogeneous pigment layer identified as lead white. Stereomicroscopic observation shows the surface morphology that reveals the woven structure of the canvas support, and several cracks on the pigment layer indicating degradation processes that have affected the material over time. Some dark areas are also visible, probably due to degradation phenomena commonly affecting lead-based pigments. Lead white is sensitive to the presence of sulfur detected in most of the investigated areas with XRF analysis,

therefore, the exact origin of these darkened regions needs further investigation. Sample C5, collected from the greenish-gold painted area, shows a different morphology. The pigment layer is heterogeneous, and numerous metallic particles are visible due to the application of brass powder to simulate the gold effect on the surface confirmed with XRF analysis. The pigment layer in C5 is different from the one of C3. It shows a more irregular texture and a less compact structure, suggesting a different application technique.

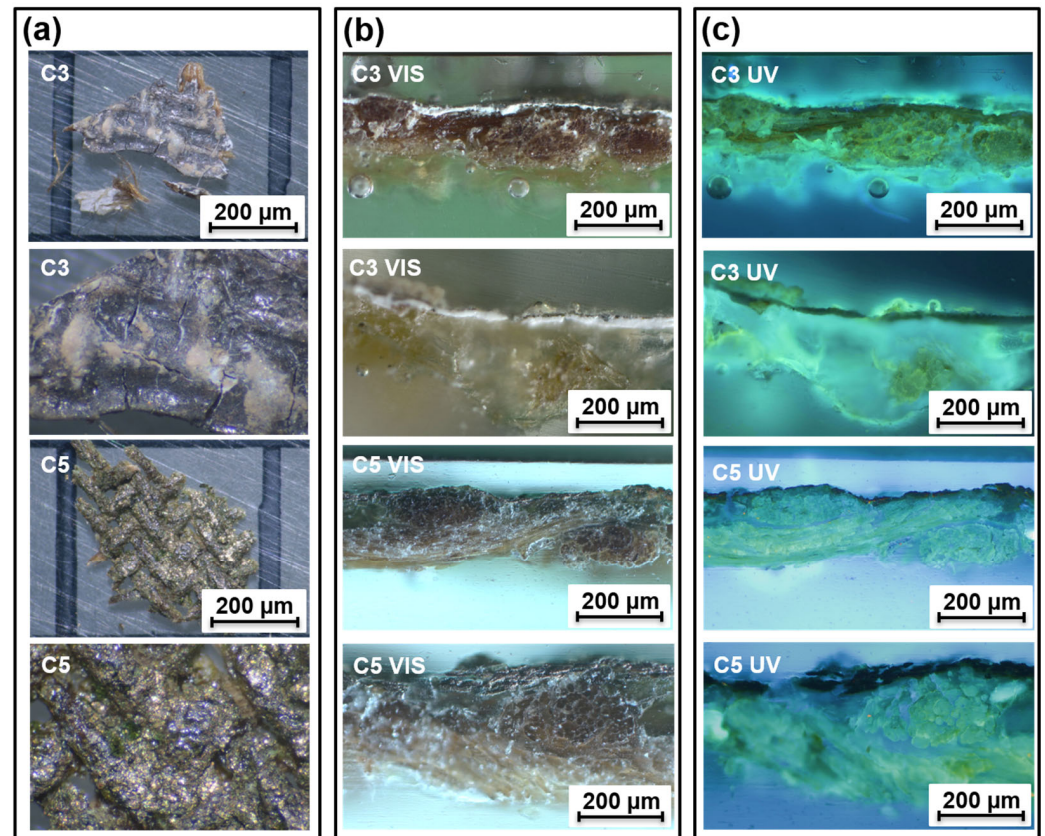


Figure 8. Images of samples from stereomicroscopic observation (a) and microscopic-stratigraphic observation in VIS (b) and UV (c) reflected light on the cross-section of samples C3 and C5.

The cross-section observation, in both the samples, did not show a preparatory layer between the textile support and the paint layer, suggesting that the pictorial layer may have been applied directly onto the textile support. The thickness of both *Biacca* and *Orone* layers are around 30 microns. The morphology of the canvas fibers is clearly visible in the cross-sections. Both transverse and longitudinal views reveal the characteristic features of cellulose-based textile fibers. The fiber transversal section shows the typical shape of rounded polygons with a small central lumen [30], while longitudinal sections show elongated structures consistent with woven textile fibers. The average diameter of the single fiber is approximately 300 microns, in agreement with the dimensions expected for the type of textile support employed.

Examination under ultraviolet (UV) illumination provides additional information regarding the organic materials present in the samples. The fibers and some localized areas exhibit moderate fluorescence, which is compatible with the presence of a proteinaceous binder identified through FT-IR analysis. Both the white and the greenish-gold pigments did not show fluorescence.

