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Technological Examination of the Warsaw and Boston Versions of *The Holy Family with Saint John and Saint Catherine* by Gianfrancesco Penni

The Meeting of the Two Paintings

On 14 January 2013, the "Late Raphael" exhibition which had previously been displayed in the Museo Nacional del Prado, Madrid, came to an end in the Louvre, Paris.[1] It aimed to present the seven years of Raphael's work in Rome, where his largest and most ambitious projects were conceived, as well as to show what became of Raphael's artistic legacy after his premature death. The central figures of the exhibition were thus Raphael himself, together with his two closest collaborators: Giulio Romano and Gianfrancesco Penni. Both of these painters assisted in the realisation of their master's Roman commissions, but, after he died, they also had careers of their own where they creatively used their earlier artistic and practical experience together with designs, drawings, and cartoons inherited from Raphael.

The organizers of the exhibition attempted in vain to borrow the painting *The Holy Family with Saint John and Saint Catherine* by Gianfrancesco Penni, a deposit of the Potocki family of Krzeszowice and Krakow in the National Museum in Warsaw (**fig. 1**). This composition is rightly believed to be one of the most interesting works from Raphael's circle. For legal reasons, however, the painting could be loaned neither to Madrid nor to Paris.

After the exhibition concluded, due to the efforts of one of its curators, Prof. Paul Joannides and courtesy of the Childs Gallery, Boston, another version of the painting came to the National Museum in Warsaw (**fig. 2**). As recent research has proved, both paintings were executed simultaneously in the same studio, only to reunite after five hundred years.[2]

They were exhibited in the Gallery of European Old Masters from 5 February until the end of March, 2013. An academic seminar, devoted to a comparison of both versions and the results

[1] "Late Raphael," Museo Nacional del Prado, Madrid, 12 June – 16 September 2012; Musée du Louvre, Paris, 8 October 2012 – 14 January 2013. The exhibition catalogue: *Late Raphael*, Tom Henry and Paul Joannides, eds, exh. cat., Museo Nacional del Prado, Madrid; Musée du Louvre, Paris, 2012–2013 (Madrid, 2012).

[2] In a private collection in Great Britain there is another version of *The Holy Family* or a later copy thereof painted on panel measuring 115.9 × 96.9 cm. The status of the painting will remain unclear unless physicochemical examination is performed, especially IR reflectography, which could reveal the underdrawing.

of technological research conducted thus far, was held on 4 February.[3] The participants of the seminar agreed that both versions of *The Holy Family* should be attributed to Gianfrancesco Penni, except for Dr Józef Grabski, who believes that the Warsaw version was painted by Giulio Romano. A preliminary comparison of the compositions confirmed that they had been based on the same cartoon and executed with very similar painting materials. A hypothesis also emerged that this panel had been the initial support of the Boston painting whose polychrome was transferred onto canvas. Dr Agnieszka Morawińska, the director of the National Museum in Warsaw and Roger Howlett from the Childs Gallery agreed that further research on the style and substance of both works should be conducted. The results thereof are presented below.[4]

Analysis of the Underdrawing

Both versions of *The Holy Family* – from Warsaw and from Boston – are perfect examples of Penni's work, and albeit modelled after Raphael, they prove their author not only to be a skilful assistant but also a true artist capable of effecting commissions on his own. They were probably both executed in Rome c. 1521–22 (see contribution by Paul Joannides).

The compositions are almost identical in size and the figural groups in both of them are alike with the only difference being the surface covered by landscape (the Boston version is a few centimetres higher). There is evidence that both paintings were based on the same cartoon, the underdrawing being indented on the support (Italian *calcare*). After projecting the outline of the Warsaw painting on the Boston using transparent plastic film it appeared that the contours of the figures matched (**fig. 3**).

It is highly probable – and would be typical of Raphael's and his co-workers' craft – that the cartoon included only the figural group with an outline of the main plans (the scarp behind the figures closing the foreground and the landscape together with the buildings on the horizon line). The differences in the background (the overgrown scarp in the Warsaw version and ruins of the Roman building in the Boston one) would have emerged in both works independently. X-ray analysis (**figs 4–5**) and IRR did not reveal any considerable *pentimenti*.

The drawing was transferred onto canvas with the use of a cartoon, its reverse blackened with charcoal. After placing the cartoon against the white ground of the support, its contours were indented with a metal stylus. This furnished black outlines that were subsequently

[3] The seminar was attended by: Roger Howlett, representative of the Childs Gallery, Boston, Prof. Paul Joannides from the University of Cambridge, David Love, independent art historian from London, Dr Józef Grabski, Dr Barbara Łydżba-Kopczyńska from the University of Wrocław and the specialists from the National Museum in Warsaw: Dr Grażyna Bastek, Dr Elżbieta Pilecka-Pietrusińska, Iwona Maria Stefańska, Prof. Antoni Ziemba together as conservators from the Conservation Workshop of the Canvas Painting and the Collection of Old Master European Art of the Museum. During the seminar Dr Grażyna Bastek compared the results of X-ray examination, infrared reflectography (IRR), UV fluorescence of the Warsaw version; Dr Barbara Łydżba-Kopczyńska discussed the analyses of pigments performed with X-ray fluorescence spectroscopy (XRF), Dr Elżbieta Pilecka-Pietrusińska and Iwona Maria Stefańska presented the preservation state of the Warsaw painting and stated a hypothesis that the polychrome of the Boston version had been transferred from panel onto canvas.

