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Unveiling Raphael's Christ Blessing: Chemical Analysis Reveals Distinctive Underdrawing Techniques and a Rare Early Use of Egyptian Blue in Renaissance Art

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Cite This: *ACS Omega* 2026, 11, 3509−3517

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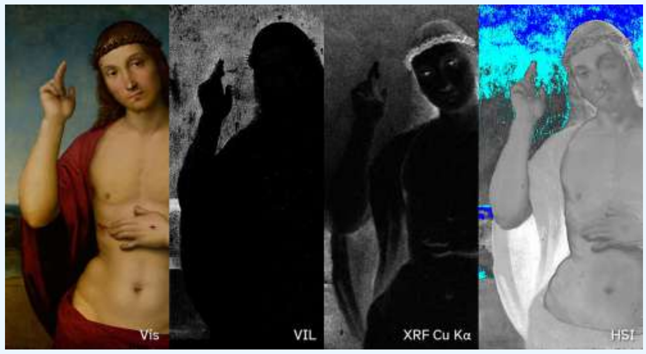
ABSTRACT: This article highlights how advanced chemical analysis led to groundbreaking discoveries in *Christ Blessing* (1505−1506), a painting attributed to Raphael and housed in the Pinacoteca Tosio Martinengo, Brescia, Italy. Through a comprehensive, noninvasive scientific investigation conducted in situ at the museum, our team identified a distinctive freehand underdrawing executed in a dry medium with a pointed tool and a rare early use of Egyptian blue in Renaissance art. Crucially, the presence of this ancient synthetic pigment—long thought to have vanished after antiquity—was chemically confirmed in the background of the composition, where it was used alongside azurite and ultramarine blue. This marks the only documented instance of Egyptian blue in a panel painting by Raphael and its only known application in a sacred subject within his oeuvre. These findings were made possible by a suite of imaging and spot-based spectroscopic techniques, including multiband and hyperspectral imaging, reflectance transformation imaging, fiber optics reflectance spectroscopy, and both spot and scanning X-ray fluorescence spectroscopy. The integration of these methods not only offered new insights into Raphael's working practice but also demonstrated the transformative potential of chemical analysis in art historical research, enhancing our ability to study and understand complex, multilayered artworks.



■ INTRODUCTION

In recent decades, advances in cutting-edge scientific instrumentation for chemical analysis have revolutionized the study and conservation of cultural heritage.[1] By integrating chemical imaging with spot-based spectroscopies, researchers can now analyze the composition and conservation condition of artworks in situ and noninvasively, with unprecedented precision. Imaging methods—such as multiband and hyperspectral imaging (MBI and HSI), as well as scanning X-ray fluorescence (XRF) spectroscopy—enable the mapping of material distributions and the detection of underlying features across entire surfaces. Complementarily, spot-based spectroscopic techniques—including XRF, fiber optics reflectance spectroscopy (FORS), Raman, and Fourier-transform infrared (FTIR) spectroscopy—offer detailed elemental and molecular identification of a wide range of organic and inorganic compounds at specific locations of interest.

This integrated analytical approach enables a comprehensive understanding of artworks, guiding the development of science-informed conservation strategies while reducing the need for sampling or invasive testing. Some of these techniques—particularly those involving chemical imaging—have been applied, in recent years, to the multimodal analysis of Old Master paintings, offering new insights into artists' palettes and workshop practices.[2] One artist whose oeuvre stands to benefit greatly from a multitechnique analytical approach is Raphael (Urbino, 1483—Rome, 1520). His paintings have been the focus of numerous investigations aimed at elucidating the materials, techniques, and working practices that underpinned his celebrated artistic production, as well as assessing the conservation condition of some of his works.[3−22] These studies have revealed, for example, the main characteristics of Raphael's wooden supports and his preparatory practices, including the use of full-scale cartoons, squaring, and pouncing (or spolvero) for transferring designs. One aspect that has been extensively studied is the distinctive use of color in the artist's paintings. Pigment analysis has identified a relatively broad color palette comprising mineral

Received: October 23, 2025
Revised: December 2, 2025
Accepted: December 9, 2025
Published: December 26, 2025

ACS Publications

https://doi.org/10.1021/acsomega.5c11121
ACS Omega 2026, 11, 3509−3517

pigments and organic lakes derived from plants and insects, in some cases accompanied by precise mapping of their spatial distribution. Notably, scientific analysis has also uncovered Raphael's use of unconventional materials, such as a previously undocumented bismuth-based black pigment, which was detected in works such as the *Ansidei Madonna*, *Procession to Calvary*, and *Madonna of the Pinks* (National Gallery, London). Further investigations into his paint stratigraphy have provided insights into the composition and layering of the ground and imprimitura, as well as the integration of powdered glass particles—particularly in red lake glazes and other pigment mixtures. Studies have also documented his varied use of metals—such as gold leaf and shell gold—highlighting his experimentation with different surface textures and reflective effects.