3.6. Integrated Interpretation of the Multi-Analytical Results

The combination of non-invasive and micro-invasive techniques allowed the results obtained from each analytical approach to be interpreted within a single diagnostic framework. Hygrometric tomography provided information on the spatial distribution of moisture across the canvas, highlighting areas of potential conservation concern, especially near structural discontinuities and panel joints. IR-R complemented this information by revealing hidden features, preparatory traces, and areas related to previous restoration interventions that were not clearly visible under ordinary observation. XRF analysis provided the elemental basis for pigment interpretation, while PCA and HCA allowed the XRF dataset to be evaluated globally, highlighting compositional similarities and anomalies among the analyzed points. In this respect, the multivariate analysis was particularly useful for recognizing chemically distinct areas within visually similar chromatic classes, such as the anomalous behavior of point 29 among the blue/light-blue regions. FT-IR and microscopic observations provided further confirmation on selected micro-samples, revealing the presence of organic materials related to binders or restoration practices, as well as morphological features associated with degradation phenomena and the heterogeneous structure of the green-gold background. Finally, the integration of these techniques showed that the painting is characterized by a complex stratigraphy and conservation history. The green-gold background can be interpreted as a brass-based layer affected by alteration processes, supported by the XRF detection of Cu and Zn and by the microscopic observation of metallic particles. The white and yellowish areas reflect the presence and alteration of lead-based materials, further supported by FT-IR and microscopic evidence. Finally, the correspondence between IR-R evidence of restoration features, FT-IR detection of restoration-related materials, and the compositional variability highlighted by XRF/PCA/HCA confirms that the painting surface is not chemically homogeneous, even where the chromatic appearance is apparently similar.

4. Discussion

The multi-analytical approach adopted in this study, based on a combination of non-destructive and micro-invasive techniques, provides essential information on both the pigment palette and the state of preservation of the *Cristo in Trono* painting by Domenico Morelli and Paolo Vetri, thereby offering restorers a sound scientific basis for future work.

Firstly, superficial moisture values detected on the surface of the canvas are mostly low (2–5 units); however, it is clearly visible the presence of evident anomalies which correspond to the edges of the canvas and the wooden joints separating the three panels (with moisture values of 23 units), indicating the areas requiring particular attention during restoration work.

The IR-R analyses carried out on the entire canvas of the *Cristo in Trono* painting reveal the presence of numerous hidden details such as preparatory drawings, compositional changes (*pentimenti*), and possible restoration interventions in several areas of the painting, observable at both 715 nm and 1000 nm (Figure 4c–g). The restoration work mainly concerns the lower part of the painting, suggesting that this artwork may have deteriorated significantly.

XRF analyses on the main pigments—blue, green, white, red and greenish-gold (Figure 5)—of the *Cristo in Trono* painting made it possible to identify the presence of different pigments, including *cinnabar* (or *vermilion*) and *lapis lazuli* (or *ultramarine*), mixed with *ochres* and *Bianca* (i.e., *Lead white*, the most used pigment by artists all around Europe in the nineteenth century, due to its high dense covering power). The pigments identified are consistent with the findings of studies in the literature concerning paintings by Italian artists from the same historical period of Morelli [31,32]. For instance, a literature study

of 2010 presented the pigments characterization of ten paintings made by Giovanni Fattori between 1854 and 1893 using Scanning Electron Microscopy Energy Dispersive X-ray (SEM-EDS) spectroscopy: this destructive technique allowed to identify *lead white*, *red* and *yellow ochre*, *cinnabar* or *vermilion*, *Naples* and *chrome yellow*, *Cobalt blue*, *Prussian blue*, and *ultramarine* [32]. A more recent study, which involved the use of non-invasive techniques such as XRF, External Reflection FT-IR and Raman spectroscopy, to characterize ten paintings dating from 1889 and 1940 by the Venetian painter Alessandro Milesi, revealed the presence of *lead white* in the oldest paintings (replaced by *zinc* and *titanium white* in the more recent ones) *vermilion*, *red ochre*, *cadmium red* and *Cobalt blue* [31].

The high quantities of Cu and Zn on the greenish-gold background are attributable to the presence of degraded brass (*Orone*), used by the artists as a cost-effective substitute for gold [25] to give a golden color. Concerning the corrosion path of Cu-Zn alloy, it is well known that zinc is more reactive than copper, due to its lower reduction potential (−0.763 V for Zn respect 0.340 V for Cu) and so Zn reacts more readily than Cu. In marine atmospheric environment, the high amount of chloride ions accelerates the corrosion process by reaction of zinc [33,34]. A literature study [35] on brass containing 37% of Zn has shown that, after exposure to marine atmosphere, basic zinc and copper chlorides are formed, according to the reactions reported in Figure 9.