[4] Physicochemical examination of the Boston painting: Harvard Art Museums/Straus Center for Conservation and Technical Studies, Cambridge (Mass.), USA. Physicochemical examination of the Warsaw version: Roman Stasiuk from the Academy of Fine Arts in Warsaw (X-ray, IRR, UV fluorescence); Dr Barbara Łydżba-Kopczyńska from the University of Wrocław and Piotr Linke from Bruker Poland (XRF); Dr Barbara Łydżba-Kopczyńska: optical microscopy, XRF, SEM-EDS, Raman spectroscopy.

made bolder by hand, a method frequently applied in Raphael's Roman studio during the work on easel paintings.[5] IRR of the Warsaw painting showed that the drawing had been transferred from the cartoon rather loosely, and only the most important contours had been strengthened (**fig. 6**). The underdrawing of the Boston version was transferred more carefully and accurately, yet more automatically, and all of the contours were strengthened with charcoal or another dry material (e.g., charcoal stick, **fig. 7**).

It is noteworthy that identical changes in the composition took place upon preparing the underdrawings for both versions. The head of Christ bears a similar shape – an outline of curly hair, maybe even of an ear, that might have resulted in a shift of the head's position, not visible in the underdrawing (**fig. 8–9**) or on the surface. In the landscape on the right at the level of Saint Joseph's hand is an outline of houses seen in the underdrawing but never actually painted (covered by a river with a cascade). The fact that some compositional elements, apparent in the underdrawing but not in the final work, appear in both paintings is a sign that they were executed simultaneously, either by a single painter or by a closely cooperating tandem, working hand in hand.[6]

Why would anybody make two or even three almost identical versions of the same composition? Such practice was not exceptional, although it was more common in the studios of Venetian painters, such as Titian. He used to execute the first version following a specific commission, whereas the second version (and often other ones) waited in the studio to be purchased or served as *modelli* for other compositions. The comparisons made in the *Late Raphael* exhibition catalogue show that the studio of Raphael, as well as the studios of the painters of his circle, produced numerous replicas of devotional paintings.[7]

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Transfer of the Painting Layers of the Boston *Holy Family*

During the Warsaw seminar held in 2013, a hypothesis was put forward for the first time that the Boston version of *The Holy Family* by Penni had not originally been painted on canvas[8] but on panel, and subsequently – at an unknown moment – the painting layers were transferred onto canvas. This would mean that the painting is a transfer.

This hypothesis was based on detailed examinations of the surface of the painting in diffuse and oblique illumination together with X-ray and IRR analyses carried out in the Straus Center for Conservation and Technical Studies, Cambridge, Massachusetts. It was also useful to compare the Boston version with the Warsaw one, which had been painted on a well-preserved poplar panel.

[5] Anna González Mozo, "Raphael's Painting Technique in Rome in Late Raphael," op. cit., pp. 323–24.

[6] No infrared examination was performed of the painting from the private collection (see n. 2). Its composition is almost identical with that of the Warsaw version, however, only an analysis of its IRR could reveal whether it was based on the same cartoon or the contours were copied with calque after the original was finished.

[7] E.g., the versions of *Madonna della Quercia* of a similar size, repeating quite accurately the figural group and differing in the landscape composition, see *Late Raphael*, op. cit., p. 212.

[8] Narayan Khandekar, *Holy Family with St. Catherine of Alexandria and the young St. John the Baptist*, Harvard Art Museum, Painting Laboratory, Investigation Report, 2011. The Authors would like to acknowledge Roger Howlett, representative of Childs Gallery, for providing them with the report.

The first indications that the painting had been transferred were characteristic surface cracks typical of panel paintings, which are mainly vertical following the direction of wood fibres. The cracks are due to multiple changes in the relative air humidity. In the Boston version they are not discernible throughout the painting because they are partially covered by *craquelure* characteristic of the canvas support the painting currently has. Nonetheless, places may be specified where they are analogous to those in the Warsaw version and characteristic of a wooden support (**figs 10–11**).

Other indicators are manifested in the painting's state of preservation. For the most part the paint layers are damaged, especially at the top and bottom edges. Overpaintings introduced at different times can be seen in diffuse light and in ultraviolet-induced luminescence of the surface.[9]

In the lower part of Saint Catherine's mantle, where the original paint layers are missing, a fragment of glossy canvas (a result of using glue or possibly varnish) is visible with no remains of any ground in the concavities of the weaves (**fig. 12**). No traces of ground were also found in lateral edges of the canvas wound on the stretcher; there is, however, a locally preserved layer of white-blue, light grey and dark blue paint (**fig. 13**). Moreover, there are small round holes in different places on the surface, which are evidence of xylophagous insects feeding on wood,[10] as well as random fragments of insect galleries, filled with sealing substance (damages made by insects are also visible on X-ray and IRR, and the sealing substance is present in samples collected from the painting, see **fig. 10**).

The IRR revealed a horizontal crack going through the figure of Saint Joseph and the background behind him, which is not typical of a canvas support or a panel, but it is characteristic of damages caused upon transfer and resulting from high pressure necessary to adhere the transferring canvas (**fig. 14**).[11]

The X-ray of the Boston painting showed no traces of joining the panels, such as those that may be seen in the X-ray of the Warsaw painting. The absence thereof, however, does not mean that the original support could not have been a panel. On the contrary, it may suggest that the supports of both paintings were constructed likewise. Although the support of the Warsaw version is made of three vertically contiguous panels, it has been preserved without cracks along the joints, which is why the joints are not seen on the surface. There are only minor ones along wood fibres at the upper and lower edge of the painting. Both the X-ray and the IRR images reveal similar cracks, but they are less visible due to having been overpainted (**fig. 15**).