Despite these relevant findings, several questions related to Raphael's material practice remain either largely unexplored or insufficiently studied. Among these, two areas of significant scholarly interest are the study of underdrawings—which can reveal pentimenti, compositional changes, and other relevant details of his creative process—and the recent discovery of Egyptian blue in some of his wall paintings.[23−27] This latter finding has sparked renewed discussion about pigment reuse and material circulation during the Renaissance.

In terms of underdrawing, recent investigations based on advanced imaging revealed that Raphael employed a variety of media in his works, either individually or in combination. Of particular interest are numerous examples of freehand brush drawings that have been documented in paintings included in the exhibition "Raphael: From Urbino to Rome" at the National Gallery in London, which focused on the artist's development from the Duchy of Urbino to the papal court.[10] Additional instances of freehand drawing can be found in *Madonna of the Pinks* (1506−1507) and *Saint Catherine of Alexandria* (1508). In the *Aldobrandini Madonna* (1510) and *Madonna of the Rose* (1518), the underdrawing was finely executed using metalpoint—specifically silverpoint and a lead−tin stylus, respectively.[5,9] For the *Alba Madonna* (1510), the use of a pointed dry medium has been proposed, though the exact material was not identified,[3] while black stone was found in recent studies of the *Lady with a Unicorn* (1505−1506).[28] The *Baglioni Entombment* (1507) is characterized by a dry medium such as black stone, an incising tool, and a fluid medium; this painting also features freehand drawing, and the varying thickness and saturation of the dry lines have been attributed to differences in the applied pressure.[29] The use of multidisciplinary imaging techniques to visualize Raphael's freehand drawing offers deeper insight into the master's work, revealing not only the materials employed but also the artistic gestures that shaped the composition, where the underlying drawing represents the essential creative act that initiates the work.

Similarly, scientific investigations of Raphael's works have revealed his deliberate reintroduction of Egyptian blue—an ancient pigment long thought to have disappeared after antiquity. First synthesized in ancient Egypt in the fourth millennium B.C.E., this pigment remained the main blue throughout the Mediterranean and Western Asia for centuries due to its vibrant hue and high stability. In ancient Rome, it was widely employed in frescoes and wall decorations, reaching the height of its popularity by the end of the first century C.E.[25−27,30] Egyptian blue was long believed to have been lost after Roman times; however, recent studies have challenged this assumption by identifying its presence in a handful of Medieval and Renaissance artworks. Its reported use in Medieval artifacts is quite sporadic: to date, around 20 instances have been documented in artifacts dated to the 7th−8th centuries, with the latest examples—both from the 13th century—found in wall paintings at the *Loggia of the Knights* in Treviso and in the polychrome lunette over the Genoa Cathedral's portal.[26] Notably, rare but significant discoveries of Egyptian blue have emerged in a few Italian Renaissance works as well, with some of the main documented cases in 16th-century painting, as follows: two frescoes by Raphael at Villa Farnesina in Rome—*The Triumph of Galatea* (1511−1512) and the *Loggia of Cupid and Psyche* (1518);[23−27] a painting by Perugino, *The Battle of Love and Chastity* (1503−1506), and an altarpiece by Giovanni di Pietro, known as Lo Spagna (commissioned in 1506), both in the Louvre collection;[31] an altarpiece depicting *Saint Margaret* by Giovanni Battista Benvenuti, known as L'Ortolano (1524), held at the Statens Museum for Kunst in Copenhagen;[32,33] and two panel paintings by Benvenuto Tisi, known as Il Garofalo—namely, the *Holy Family with Saints Elizabeth, Zacharias, John the Baptist (and Francis?)* (ca. 1520−1535) at the National Gallery in London,[34] and an *Adoration of the Magi* at the Rijksmuseum in Amsterdam (ca. 1530−1540).[33] Apart from these exceptions, Egyptian blue re-emerged in the 19th and 20th centuries, when its chemical and mineralogical properties were widely studied and a few related pigments became available.[25−27]

Building on previous analytical research, this article presents the results of a scientific investigation conducted on *Christ Blessing* (1505−1506), a painting on wooden panel housed in the Pinacoteca Tosio Martinengo in Brescia, Italy[35] (Figure 1).

Figure 1. Raphael, *Christ Blessing* (1505−1506). Pinacoteca Tosio Martinengo, Brescia, Italy.

https://doi.org/10.1021/acsomega.5c11121
ACS Omega 2026, 11, 3509−3517

The study was undertaken in 2023−2024 at the request of the Italian National Committee for the Celebration of the 500th Anniversary of Raphael's Death, with the goal of contributing to ongoing scholarship on the artist's oeuvre. Prior to this study, the painting had been the subject of only one documented analytical campaign, carried out in 1983 in conjunction with a conservation treatment. The intervention involved the removal of varnish, overpaints, and previous fills, as well as the filling of losses, reintegration of the paint layer, and revarnishing.[36] Scientific analysis, carried out using the instrumentation available at the time, detected traces of an underdrawing in Christ's eyes, mouth, lower robe, and right hand. Three paint samples taken from the red mantle and green vegetation along the right edge were examined, revealing a double preparation layer: a base of gypsum and glue topped with a thinner imprimitura of lead white and oil. Vermilion with iron oxide particles were identified in the reds, and malachite mixed with lead white in the greens. A separate sample confirmed that the panel is made of poplar (*Populus alba* L.).[37]