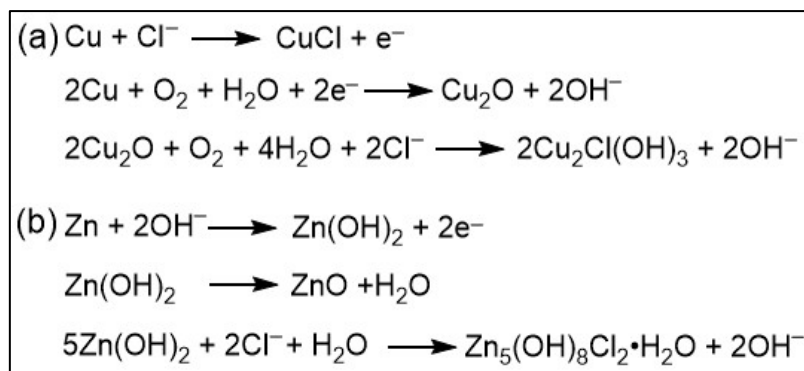


Figure 9. Reaction scheme of formation of basic chlorides of Cu (a) and Zn (b) after exposure to marine atmosphere.

In our study, Cu/Zn ratios obtained by XRF analysis are in the range 8.6–9.2, in line with the proportions given for brass alloys used as golden pigment, namely 90% of Cu and 10% of Zn [15]. However, no study reports an analysis of this type of brass, which contains low percentages of zinc (less than 15%), making it not susceptible to dezincification process [36]. Based on these considerations, the most likely scenario is the formation of metal chloride as degradation products of brass; however, this cannot be demonstrated by the investigations carried out since XRF provides no information on the nature of the chemical compound in which the detected elements are found and ATR-FT-IR analyses performed on microsamples are not able to reveal any brass corrosion products. It should be noted that FT-IR was carried out on the entire sample, which therefore also contained canvas backing and binders, in addition to the surface pigments. Due to the small sample quantities, it was not possible to carry out more detailed FT-IR analyses or a Raman analysis; according to the literature [37] the latter might have more readily revealed the presence of copper degradation products.

The canvas is therefore in a precarious state of preservation, given the severe deterioration of the gilded ground caused by the copper's exposure to the atmosphere; this is also visible in the stereomicroscopic examination of the small fragments collected, showing dark areas on the surface of the pigments, mainly caused by pigment exposure to the salts-enriched environment (Figure 8). Furthermore, significant concentrations of chlorine

(attributable to impurities in the pigments, marine aerosol deposition from the coastal town of Amalfi, and previous restoration or cleaning work) have been detected in certain areas of the canvas showing advanced signs of deterioration.

PCA on XRF data supports the presence of compositional heterogeneity amongst areas in the same color class. Some points related to the blue mantle and the celestial arc are in the positive PC1 region and are associated with elemental contributions such as Ca, S, K, and Sr, whereas other blue points occupy distinct positions (e.g., point 29). Green areas are mainly distributed toward positive PC1 and negative PC2, in the direction of elements such as Ba, Sr, Cr, V, Ti, and Pb. This distribution suggests that these areas are characterized by an elemental profile different from most red, white, and yellow/gilded regions. The HCA clustering provides complementary information to the PCA by visualizing similarities among the measurement points based on their overall elemental profiles: some green and blue-green points show relatively similar compositional behavior, whereas red, yellow/gilded, white, brown, and background-related areas are distributed across different branches of the dendrogram. The distribution of some color across separate branches further supports the complexity of the painted surface and the absence of a simple one-to-one relationship between visible color and elemental composition.

Based on these results, certain areas of the canvas were selected for micro-invasive analysis. The results of FT-IR analyses on micro-samples collected from the canvas show: a significant contribution from cellulose fibers; the presence of PVA, attributed to restoration practices [26], responsible for the change of the white pigment (*Bianca*) from a cold to a yellowish white color; the presence of bands associated with protein compounds [28], suggesting that protein-based binder (such as animal glue, casein or egg white) was used to apply both the brass ground and the pigments.