Other features of the Boston version include lunar deformations of the canvas directly contiguous to the paint layer which may have emerged during the transfer process. Furthermore, a clear imprint of the canvas structure may have been due to pressure applied during the transfer (which additionally underpins the possible cause of the horizontal crack on Saint Joseph).

The difference in the dimensions of both paintings (regardless of the fact that the edges of the Warsaw version have been cut) may result from the transferring technique, which involved softening the ground, separating the paint layers from the support and applying pressure from the transferring canvas, slightly bigger than the original painting.

9 As observed before the conservation of the painting in February 2013.

10 Marco Cardinali, Maria Beatrice De Ruggieri, Claudio Falcucci, *Diagnostica artistica. Tracce materiali per la storia dell'arte e per la conservazione* (Roma, 2007), p. 143.

11 Élisabeth Ravaud, Élisabeth Martin, "Diagnostic radiologique des transpositions," *Technè*, nos 13–14 (2001), p. 116.

Descriptions of various transfer methods are known, including those consisting in softening or washing out the ground.[12] Such methods may also have caused differences in the appearance of the underdrawing lines in the paintings in question.

Examples of paintings are known that were transferred from the original support onto an auxiliary (transferring) support using an array of two different canvases.[13] The lateral edges of the Boston version indicate two of them: an outer one, with a sparse weave (gauze), and the inner one, closer to the painting layer, which is thin and densely woven. Nowadays both canvases are equally damaged and strongly yellowed (**fig. 16**).

All of the above observations and analyses led us to conclude that the Boston version of *The Holy Family* had been subjected to transfer. Nevertheless, in order to confirm it, physicochemical examination was required.[14]

At the time when the two paintings were being executed, significant changes in the technology of making easel paintings were underway. Canvas support was becoming more and more popular and gradually replaced wooden panels. Painters experimented to obtain good canvas support – they modified grounds by adding various substances, mainly plastifying ones. Traditional gypsum grounds which were suitable for wooden panels proved too hard and brittle for the new textile supports.[15]

No gypsum was identified directly underneath the paint layers of the Boston version, though it was commonly used as ground in 16th-century Italy. Stratigraphic examination of the samples revealed that where the ground should be there is a dark blue layer of a different consistency from that of the painting layers and which adheres weakly to them (**fig. 17**). It consists of aluminosilicates, calcium compounds, locally some ochre and white lead. A mixture of similar ingredients was used as a transferring mass to bond the paint layer to the transferring canvas or served as smoothing putty.[16]

Thanks to an analysis of the preservation of the Boston version and physicochemical examinations, it was possible to formulate a thesis that the painting layers had been transferred and to establish how this had been done. The original wooden support was probably removed by softening the ground and carefully eliminating its remains. During the preparation of an auxiliary support, on an auxiliary stretcher thin, densely woven canvas was stretched and tightly adhered to the surface. On the back of the paint layer, after refilling the insect holes with the red substance (see **fig. 10**), transfer mass was applied to make the fragile paint layers

[12] Giovanni Secco-Suardo, *Il Restauratore dei dipinti* (Milano, 1918), pp. 132–34; Emmanuelle Philippe, "Innover, connaître et transmettre. L'art de la restauration selon François-Toussaint Hacquin (1756–1832)," *Technè*, nos 27–28 (2008), pp. 53–59; Marta Lempart-Geratowska, *Transfer malowideł sztalugowych. Cz. 1, Historia, metodyka, stan badań / Transfer of easel paintings. Pt. 1, History, methodology, current state of research* (Krakow, 2010). Studia i Materiały Wydziału Konserwacji i Restauracji Dział Sztuki Akademii Sztuk Pięknych w Krakowie, vol. 20.

[13] Ségolène Bergeon, *Science et patience ou la restauration des peintures* (Paris, 1990), p. 79.

[14] See further in the paper.

[15] *Il riposo di Raffaello Borghini...*, Giovanni Gaetano Bottari, ed. (Firenze, 1730), pp. 136–38; Cennino Cennini, *Rzecz o malarstwie* (Wrocław, 1955), pp. 64–68, 96–97; *Preparazione e finitura delle opere pittoriche. Materiali e metodi*, Corrado Maltese ed. (Milano–Mursia, 1993); Grażyna Bastek, *Warsztaty weneckie w drugiej połowie XV i w XVI wieku* (Warsaw, 2010), pp. 36–37.

[16] Frankline Barrès, "Les peintures transposées du Musée du Louvre, étude des techniques de transposition en France, de 1750 jusqu'à la fin du XIXème siècle," in *ICOM Committee for Conservation, 14th Triennial Meeting, The Hague 12–16 September 2005, Preprints, 2*, pp. 1002 and 1008; Lempart-Geratowska, op. cit., passim.

more flexible and to serve as adhesive between them and the secondary support. Next, the canvas was put on the back of the paint layers and intense pressure was applied to obtain better adhesion of the binding agent. This resulted in a partial overflow on the edges of the canvas. Afterwards the painting was wound onto the final stretcher and gaps in the paint were filled, sometimes excessively, as in the blue of the sky that also appeared on the fringes of the canvas. These fringes were eventually unified in colour with the use of light grey paint. The outer canvas (gauze) visible on the Boston version could have been added when the preceding canvas had been damaged on the edges of the stretcher.

The method of transfer and the materials used indicate that it may have taken place in the 18th century. In order to confirm this, further physicochemical investigation ought to be undertaken; above all, vehicles of particular layers should be analysed (no such examination of either painting was executed).