This work advances earlier studies by presenting two significant new findings, namely, the identification of a unique freehand underdrawing, executed with a pointed tool, and the use of Egyptian blue. Remarkably, this appears to be one of the earliest documented instances of the pigment's use in Renaissance art and the earliest within Raphael's oeuvre. It also corresponds to the first—and so far only—confirmed use of Egyptian blue by Raphael in both a panel painting and a work depicting a sacred subject, marking a rare and noteworthy convergence of historical technique and artistic innovation. We also emphasize the multimodal analytical approach employed in this research, which integrates advanced imaging technologies—including MBI, HSI, reflectance transformation imaging (RTI), X-radiography, and scanning XRF—with spot-based methods such as FORS and XRF. This comprehensive methodology moves beyond basic material identification to explore the intricate interactions of materials within Raphael's technique. Notably, this was achieved without the need for sampling, thus preserving the integrity of the artwork. The resulting high-resolution visualizations not only support material identification and condition assessment but may also enhance public engagement through exhibitions and educational initiatives.

EXPERIMENTAL SECTION

The scientific investigation in this study was organized as a comprehensive, multitechnique analytical campaign aimed at documenting the artwork's materials and techniques through a fully noninvasive approach. The analytical campaign integrated a wide range of imaging and spot-based spectroscopic methods, combining macroscopic and microscopic levels of examination and analysis. High-resolution imaging techniques included diffuse visible light photography (Vis-D) for general documentation; infrared reflectography (IRR) in both the near-infrared (NIR, 850−1100 nm) and short-wave infrared (SWIR, 1000−1700 nm) ranges to visualize the underdrawing and any additional subsurface features; and visible-induced infrared luminescence (VIL) to detect the possible presence of luminescent pigments like Egyptian blue. RTI was employed to investigate the surface morphology and texture, while HSI in the Vis, NIR, and SWIR ranges (400−1700 nm) provided spatially resolved reflectance spectra for material identification, pigment mapping, and the creation of enhanced diagnostic images through multivariate analysis. X-radiography complemented the imaging data set by revealing the work's internal structure, any compositional changes, and density variations of the paint and support layers. Elemental distribution maps were then obtained through scanning XRF spectroscopy, providing spatially resolved information about the composition of selected areas. To complement these imaging methods, targeted point analyses were performed to obtain more localized elemental and molecular information. Spot XRF analyses yielded detailed elemental data at specific points of interest, while FORS was applied for noninvasive pigment identification through comparison with reference spectral databases. Together, these complementary techniques enabled a holistic understanding of the artwork's techniques and material composition, supporting both art historical interpretation and conservation decision-making.

Vis-D, IRR in the NIR spectral range, VIL, RTI, spot XRF, and FORS analyses were conducted using portable or mobile instruments available at the Scientific Laboratories of the Centro per la Conservazione ed il Restauro dei Beni Culturali (CCR) "La Venaria Reale", Turin, Italy. IRR in the SWIR spectral range and X-radiography were performed with equipment owned by the University of Milan's "Aldo Pontremoli" Department of Physics. HSI was conducted using a scanner designed and assembled at the "Nello Carrara" Institute for Applied Physics of Italy's National Research Council (IFAC−CNR). Scanning XRF was carried out with a system developed at the National Institute of Nuclear Physics (INFN), Florence branch, within the related Cultural Heritage Network (CHNet). Details of the analytical techniques employed and related experimental parameters are reported in the Supporting Information.

RESULTS AND DISCUSSION

Underdrawing: Revealing the Invisible. IRR applied in the SWIR spectral region (1000−1700 nm) significantly enriches the information obtained from the 1983 studies.[37] This technique reveals the presence of a freehand drawing made with a dry medium on the prepared panel without evidence of transfer from a preparatory cartoon. The shape and distribution of the drawn lines, which appear in general quite delicate, suggest the use of a pointed tool, such as a metalpoint or black stone. Most of the visible marks in the SWIR image appear as very thin, dark gray lines, characterized by regular contours and uniform saturation; in some areas, however, the strokes are darker and more pronounced. In the detail shown in Figure 2a, the presence of a thin gray line is accompanied by darker anatomical features, as if the artist had gone over certain points—such as the eyes, nose, and mouth—to define and reinforce their shape. As for the specific nature of the drawing medium used, no evidence of metalpoint is detected in the scanning XRF maps due to various factors, likely including the resolution adopted for the analysis. A careful comparison of the IRR, RTI, and X-ray images, however, allows for hypotheses to be formulated based on the differences in saturation and morphology of the lines: for instance, in some areas, a dark stroke may suggest the use of a black stone. SWIR reflectography and the normal map obtained through RTI highlight the simultaneous presence of raised and incised lines (Figure 2). Notably, some of the thinner gray lines correspond to incisions defining the eyebrows, eyelids, and eyes, whereas there is no such correspondence for the thicker strokes. Interestingly, the stratigraphic profile reconstructed via RTI of