Examination under a stereomicroscope of the same micro-samples taken from the canvas, and also their consequent stratigraphic examination by optical microscope of prepared cross-sections, reveals the interwoven structure of the support and several cracks in the pigment layer, indicative of the degradation processes that have affected the material over time, and some dark areas. The optical microscopy analysis carried out provides no information on the chemical nature of the substances responsible for the formation of these black areas, allowing only their identification. However, the limited amount of sample did not permit the use of techniques such as XRD, which would have enabled a complete chemical characterization of the degraded areas. Based on the nature of the pigment used by the artists, namely lead white, and the information reported in the literature, we can assume that these areas are associated with the formation of lead sulphides and/or oxides: indeed, in the absence of appropriate conservation strategies, exposing paintings to the air (especially in presence of humidity, light, oxidizing agents and alkaline environment) [38] and to significant concentrations of volatile sulphur-rich pollutants can lead to the formation of by-products such as oxides (e.g., PbO_2), sulphates (e.g., PbSO_4) and sulphides (e.g., PbS), which are responsible for the blackening of lead white [39].

Although it is not possible to observe an overall correlation between the different types of investigation considered in this study, also because the micro-sampling was limited to certain areas of the canvas where signs of deterioration were already visible to the naked eye, the results of all techniques lead to the same conclusion on the state of preservation of the tempera painting *Cristo in Trono*. Greater degree of deterioration is observed in the lower part of the canvas, where higher surface moisture levels are observed, along with the greatest number of restoration and/or cleaning interventions, as evidenced by both the IR-R measurements and the ATR-FT-IR analysis of the micro-samples. It is also possible to observe that the most appropriate strategies were not employed in previous restoration work, such as the use of PVA, which caused a change in the original color of the lead white.

Nevertheless, it was possible to observe the effect of exposure to the air on the deterioration of the pigments used. Abnormal levels of chlorine and sulphur suggest that the pigments have degraded as a result of exposure to humidity and/or sulphur-containing atmospheric pollutants (see the blackening of the lead white) and marine aerosols (see the greening of the brass background). All these aspects must be taken into account when planning a proper restoration and improving the conservation strategies for the canvas.

5. Conclusions

In this study, a multi-analytical approach based on non-invasive and micro-invasive was applied to the analysis of the painting *Cristo in Trono* by Domenico Morelli and Paolo Vetri (Amalfi, SA, Italy).

Hygrometry and IR-R showed some restoration interventions thus confirming the degradation of the painting layer. XRF analysis highlighted the use of pigments such as *ultramarine* (or *lapis lazuli*) and *cinnabar* (or *vermilion*), whilst also providing information regarding the condition of the work, such as the deterioration of the brass originally used for the gilded background and the presence of significant concentrations of chlorine in certain areas of the canvas that show advanced signs of deterioration. The results of PCA and HCA provided a global and comparative interpretation of the XRF dataset, allowing the simultaneous evaluation of all analyzed points and elemental variables. The multivariate approach highlighted that visually similar chromatic areas do not always correspond to homogeneous elemental compositions. PCA/HCA revealed compositional variability among red and blue regions and identified point 29, visually classified as a blue area of the baptismal font, as chemically distinct from the main group of blue/light-blue areas. This behavior suggests possible differences in pigment mixtures, stratigraphic contributions from underlying layers, or later restoration interventions. Therefore, PCA and HCA did not merely confirm the direct XRF interpretation but provided an additional interpretative layer by identifying chemically distinct areas within apparently similar chromatic classes. These results are consistent with the complex conservation history of the painting and with the restoration features observed by IR-R. FT-IR analysis of the micro-samples taken revealed the presence of bands associated with protein compounds, suggesting that suggesting that protein-based binder (such as animal glue, casein or egg white) was used to apply both the brass ground and the pigments. Microscopic examination of the same micro-samples confirmed the state of deterioration of the canvas and revealed a heterogeneous and irregular morphology of the green-gold background, providing some insight into the technique used by the artists to apply the pigments. The lower part of the canvas exhibited the most severe deterioration, resulting from higher moisture levels, unsuitable past restoration treatments, and prolonged exposure to humidity, atmospheric pollutants, and marine aerosols.

Ultimately, the multi-analytical applied in this study provided useful information on the nature and state of degradation of pictorial materials of the investigated tempera painting on canvas in order to plan the best conservation strategy and any targeted interventions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16146934/s1>, Figure S1: XRF spectra of the 30 points analyzed, grouped according to the type of color observed and similarities/differences in elemental composition: blue (a); green (b); mainly white-yellow (c); mainly greenish-gold (d); red-brown (e,f). The label for each point is shown to the right of the spectrum, displayed as an overlay of the spectra obtained at the three selected voltages: 8 kV (blue line)–15 kV (orange line)–45 kV (magenta line). The assignment of the principal peaks is also shown (the Rh signal caused by the X-ray source is also indicated); Table S1: Points of XRF analysis.

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

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Conflicts of Interest: Authors C.G., S.C. and E.C. were employed by the company Istemi S.r.l. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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