To sum up, the arguments to support the thesis that the Boston version has been transferred from panel onto canvas are:

- presence of cracks in the technological layers which are typical only of wood;
- interference of cracks that would occur only upon transfer, caused by wooden support and generated by canvas support;
- traces of xylophagous insects' destructive influence on the wood observable in diffused lighting, and in X-ray and IRR images;
- a horizontal crack in the paint layers (through the figure of Saint Joseph and the background), frequently occurring during transfer;
- absence of ground in the concavities of the weaves of the canvas on the surface of the painting, on its edges and fringes;
- neither the stratigraphic examination nor physicochemical analysis of the painting materials revealed any traces of gypsum ground, which would be typical of Italian painting at this time;
- the composition of the layer directly underneath the paint layers matches the substances used for transfers (transfer mass).

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X-ray Fluorescence Spectroscopy (XRF) Examination

Comparative analysis of the painting materials was used to determine whether or not both versions of *The Holy Family* were executed simultaneously in the same studio.

In order to identify painting materials a non-invasive and non-destructive analytical method was used: X-ray fluorescence spectroscopy (XRF).[17] The examination is carried out directly on the object and does not require collecting or preparing samples. Data obtained through interaction of X-rays with a specific area of the object allow for identifying the chemical elements in it.[18]

[17] Barbara H. Stuart, *Analytical Techniques in Materials Conservation* (Chichester, 2007), pp. 234–38; Krystian Książek et al., *Skarb średniowieczny z Głogowa: analizy specjalistyczne i konserwacja wybranych zabytków / Medieval hoard from Głogów: specialist analyses and conservation of selected objects*, Borys Paszkiewicz, scientific ed. (Głogów, 2013), p. 9; Koen Janssens et al., "Recent trends in quantitative aspects of microscopic X-ray fluorescence analysis," *Trends in Analytical Chemistry*, vol. 29, no. 6 (2010), pp. 464–78.

[18] The XRF examination of the paintings provides information about the chemical elements in both the upper paint layers and in the ground. During the examination no helium was used that would have made it possible

The examination of the Warsaw version of *The Holy Family* was performed in 2013 in the National Museum in Warsaw with the use of a manual XRF – TRACER IV spectrometer manufactured by Bruker, with a rhodium anode lamp working at an intensity of 14,80 μA and at a voltage of 40 kV. The examination of the Boston painting took place in the Harvard Art Museum / Straus Center for Conservation and Technical Studies in Cambridge (Mass.).[19] In order to perform a comparative analysis of the results of both examinations, measurement points were most carefully set in analogous places. An effort was made to ensure the best comparability of the environment of the examination.

The measurements in the Warsaw painting were made in different colour areas: red (Mary's dress: P2, P3); purple (Saint Catherine's dress: P7); blue (Mary's mantle: P1, Saint Joseph's robe: P6, blue landscape in the background: P13); green (lining of Saint Catherine's mantle: P8, landscape in the background: P11a and b); yellow (Saint Joseph's mantle: P5a, b and c, cradle: P12); white (stone pedestal: P4); and brown (Saint Catherine's plait: P9) (**fig. 17**).

The XRF spectra for measuring points located on Mary's red dress (P2 and P3) showed the occurrence of lead, possibly coming from lead white used in the underpainting and also served to differentiate the tonal modulation. Trace amounts of iron (Fe) and manganese (Mn) may indicate that umber is present. The absence of characteristic signals of metals that could give red colouring to the dress may suggest that an organic pigment, like carmine, was used.[20] Carmine contains such elements as carbon (C), oxygen (O) and hydrogen (H), which could not be detected by the spectrometer used as their mass number is below the range of this device. A result that suggests the presence of an organic pigment was also obtained in measurements on the purple sleeve of Saint Catherine's dress (P7). Additionally, signals of copper (Cu) were found in the spectra for P2, P3 and P7 measuring points. A much more intensive signal of this element was recorded on Mary's blue mantle (P1), which indicates the presence of a copper pigment, probably azurite. Lead (possibly coming from lead white) and significant signals of calcium (Ca, possibly used in the ground) were identified. It is most likely that gypsum (calcium sulphate) was utilized, which would be a typical material for grounds in Italian easel paintings,[21] yet the use of calcium carbonate (chalk) cannot be entirely excluded as the detection range for the spectrometer does not include sulphur signals.[22]

The trace amount of iron recorded may be due to the presence of iron oxides in ochre, whereas traces of titanium (Ti) may come from such minerals as ilmenite or rutile that are naturally present in this pigment.[23] Of note, is that both elements were registered at numerous measuring points (e.g., P1, P4, P7), with measurement signals of calcium, iron and titanium recorded, analogous to those from Mary's mantle and dress. Saint Joseph's blue robe (P6) and

to detect light metals, such as sodium (Na) or aluminium (Al), that are the main components of lapis lazuli. In addition, this technique cannot be used for identifying organic pigments.

19 Khandekar, op. cit.

20 *Artists' Pigments. A Handbook of Their History and Characteristics*, Ashok Roy, ed. (Cambridge, 1993), vol. 2, p. 255.

21 Gypsum – as the main ingredient of the ground in the painting – was identified during research carried out in the National Museum in Warsaw. See Jan Białostocki, Maria Skubiszewska, *Malarstwo francuskie, niderlandzkie, włoskie do 1600*, collection catalogue (Warsaw, 1979), pp. 138–39.