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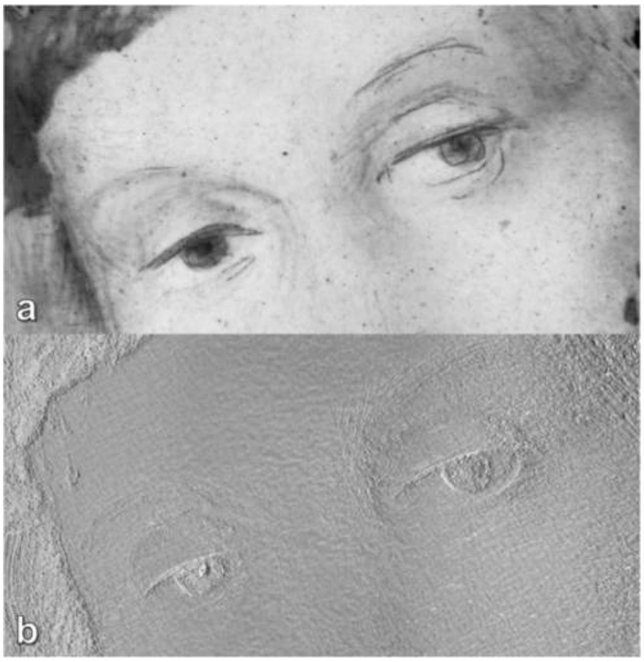

Figure 2. Comparison between images acquired in (a) IRR SWIR and (b) RTI of the upper portion of Christ's face. Two distinct traces are visible in the underdrawing: a lighter one for the facial details and a darker one to emphasize the eyes and eyebrows.

the left pupil is perfectly circular, while in IRR, the darker lines sketch out a more irregular and flattened shape. Based on these observations, it may be hypothesized that, rather than reinforcing key features, the darker strokes were originally meant to outline this portion of the figure's face.

These dark lines, used solely as preliminary guides for the subsequent painting phase, sketch the outlines of some anatomical details. For example, compared to the final version of the work, the iris was later broadened and the eyelid reshaped with a more rounded contour. Additional compositional changes can be observed around the right ear, whose profile is only faintly visible beneath the brown curls: in the underdrawing, the ear appears larger and is defined by a double line suggesting later adjustments. The contour of the head, later resized, was also reworked several times to refine its shape, while the chin appears to have been slightly shifted downward and may even bear traces of a short beard. The anatomical lines defining the pectoral and abdominal muscles, collarbones, and the left shoulder—now slightly reduced in proportion—are clearly visible. These variations, which testify to Raphael's creative process, are particularly evident in the definition of the left arm and hand. Specifically, the contours of the biceps, elbow, and forearm differ slightly from the painted version, while the hand shows a more marked modification, with the fingers originally extended more toward the figure's right side (Figure 3a). On the left pectoral, in addition to an overall sketch aimed at defining its volume, graphic marks around the nipple suggest a series of reworkings leading to the final version (Figure 3b). The right hand, depicted in the act of blessing, shows a carefully composed preparatory drawing: the outlines of the ring and little fingers differ slightly from the completed painting, while the thumb appears to have been painted in a more retracted position compared to what is revealed by the reflectographic image, where it was originally extended further upward (Figure 4). The red mantle, which falls from Christ's right shoulder and wraps around his waist, reveals in the IRR images a series of drapery folds that are not visible to the naked eye, as well as hatching near the hair, the right side of the torso, and the lower part of the garment that define shadowed areas. In the background vegetation, aside from a fine dividing line between the light and dark areas of the hills on the right, no drawing is visible—even in painted passages that depict trees.

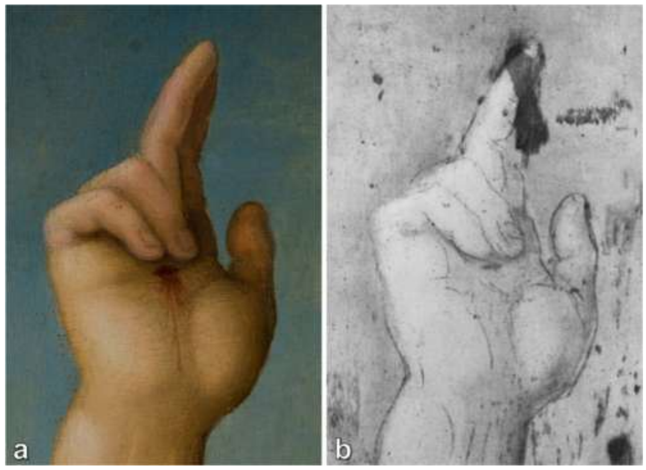

Figure 4. Comparison between images acquired in (a) Vis-D and (b) IRR SWIR of the right hand, showing a series of compositional changes in the shape and position of some fingers.

