National Gallery Technical Bulletin

VOLUME 32 Leonardo da Vinci: Pupil, Painter and Master







National Gallery Company London

Distributed by Yale University Press

This edition of the *Technical Bulletin* has been funded by the American Friends of the National Gallery, London with a generous donation from Mrs Charles Wrightsman

Series editor: Ashok Roy

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First published in Great Britain in 2011 by National Gallery Company Limited St Vincent House, 30 Orange Street London WC2H 7HH

www.nationalgallery.org.uk

British Library Cataloguing-in-Publication Data. A catalogue record is available from the British Library.

ISBN: 978 1 85709 530 2 ISSN: 0140 7430 1032030

Managing Editor: Jan Green Project Manager: Giselle Sonnenschein Editor: Rebecca McKie Design: Libanus Press Picture Research: Maria Ranauro and Giulia Ariete Production: Jane Hyne and Penny Le Tissier Repro by Alta Image Printed in Italy by Conti Tipocolor

FRONT COVER

Leonardo da Vinci, *The Virgin of the Rocks* (NG 1093), c.1491/2-9 and 1506-8 (detail).

TITLE PAGE

Top left: Andrea del Verrocchio, *The Virgin and Child with Two Angels* (NG 2508), *c*.1467–9 (detail).

Bottom left: Master of the Pala Sforzesca, *The Virgin and Child with Four Saints and Twelve Devotees* (NG 4444), probably *c*.1490–5 (detail).

Right: Leonardo da Vinci, *The Virgin of the Rocks* (NG 1093), *c*.1491/2–9 and 1506–8 (detail).

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Painting Practice in Milan in the 1490s: The Influence of Leonardo

MARIKA SPRING, ANTONIO MAZZOTTA, ASHOK ROY, RACHEL BILLINGE AND DAVID PEGGIE

In spite of intense and continuous interest in all aspects of the life and art of Leonardo da Vinci, rather little has been known from direct evidence about the material side of his painting techniques, based on physical and analytical study of his easel pictures. This is understandable, since it is only under the circumstances of a comprehensive conservation treatment, when a painting is fully examined and analysed, that this kind of information can be assembled. The recent treatment of Leonardo's London version of The Virgin of the Rocks (NG 1093) has afforded just such an opportunity, as explained in the article on the picture in this issue of the *Bulletin* (pp. 32-56). It is also noted there that as a prelude to the cleaning and restoration of The Virgin of the Rocks, a number of Milanese panel paintings of the late fifteenth and early sixteenth centuries were cleaned and restored at the National Gallery in the mid-1990s in order to gain critical experience of the conservation behaviour of these types of pictures. These included a group of works by Ambrogio de Predis, Giovanni Antonio Boltraffio and Giampietrino, for which some of the results of the examination undertaken during the course of treatment have already been published.1

Study of the technique of pictures by artists connected to Leonardo has been given an additional impetus by the Gallery's decision to mount the loan exhibition Leonardo da Vinci: Painter at the Court of Milan (9 November 2011 – 5 February 2012). A further group of paintings, which will be described here, was examined and analysed in order to understand their technique more fully and to relate these findings to what is known of Leonardo's own studio practice. New observations on some of the paintings that were part of the earlier study are also presented. They are all connected by an association with Leonardo's sphere, either as the products of direct pupils, or as cases showing some clear contemporary Leonardesque style arising from the Milanese milieu of picture production. Although it is not possible to explore every strand of Leonardo's technical influence solely with these particular examples, taken from the National Gallery's own collection, they represent many of the main elements of his technical reach and also reveal some alternative practical responses to his distinctive visual and compositional inventions.

The terms 'Leonardesco' ('Leonardesque') and 'Leonardismo' ('Leonardism') have had rather a negative association for much of the twentieth century. It is noticeable that no particularly relevant or systematic studies of Leonardo's followers were pursued between 1929, the year of Wilhelm Suida's fundamental publication *Leonardo und sein Kreis* (Leonardo and his circle), and the early 1980s, when renewed interest in Leonardism first appeared. This long period of neglect has resulted in the attribution and chronology of the paintings by Leonardo's followers continuing to be a matter of great and unresolved debate. This difficulty is exacerbated by the powerful influence of Leonardo on the development of painting style in Milan at the end of the fifteenth century, which only a few artists managed to evade.

The forthcoming National Gallery exhibition focuses on Leonardo's first Milanese period, from about 1482 until 1499, and, in keeping with this, the selection of paintings examined and discussed here are all works produced by artists who were particularly close to Leonardo during his period in the city – the first generation of so-called 'Leonardeschi'. The National Gallery *Virgin of the Rocks* was very likely the most important exemplar for Leonardo's pupils during the 1490s.²

Although Leonardo arrived in Milan in the early 1480s, Leonardism was not a force until about 1490. The existence of two notes by him, dated 1490 and 1491, makes it possible to be almost certain that Marco d'Oggiono and Giovanni Antonio Boltraffio were training at that time in his workshop, since Leonardo reported that both were victims of the theft of a silverpoint by Salaì, a mendacious associate. These records not only provide a link between Marco d'Oggiono, Boltraffio and Leonardo, but are also evidence that Leonardo's pupils were experimenting with silverpoint, which became more generally employed in Milan under Leonardo's influence.