22 Corresponding results were obtained by researchers from the Straus Center. See Khandekar, op. cit.

23 Marcin Ciba, Andrzej Kozieł, Barbara Łydżba-Kopczyńska, "Badania fizykochemiczne wybranych obrazów Michaela Willmanna oraz palety pochodzącej z jego pracowni," in *Obrazy Michaela Willmanna pod lupą* (Jawor, 2010), pp. 25–49.

blue fragments of the landscape (P13) contain copper, lead, iron and manganese, the presence of which implies the use of the same pigments that appear in Mary's blue mantle, i.e., the blue copper pigment (perhaps azurite), lead white and umber.

In the spectra obtained from Saint Joseph's yellow mantle (P5a, b and c) and from the cradle (P12) iron and lead signals were registered, implying the use of yellow ochre and lead white. In the green, and greenish-brown parts of the picture – Saint Catherine's mantle (P8) and the overgrown scarp in the background (P11a and P11b) – distinct signals of copper and lead were found, as well as iron and traces of tin (Sn). The connection between lead and lead white pigment would not be surprising, whereas the presence of tin would suggest lead-tin yellow. If the presence of iron results from the use of yellow ochre or lead-tin yellow, it seems natural that the green colour was obtained using blue copper based pigment, probably azurite. Yet, it cannot be excluded that copper acetate (verdigris)[24] or copper resinate[25] was used, for their signals would exceed the range of the used spectrometer. In Old Masters, painting verdigris would be utilized for its transparent properties that facilitate glazing effects in green landscapes. For the same reasons copper resinate together with lead-tin yellow were used (signals of tin may be a sign of it).[26]

In order to identify the white pigment, two areas in the painting were chosen: the stone pedestal (P4) and Mary's face (P10a). In both cases a distinct signal of lead was identified, which means that lead white had been used. However, in the measuring point on Mary's cheek (P10a) signals of mercury (Hg) were detected, which means vermillion (HgS) had been utilized to obtain pink tone of the complexion.[27]

The last measuring point was the brown plait of Saint Catherine's. Here, strong signals of lead, iron, mercury, calcium and traces of tin were recorded. Similarly to the previous cases, signals of calcium would come from the ground, while other elements imply the use of lead white, vermillion, ochre and possibly lead-tin yellow.

The results of the pigment examination, using XRF spectroscopy in both paintings, are presented in the table (p. 189). There is considerable consistency in the identified pigments. Utilizing lead white not only for complexion but also in other parts of the painting is justified by the need to obtain a certain colour. White lead was widely used in Old Master paintings for lightening colours and building chiaroscuro. In both paintings vermillion was used for obtaining a proper tone of the persons' complexion. The main material responsible for the colour of Mary's red dress and Saint Catherine's purple one and their tones was likely an organic pigment together with lead white, azurite and umber. Mary's blue mantle and Saint Joseph's robe plausibly owe their colour to azurite. Comparable results for both paintings were also obtained during examination of Saint Catherine's mantle and the green plants of the scarp in the background. In both cases the XRF spectra display signals corresponding to copper and lead. The presence of the latter implies that white lead pigment had been used; however, identifying the copper based pigment is not so obvious. The signal may correspond to blue azurite or to green copper based pigments, such as copper acetate (verdigris) or copper resinate. The XRF analysis did not give unambiguous results that would make it possible to identify one of the pigments.

24 *Artists' Pigments*..., op. cit., p. 131.

25 Ibid., p. 141.

26 Ibid., pp. 131–47.

27 Nicolas Eastaugh et al., *Pigments Compendium. Optical Microscopy of Historical Pigments* (Oxford, 2008), p. 392. XRF examination does not allow for differentiating between mineral cinnabar and vermillion.

Table
The results of the pigment examination of the Warsaw and Boston paintings with XRF spectroscopy (the symbols of the elements recorded in trace amounts are given in brackets)

Painting	***The Holy Family*** **The National Museum in Warsaw**		***The Holy Family*** **Childs Gallery in Boston**	
Colour	**Elements**	**Pigments**	**Elements**	**Pigments**
Blue	Pb, Cu, Ca, Fe, Mn, Ti, (Sn)	azurite, lead white, umber	Cu, Pb, Fe, Mn, (Ti)	azurite, lead white, umber
Green	Cu, Pb, Fe, Ca, Sn	copper resinate / verdigris / azurite, lead-tin yellow, lead white	Pb, Cu, Sn, Fe, Ca	azurite, lead-tin yellow, lead white
Red	Pb, Cu, Fe, Ca, Ti, Mn, Sr	lead white, azurite umber, organic pigment	Pb, Fe, Mn, Ca, Cu, (Ti)	lead white, umber, azurite, organic pigment
White	Pb, Fe, Cu, Ca, Ti, Pb, Fe, Hg, Sn, Cu, Ca	lead white, vermilion	Pb, Hg, Ca, Fe, Cu, (Ti)	lead white, vermilion
Yellow	Pb, Fe, Cu, Ca, Sn, (Ti)	Lead white, yellow ochre / lead-tin yellow	Pb, Fe, Sn, Ca, Cu, Ti	yellow ochre, lead-tin yellow

XRF spectroscopy of the Boston painting suggested several times that lead-tin-yellow had been used. Unfortunately, the analysis of the Warsaw version showed that the signal of tin in XRF spectra was relatively weak, hence the use of lead-tin yellow could not be fully confirmed. Nerveless, it should be borne in mind that each painting was examined in a different laboratory and with a different spectrometer. Therefore, this discrepancy in the results might be attributed to dissimilar measurement conditions and not to significant differences in the painting materials. However, signals that proved the presence of calcium, iron and titanium were recorded for almost all measuring points.