In addition to outlining the figure of Christ freehand, the medium used for the thinner gray lines is also employed to define certain shadows with broad, parallel hatching, visible, for

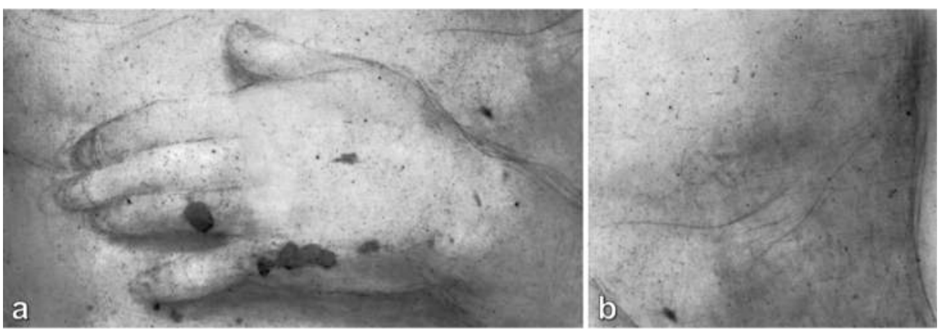

Figure 3. Reflectographic images obtained in the SWIR spectral region: (a) left hand, where a change is evident in correspondence with the fingers; (b) left breastplate, where several repositioning marks are visible.

https://doi.org/10.1021/acsomega.5c11121
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example, above the eyes and on the right side of the neck, where the hair falls. If a metalpoint was used, the quantity of metal—whether lead or another material—deposited is usually minimal and thus difficult to detect in X-radiography, especially when compared to the larger amounts of lead or other heavy elements typically found in a lead white-based paint layer of significantly greater thickness. Regardless of whether the tool was a metalpoint or a black stone, the incision it produced left a groove of varying depth, which was later filled with the imprimitura and paint layers. This effect is recognizable in areas of the drawing such as the left wrist, where the comparison shown in Figure 5 highlights the exact match between the radiopaque stroke in X-ray and the dark line in SWIR reflectography, confirming the use of a pointed tool for the drawing. For most of the drawn lines, however, the pressure applied was not sufficient to fill the groove with a detectable quantity of radiopaque material for clear identification in the X-radiograph.

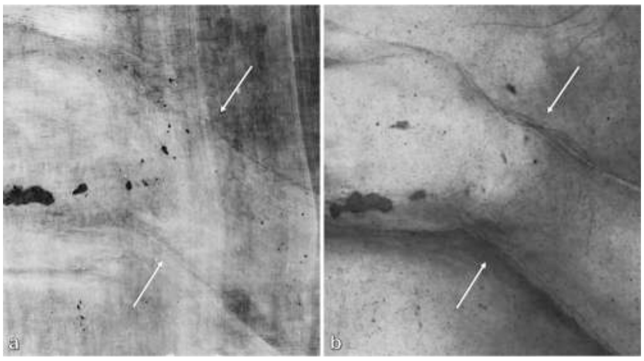

Figure 5. Comparison between images acquired in (a) X-radiography and (b) IRR SWIR of the left wrist, highlighting the presence of an underlying drawing executed with a sharp dry medium.

Among the extant comparisons, a particularly relevant work for the purposes of this study is that concerning the *Baglioni Entombment* (1507), a painting that reveals—like the *Christ Blessing* analyzed here— the use of diverse underdrawing techniques and materials, including a dry medium such as black stone, an incising tool, and a fluid medium, with freehand execution and pressure-sensitive line variation.[29]

Egyptian Blue: Identification and Technical Use. Despite its rare use during the Renaissance, Egyptian blue was unequivocally identified through three independent techniques—VIL, XRF, and HSI—each confirming the presence of this pigment in the sky and in parts of the landscape.

In detail, the VIL reveals the typical response of Egyptian blue in the blue and light blue tones of the sky (Figure 6a). This result is corroborated by XRF analysis, which identifies the characteristic elements of its dominant crystalline phase, the mineral cuprorivaite (a copper and calcium tetrasilicate with the formula $CaCuSi_4O_{10}$)—namely, copper, along with calcium and silicon (Figure 6b).[38] The same material is also detected in the upper bands of the hills in the background. In both of these areas, it appears to be frequently used in combination with other pigments. VNIR reflectance spectra extracted from the HSI data from the sky also feature the spectral markers of Egyptian blue, which consist of a triplet in the 540−630 nm region and a band at 800 nm (Figure 7).[39] However, in other areas of the blue background where the color is deep blue, such as the upper portions of the sky and hills, the Vis spectra show the typical behavior of ultramarine blue—with an absorption band centered at 600 nm with a paraboloid shape, also observed in the FORS spectra (Figures 7 and S1, Supporting Information). Additionally, NIR false-color imaging shows a burgundy-toned response in the sky and in the upper portion of the hills (Figure S2, Supporting Information). Overall, this is consistent with the presence, above Egyptian blue, of a superficial glaze of ultramarine blue, which appears to gradually thin out from the top to the bottom of the composition. In particular, the application of the Spectral Angle Mapping (SAM) classification algorithm to the hyperspectral imaging data shows how the gradation from dark blue to light blue in the sky was achieved starting from a base layer of Egyptian blue, over which a thin layer of ultramarine blue was applied in the upper section and a mixture of lead white and possibly azurite in the lower one. The use of ultramarine blue as a surface glaze is confirmed by the detection of potassium in the XRF maps. Although potassium is not part of the commonly accepted chemical formula of lazurite, it is frequently found as an interstitial cation in hauyne—another member of the sodalite group often occurring in association with lazurite;[40] another potassium-bearing mineral associated with lazurite in the Badakhshan mine, Afghanistan, is the feldspathoid afghanite.[41] The possible presence of azurite, on the other hand, is suggested by reflectance analysis, although in low concentration, for areas that appear blue and contain copper but lack the typical VIL of the Egyptian blue pigment.

Figure 6. Comparison between (a) VIL image and (b) Cu Kα elemental map obtained by scanning XRF, highlighting the distribution of Egyptian blue and copper-based pigments (including Egyptian blue), respectively.

The vegetation, on the other hand, appears to have been rendered by using complex combinations of blue, green, and yellow pigments. In addition to the dark blue tones of the background hills, the joint use of VIL and HSI made it possible to precisely identify the presence of Egyptian blue, in varying concentrations, also in certain greenish areas of these regions, such as the section below Christ's right elbow. An exception to this is the intermediate zone between the left arm and the lateral edge of the painting. The XRF distribution of copper in the green tones of the grass and trees—especially intense in this latter area—suggests the presence of a copper-based pigment different from Egyptian blue (Figure 6b). In this and other areas of the vegetation, HSI analysis suggests the use of azurite mixed with variable amounts of a yellow pigment, likely

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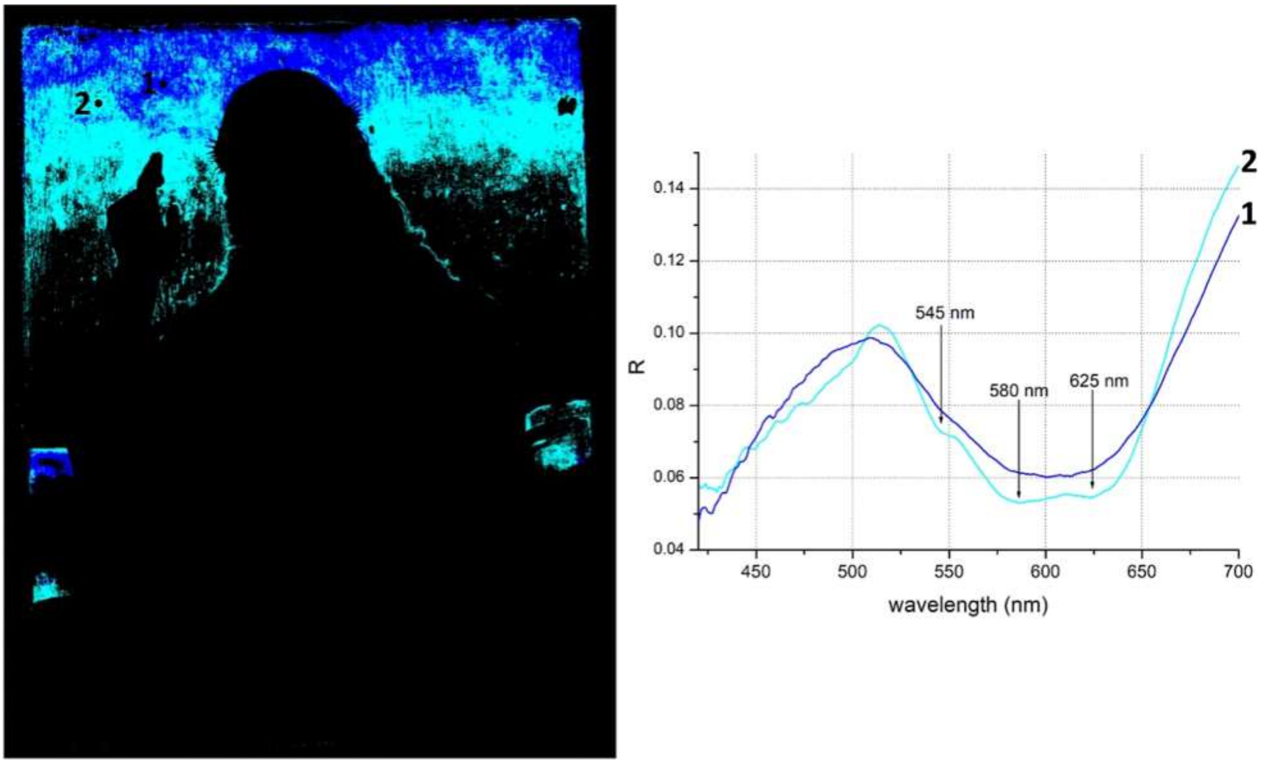