The results of the examination show that in analogous parts of both paintings the same pigments were used to obtain certain colour effects. The XRF does not enable an unambiguous identification of the copper pigment appearing in the green parts of the Warsaw painting[28] and it is impossible to state whether the material used in the ground layer and in the transfer layer was gypsum or chalk (the latter being historically less likely). Given that the questions concerning both the Warsaw and Boston versions that were not answered with XRF concern similar issues, it can be taken as another argument that both paintings had been executed in the same studio.

BŁK

Examination of Painting Layer Samples Using SEM-EDS Microscopy and Raman Spectroscopy

Non-invasive examination of the Warsaw and Boston versions using XRF spectroscopy made it possible to define the palette of both works. However, a fuller image that would reveal the order and manner of applying subsequent layers was obtained due to a stratigraphic examination of the samples. To carry it out, two samples were taken from each of the paintings at the Conservation Workshop of Sculpture and Painting on Wooden Supports of the National Museum in Warsaw (**figs 18–19**).[29]

The first sample from the Warsaw painting, marked WAW1 (**fig. 20**), was taken from the white sheet in the cradle, and the other one (WAW2) came from the hem of the green lining of Saint Catherine's mantle. Neither cross-section shows the full stratigraphy with both the ground and the paint layers. WAW1 sample shows the white ground and traces of the *imprimitura* or paint layer, whereas WAW2 has the upper layer in white, the middle layer in brown-grey with sparse grains of light green and the lower layer of white ground.

Upon illumination with UV light, the WAW1 sample showed yellow fluorescence characteristic for oil binding media typical of Raphael's studio.[30] In the WAW2 sample there is strong white fluorescence on the paint layer, possibly originating from the varnish.

28 Researchers from the Straus Center point out that azurite was used in the Boston painting.

29 After preparing the necessary documentation of the samples selected for cross-sections they were immersed in epoxide resin and subsequently cross-sectioned with a manual grinder. Next, stratigraphic analysis of the cross-sections was performed using a stereoscopic Opta-tech microscope and an optical MBL microscope with the epifluorescence setup FL-800. The examinations took place in the Cultural Heritage Research Laboratory, Faculty of Chemistry, University of Wrocław, in 2013.

30 Marika Spring, "Raphael's Materials: Some New Discoveries and Their Context within Early Sixteenth-Century Painting," in *Raphael's Painting Technique: Working Practices before Rome. Proceedings of the Eu-ARTECH Workshop*, Ashok Roy, Marika Spring, eds (Firenze, 2007), pp. 77–86; the examination of paintings by Raphael carried out in the National Gallery, London, confirmed that the binding media was based on linseed and walnut oil. Ashok Roy, Marika Spring, Carol Plazzotta, "Raphael's Early Work in the National Gallery: Paintings before Rome," *National Gallery Technical Bulletin*, 25 (2004), pp. 4–35.

The first sample from the Boston painting (BOS1) comes from the left edge of the work – of a fringe wound over the stretcher. The other one (BOS2) was also taken from the fringe at the height of the middle of the composition, on the left as well. When the samples were being collected, a dark layer was found, probably a secondary one, added upon transfer after removing the original ground.[31]

In the cross-section of BOS1 three layers can be seen (**fig. 21**). The upper one is light grey; the middle one is white-blue with blue crystals whose morphology is similar to azurite. In UV light both layers show mediocre yellow fluorescence, which – similarly to the Warsaw version – implies the use of oil as a binding medium.[32] The lower layer is dark blue – lack of fluorescence suggests that it may contain aluminosilicates, such as clay. Between the white-blue and dark blue layer there is a local red layer (most probably it is a sealing substance also coming from the transfer).

In the upper part of the cross-section of BOS2 (**fig. 22a**) one can see a light grey layer, and in the lower part – a dark blue one. The compositions of each of the samples from the Boston painting are alike, though in BOS2 more white is contained. Below the light grey layer there is a double layer consisting of an intensely green finish and a light green underpainting with numerous grains of light green morphologically more similar to verdigris or copper resinate than to malachite. Upon UV illumination a distinct yellowish fluorescence appears only in the upper, light grey layer. Between the two lower layers (the dark green and the dark blue one) stands out another, very thin layer of a noticeable fluorescence (**fig. 22b**). It may be a remnant of some original *imprimitura*, although it was not found in BOS1 sample. Both, in turn, have that local red layer, that must have been a sealing substance used during the transfer.

The next step on the way to identification of painting materials in cross-sections was the analysis using scanning electron microscopy with EDS (SEM-EDS).[33] The measurements were taken in 2013 at the Faculty of Chemistry, University of Wrocław, using a Hitachi S-3400N scanning electron microscope with an EDS Thermo Scientific Ultra Dry detector. All of the measurements were performed at low vacuum with an energy of 30 kV and magnifications of the order from 120 to 20,000 times. For each cross-section their elemental compositions was examined in over a dozen single points measurements and was mapped.[34] An important advantage of this technique is the possibility to determine the distribution of elements in the sample, which is of particular significance when analysing cross-sections.[35]

SEM-EDS examination of WAW1 and WAW2 samples confirmed the previous conclusions based on stratigraphic analysis. Single point measurements, as well as mapping the surface of WAW1, showed that in the lower layer (ground) there is calcium, sulphur and oxygen, indicating the presence of calcium sulphate – possibly gypsum (**fig. 23**). Raphael and his studio utilized *gesso* made of gypsum mixed with animal glue vigorously stirred and heated, which produced

31 See "Transfer of the Painting Layers of the Boston *Holy Family*" – pp. 183–86 above.

32 The research carried out in the Cultural Heritage Research Laboratory, Faculty of Chemistry, University of Wrocław, with GC-MS confirm that oil binding medium was used.