Figure 7. False-color map obtained from HSI VNIR data using the SAM algorithm, where light blue and dark blue pixels correspond to the distribution of Egyptian blue and ultramarine blue, respectively. Representative spectra of the two materials, on the right, were extracted from marked areas on the map.

lead tin yellow based on the finding of lead and tin with XRF. According to the collected data, it is further hypothesized that copper-based greens were used in the lower portion of the hilly background. In support of this hypothesis, a microscopic sample taken from a vegetation area along the right edge of the painting and analyzed during the 1983 analytical campaign was found to consist of a layer of malachite and lead white, with probable later overpainting using a mixture of red and green pigments.[37]

The identification of Egyptian blue in *Christ Blessing* should be contextualized within the framework of recent discoveries concerning the use of this pigment by Raphael and, more broadly, within the scope of Italian Renaissance art. The Renaissance works in which the use of Egyptian blue has been reported so far date from 1503 to 1540; within this timeframe, the *Christ Blessing* in Brescia—created by Raphael prior to his Roman period—currently stands as the second earliest known Renaissance painting in which Egyptian blue has been documented, after Perugino's *The Battle of Love and Chastity*.[31] Within Raphael's oeuvre, it is also noteworthy as the earliest work, and only panel painting, in which this pigment has been identified to date.

As previously noted, in *Christ Blessing*, Egyptian blue is combined with other pigments—such as ultramarine blue, lead white, and azurite in the sky, and azurite and lead tin yellow in the vegetation. This application technique aligns with a broader practice observed in many of Raphael's works, where blue areas—such as skies and drapery—are painted with two superimposed layers containing different blue pigments, typically azurite and ultramarine blue. Inherited from 15th-century painting, this approach was widely adopted by artists throughout the following century.[9,22] A similar situation where Egyptian blue is associated with other materials is also described for the frescoes at Villa Farnesina. In the *Triumph of Galatea*, the sky appears to have been built up through two superimposed layers—Egyptian blue and an iron-rich pigment—while the sea was painted using a mixture of Egyptian blue with other copper- and iron-based pigments. Additionally, Egyptian blue was detected in the putti's wings, where it appears both as a mixture with other materials and as a surface finish, applied to achieve different chromatic effects; it is also present, in combination with a white pigment, in the sclerae of Galatea and other figures gazing directly at the viewer.[23−27] In *Christ Blessing*, however, the eyes contain copper but do not exhibit the characteristic VIL response of Egyptian blue, suggesting the presence of other copper-based pigments. Examination of a macrophotograph of the eye captured with a portable optical microscope reveals a brown coloration in the iris and brown to cream hues in the scleral area. Combined with the Fe distribution map obtained by scanning XRF, these observations indicate the use of pigment mixtures containing both copper- and iron-based materials, rather than Egyptian blue (Figures S3 and S4, Supporting Information).

Microinvasive analyses by the Istituto Centrale per il Restauro (ICR) in Rome confirmed the presence of Egyptian blue in both frescoes at Villa Farnesina, possibly in association with ultramarine blue and azurite. In a cross section from the lower border of the *Triumph of Galatea*, Egyptian blue mixed with black pigment grains was found beneath a purplish glaze of ultramarine blue and vermilion. It was also detected in two fragments of the same cross section from the *Loggia of Cupid and Psyche*, where it appeared either above a dark layer or as a paint layer over azurite, which itself rested on a thin dark layer.[42] The painting technique observed in the upper sky of

https://doi.org/10.1021/acsomega.5c11121
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the *Christ Blessing*—namely, a glaze of ultramarine blue applied over an Egyptian blue layer—might be consistent with the sea near the putto's feet in the *Triumph of Galatea*. The association of Egyptian blue with other copper-based blues, such as azurite, if confirmed, would align with the findings from the *Loggia of Cupid and Psyche*.

In general, the possibility of drawing meaningful parallels between *Christ Blessing* and the frescoes at Villa Farnesina is certainly intriguing. However, as noted by the ICR researchers who conducted the most recent analysis,[42] it should be kept in mind that the samples in question were collected between the 1970s and 1990s, are often challenging to reanalyze after several decades, and frequently consist of fragments that were not documented in a comprehensive or detailed manner. For this reason, it also remains uncertain whether the ultramarine blue identified in the *Triumph of Galatea* might be a synthetic pigment introduced during later conservation treatments. Given the fragmentary nature of the available evidence concerning the paint stratigraphy, it is difficult at this stage to establish firm parallels with the frescoes at Villa Farnesina; more precise comparisons may become possible once definitive analytical data on the frescoes are available.

A comparison with the data from Ortolano and Garofalo's paintings[32−34] further supports the evidence that Egyptian blue was employed alongside ultramarine blue, in those cases possibly serving as an adulterant or extender of the latter. Specifically, in Ortolano's *Saint Margaret*, the saint's dress consists of a violet underlayer composed of azurite and red lake, overlaid by a surface application of Egyptian blue mixed with ultramarine blue. In Garofalo's *Adoration of the Magi*, all the deep blue areas contain mixtures of Egyptian blue and ultramarine blue. Similarly, in Garofalo's *Holy Family*, several blue passages—particularly the figures' cloaks and robes, as well as the soft blues of the mountains, sky, and clouds—were painted with Egyptian blue; in all these areas, this pigment was detected together with ultramarine blue and azurite. The occurrence of Egyptian blue in combination with other blue pigments, particularly ultramarine blue, in these Renaissance paintings aligns closely with our own observations for Raphael's *Christ Blessing*; however, unlike the aforementioned cases, in the Brescia panel, Egyptian blue does not appear to have been used as an adulterant or extender of ultramarine blue but rather as a deliberate and distinct pigment choice.

■ CONCLUSIONS

Thanks to the integration of advanced, noninvasive imaging and spot-based techniques of chemical analysis, this in situ study conducted at the Pinacoteca Tosio Martinengo (Brescia, Italy) has yielded new insights into the materials, techniques, and conservation condition of Raphael's *Christ Blessing* (1505–1506), a panel painting executed prior to his Roman period. While the materials and techniques largely align with those known from the artist's early practice and 16th-century workshop traditions, scientific analysis has uncovered two notable and previously unrecognized elements that not only deepen our understanding of Raphael's methods but also enrich current scholarship on his technical and material choices.

First, IRR, RTI, and X-ray images revealed a freehand underdrawing executed with a dry, pointed tool—likely metalpoint or black stone—without evidence of transfer from a preparatory cartoon. The underdrawing consists of fine gray lines of varying intensity with darker strokes used to reinforce key features such as the eyes and mouth. Incisions and hatching were also detected, indicating a combination of drawing and scoring techniques. Numerous compositional adjustments—seen in the contours of the face, torso, hands, and drapery—attest to the artist's evolving design and provide valuable insight into his direct, experimental approach during the early phase of his career. To the best of the authors' knowledge, the presence of an underdrawing revealed both as a dark line in infrared imaging and as an incision in radiography represents the first instance documented in such detail.

Second, VIL, XRF, and HSI confirmed the use of Egyptian blue in the painting's sky and hills. HSI data show that it was applied beneath glazes of ultramarine blue in the upper sky and combined with azurite and lead white in the lower areas to create tonal variation. Traces were also found in the greenish zones of the vegetation, although other copper-based pigments were used elsewhere. This marks one of the earliest known uses of Egyptian blue in a Renaissance artwork, and its earliest and only occurrence to date in a panel painting by Raphael, offering new insights into his materials and the selected revival of ancient pigments in the early 16th century.

These discoveries underscore the effectiveness of combining advanced chemical imaging with spot-based spectroscopic methods to unravel the complex material composition of multilayered artworks. The synergy between these noninvasive techniques enabled precise identification of relevant pigments, such as Egyptian blue, and revealed subtle aspects of Raphael's working practice. From an art historical perspective, these findings enrich our understanding of his material choices, contributing to broader discussions on the continuity of ancient pigment use in the Renaissance. More broadly, this work demonstrates how the convergence of scientific and historical methodologies can lead to groundbreaking insights into the field of cultural heritage research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c11121.

Additional experimental details, including a description of the analytical techniques employed and related experimental parameters, and additional figures (DOCX)

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https://doi.org/10.1021/acsomega.5c11121
ACS Omega 2026, 11, 3509−3517

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This research was co-funded by the Italian National Committee for the Celebration of the 500th Anniversary of Raphael's Death and the CCR "La Venaria Reale".

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors express their sincere gratitude to Roberta D'Adda, Giulia Paletti, and all the colleagues at the Pinacoteca Tosio Martinengo in Brescia for their generous support and for granting access to the artwork, making this research possible. The authors also thank the Italian National Committee for the Celebration of the 500th Anniversary of Raphael's Death, and in particular Dr. Carla Di Francesco and Dr. Michela Di Macco, for entrusting the CCR "La Venaria Reale" with the task of coordinating this analytical campaign.

■ ABBREVIATIONS

Vis-D, diffuse visible light photography; IRR, infrared reflectography; VNIR, visible and near-infrared; SWIR, short-wave infrared; VIL, visible-induced infrared luminescence; RTI, reflectance transformation imaging; MBI, multiband imaging; HSI, hyperspectral imaging; SAM, spectral angle mapping; XRF, X-ray fluorescence; FORS, fiber optics reflectance spectroscopy; FTIR, Fourier-transform infrared

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ACS Omega 2026, 11, 3509–3517