33 Stuart, op. cit., pp. 91–93 and 234–38.

34 Examination performed in the Cultural Heritage Research Laboratory, Department of Chemistry, University of Wrocław.

35 Ciba, Kozieł, Łydżba-Kopczyńska, op. cit., pp. 42–43.

numerous bubbles of air in the ground layer,[36] visible also in the Warsaw sample (**fig. 20**). A few red-orange grains are probably ochre (iron oxides). The upper layer, in turn, which is a part of *imprimitura* or paint layer, lead was found that will have come from lead white.

In WAW2, in the upper, white paint layer lead was recorded, which also suggests lead white pigment. Another layer contained such elements as lead (Pb), aluminium (Al) and silicon (Si) that form aluminosilicates. Traces of copper imply the use of a copper pigment. As the sample was taken from the hem of Saint Catherine's dress, it may be inferred that the painter used green or blue copper-based pigment.

During further investigation of the WAW2 sample, in its lower layer – fragmentarily preserved ground – bismuth (Bi) was identified, which had not been registered beforehand during XRF analyses (**fig. 24**). In SEM-EDS microscopy the measuring spot is far smaller (c. 4 nm),[37] thus signals that were not registered in XRF can be detected with SEM-EDS. Moreover, examination of cross-sections allows for a more insightful analysis of the painting materials used. The presence of bismuth is not unexpected in a painting by a disciple of Raphael's as its use was confirmed in previous examinations of paintings attributed to Raphael.[38]

Semi-quantitative[39] SEM-EDS results suggest the presence of glass, which is indicated not only by the presence of silicon, sodium, magnesium (Mg), aluminium, potassium (K), calcium, titanium, manganese and iron (**fig. 25**), but also by irregular shapes that make glass different from other aluminosilicates. Glass, especially containing manganese coming from vegetal ashes, was added to the paint as siccative that facilitated drying up.[40]

SEM-EDS examination of cross-sections of samples taken from the Boston painting brought more comprehensive information about paint layers and the dark blue layer in the place where white, gypsum ground would be supposed to appear.

In the cross-section of the first sample (BOS1), as stated earlier, three layers are visible: the upper one (light grey), the middle one (white-blue) and the lower one (dark blue). The upper one contains lead, aluminium, silicon, magnesium, calcium, carbon and oxygen. Considerable amounts of lead (together with carbon and oxygen) indicate that one of its main ingredients is lead white pigment mixed with material based on aluminosilicates, e.g., clay containing iron compounds. Calcium too can come from calcium carbonate owing to the presence of carbon and oxygen, which, furthermore, is also due to presence of an organic substance (e.g., binding medium) yielding strong fluorescence of this layer.

In the white-blue painting layer copper and lead were identified, which means that it is composed of a mixture of copper pigment and lead white (**fig. 26**). Semi-quantitatively[41] determined chemical composition revealed with SEM-EDS suggests it may be azurite (copper carbonate hydroxide) (**fig. 27**). This conclusion is supported by the blue colour of the grains discernible in the cross-section observed in visible light. In addition, the blue paint layer contains traces of such elements as aluminium and silicon implying the presence of aluminosilicates. Local

36 Roy, Spring, Plazzotta, op. cit., passim.

37 Spring, op. cit., pp. 77–78.

38 Książek et al., op. cit., pp. 1–102.

39 Due to measurement conditions the SEM-EDS method provides semi-quantitative and not quantitative results for the composition of the examined materials; ibid., op. cit., p. 44.

40 Spring, op. cit., pp. 79–80.

41 Książek et al., op. cit., p. 44.

occurrence of iron may suggest the use of ochre. Mapping (**fig. 28**) of the thin red layer locally observable between the white-blue paint layer and the dark blue lower one showed that its main ingredient is iron. Apart from that, aluminium, silicon and traces of lead were detected. Thus, one may suppose that this layer consists of iron oxide (ochre) mixed with some sort of clay minerals. Trace amounts of lead may result from using it as siccative.

Based on SEM-EDS results, the following elements were identified in the dark blue lower layer: silicon, aluminium, calcium, iron, carbon, oxygen, lead and traces of sulphur and titanium. This suggests that it consists of aluminosilicates (e.g., clay), an organic substance and calcium (the concentration of which here is lower than in the upper layer). Part of the calcium may come from calcium sulphate (gypsum. As there are only traces of sulphur, it may be the leftover of the ground removed before transfer. The remaining part of calcium may come from calcium carbonate. Because of the colour of the layer in question the small content of lead compounds (several per cent) means it might have been used as siccative.

The cross-section of BOS2 (**fig. 22a**) reveals three layers: the upper one (light grey), the double green layer in the middle (finish and underpainting), and the lower one (dark blue). In the sample there are local occurrences of red sealing layer coming from the transfer.

The examination showed that the light grey layer is composed of lead, aluminium, silicon, calcium, oxygen and traces of iron. It is very similar to the composition of the analogous layer in BOS1. In both cases samples probably consist of a combination of white lead, aluminosilicates, an organic substance and calcium carbonate.

Another layer (finishing layer) owes its dark green colour to the copper in verdigris or copper resinate. This layer also contains: aluminium, silicon, lead, carbon, oxygen and traces of calcium and iron (due to local occurrences of ochre).

The main component of the light green underpainting is an aluminosilicate matrix, which is proved by large amounts of aluminium and silicon together with traces of iron coming probably from red ochre (as red grains are visible). The occurrence of copper, lead, tin and antimony (Sb) may be explained by the fact that the painter used green copper based pigment (such as verdigris, copper resinate) and lead-tin yellow. The traces of antimony may arise from using antimony sulphide, also utilized in Raphael's studio.[42] This sulphide is dark grey, which is why its use in underpainting (where dark grey grains can be seen) is probable.

The lower, dark blue layer is composed of silicon, aluminium, carbon, oxygen, iron, calcium and traces of lead. Its composition, based on a combination of an organic substance, aluminosilicates and perhaps calcium carbonate, corresponds to that of the lower layer in BOS1 sample.

The last method used in investigation was Raman spectroscopy, which consists in illuminating a sample or a previously prepared cross-section with monochromatic light from a laser.[43] It confirmed the presence of lead white, red ochre (**fig. 29**) and azurite (**fig. 30**) in WAW2.[44] Regrettably, the spectra registered for BOS2, down to strong fluorescence, did not yield results that would confirm the presence of verdigris or copper resinate.

[42] Spring, op. cit., pp. 77–86.

[43] Marcin Ciba, Barbara Łydżba-Kopczyńska, "Technika malarska Jeremiasa Josepha Knechtla na podstawie badań fizykochemicznych obrazu *Święty Karol Boromeusz* z kościoła filialnego pw. świętego Wawrzyńca w Przychowej," in *Jeremias Joseph Knechtel (1679–1750): legnicki malarz doby baroku*, Andrzej Kozieł, Emilia Kłoda, eds (Legnica, 2012), p. 79.

[44] Examination performed in the Cultural Heritage Research Laboratory, University of Wrocław.

The results of SEM-EDS and Raman spectroscopy analysis of the cross-sections of samples from the Warsaw and Boston painting did confirm the use of azurite with lead white to obtain blue colour, which is conform to the XRF examination. The analysis of the green colour enables drawing the conclusion that the painter made it by creating a paint layer consisting of lead white, lead-tin yellow and azurite or a green pigment. The supposition that the latter was verdigris is supported by the stratigraphic analysis of the samples and the comparison with the results of the examination of Raphael's paintings performed in the National Gallery, London.[45]

The results of SEM-EDS show that the main component of the ground in the Warsaw painting is calcium sulphate. Although in the Boston version calcium was found in many layers, there was no white gypsum layer in any of the cross-sections. During the transfer it must have been replaced with a mixture of an organic substance, aluminosilicates and calcium compounds.

SEM-EDS and XRF examinations of both paintings allowed for identification of elements characteristic of aluminosilicates,[46] the presence of which is often connected with using clay minerals (e.g., clay). The SEM-EDS examinations confirmed that they appear in both original and secondary layers.

It is noteworthy that conclusions drawn from the results of the XRF and SEM-EDS analyses of the Warsaw and Boston paintings are consistent. The examination of cross-sections, and particularly mapping of the elemental composition of their surface, allowed for confirming the localization of signals coming from elements registered during XRF. It would be interesting to compare results obtained for samples from the Warsaw version taken from places analogous to those where the Boston samples were taken from; unfortunately, it was not practicable.[47] However, the analysis of a Warsaw sample containing ground allowed the confirmation that it was based on gypsum, which is typical of Raphael's studio.

Particular attention should be drawn to the fact that Gianfrancesco Penni preserved and continued Raphael's painting techniques. It involved using the same palette where azurite served as blue pigment and obtaining green by applying several painting layers with lead-tin yellow and probably verdigris. Moreover, Penni made use of other characteristic Raphaelite procedures, such as using bismuth in powder as pigment[48] and adding pulverized glass to *imprimitura* and to paint layers.[49]

The analysis of chemical elements in the lower, dark blue transferring layer visible in samples taken from the Boston painting demonstrated that it is a material based on aluminosilicates, e.g., clay containing iron compounds and probably traces of calcium carbonate. The hypothesis concerning the transfer of paint layers of the Boston version is supported by the conformity of the layer's elements composition and of the conclusions formulated by conservators and analogous paint layers in other paintings and their examinations that have been reported.

Using two different methods based on X-ray enables a general evaluation of their advantages and shortcomings. The conformity of the results obtained when the whole painting was

45 Spring, op. cit., pp. 80–81.

46 One cannot disprove that a certain amount of aluminosilicates occurring in paint layers may be related to the presence of ground glass; yet, such a possibility ought to be confirmed with other analytical methods.

47 Collecting samples in analogous parts of both paintings was not possible because of the fragility of paint layers of the Warsaw version, additionally covered with a thick layer of hard varnish.

48 Spring, op. cit., pp. 77–78.

49 Ibid., pp. 78–79.

examined with the use of XRF and SEM-EDS of the cross-sections leads to the conclusion that using a scanning microscope brings new information to the technological analysis of paintings. Proper interpretation of the signals registered during the XRF analysis and matching them with specific pigments and layers in the sample is mainly due to the information obtained during the stratigraphic examination of cross-sections using such techniques as SEM-EDS. What is more, the opportunity to map the spatial distribution of chemical elements in the sample is not to be undervalued. Without taking samples and preparing cross-sections it would be impossible to confirm, for instance, the occurrence of bismuth, the presence of which is characteristic of a Raphaelite artist.

BŁK

Translated by Szymon Żuchowski