In 1491, Marco d'Oggiono and Boltraffio were commissioned by the Grifi brothers to paint an altarpiece for the Oratory of Saint Leonard, which adjoined the Milanese church of San Giovanni sul Muro. After their failure to deliver the work, a second contract was drawn up in 1494. This painting is the Resurrection with Saint Leonard and Saint Lucy (also known as 'The Grifi Altarpiece') now in Berlin (Gemäldegalerie).³ Since there are clear references to Leonardo's Last Supper in the figures of Saint Leonard and Saint Lucy, the altarpiece was almost certainly completed after 1497, the year Leonardo's most celebrated masterpiece was unveiled. It is widely agreed that Boltraffio is responsible for the two saints, whereas Marco is thought to have painted the figure of the risen Christ. It is interesting in terms of workshop dynamics that a metalpoint Study of a Drapery for the Risen Christ in the British Museum may in fact be by Boltraffio,⁴ which would imply that in Leonardo's workshop, exchange of drawings and ideas also occurred between pupils. A similar exchange of ideas, once more between Boltraffio and Marco d'Oggiono, can be seen in the case of the portrait of a child (most probably Francesco Maria Sforza, 'Il Duchetto', born in 1491) in Bristol Museum and Art Gallery (FIG. 1), here attributed to Marco d'Oggiono. It is based on a metalpoint Study for the Portrait of a Child in Milan (Ambrosiana), which is probably by Boltraffio, as there is a gulf in quality between the drawing – of a striking beauty - and the painting.

In The Grifi Altarpiece mentioned above, the distinction between the two hands is therefore a good basis on which to understand the two artists. The extremely skilled Boltraffio (see FIGS 20 and 28), 'Leonardo's only pupil', as his friend the poet Girolamo Casio described him, was probably regarded as a 'second Leonardo' and he had his own followers (see FIGS 31 and 34), including the less talented Marco d'Oggiono. Marco already shows at this stage, in the head of Christ, all his inadequacies (as in, for example, the employment of an unnecessary emphasis and exaggerated sfumato for the painting of the flesh), which are also present in works here attributed to him such as the Portrait of a Man aged 20 ('The Archinto Portrait') (NG 1665, FIG. 11), which is dated 1494. The fault persists in his later and more easily recognisable work, The Virgin and Child (NG 1149, FIG. 40) of about 1520.

Another work that is key for the study of the Leonardeschi in Milan in the 1490s is *The Virgin and Child enthroned between the Four Doctors of the Church and the Sforza Ducal Family*, known as the '*Pala Sforzesca*' ('Sforza Altarpiece'), painted originally for the Milanese church of Sant'Ambrogio ad Nemus, but now in the Brera, Milan.



FIG. 1 Marco d'Oggiono, Portrait of Francesco Maria Sforza ('11 Duchetto'), c.1492–3. Oil on canvas, transferred from panel, 36.8 × 26.6 cm. Bristol Museum and Art Gallery, inv. no. K1653.

It was commissioned by Ludovico il Moro in 1494, who was at that time the ruler of Milan, and most probably finished in about 1495. Although its creator remains to be identified, this work is of importance, at the very least because it proves that the London *Virgin of the Rocks* was already in existence by the date of its execution, but also because it provides a fundamental locus for a stylistically consistent group of works which are comparable to an anonymous close follower of Leonardo known as the 'Master of the Pala Sforzesca' (see FIGS 2 and 9).

The Milanese painter Ambrogio de Predis was involved in the commission for the altarpiece that included *The Virgin of the Rocks*; he is mentioned in the original contract of 1483 and also in the subsequent disputes concerning the picture. His role, however, was marginal, since of the surviving parts of the whole altarpiece, only the *Angel in Red with a Lute* (FIG. 2, p. 58) is thought to be by him. Ambrogio was only slightly younger than Leonardo at the time of Leonardo's arrival in Milan and he probably already had an established career. He therefore never really adapted his style to that of Leonardo. This can be seen most clearly in his portraits, which remained the traditional profile type (see NG 5752, FIG. 18), still the favoured pattern for official portraiture at this period in Milan.

After Ludovico il Moro's downfall and Leonardo's departure from Milan in 1499, the first generation of 'Leonardeschi' lost their guiding stimulus. Some of them, such as Boltraffio, found new inspirational sources in other artists, for example Bramantino; others, notably Marco d'Oggiono, laboured Leonardo's formulas to such a degree that their works became mere vulgarised shadows of Leonardo's art.

General features of the technique and materials of the paintings

The individual entries for the paintings discussed here form a detailed catalogue of the techniques and materials used, including a comprehensive discussion of the panel, preparatory layers, pigments and binding media obtained not only from analysis of samples but also from examination of the surface of the paintings with a stereomicroscope. The observations made from the infrared reflectograms (IRRs) and X-ray images on underdrawing, as well as changes in the composition, are also described.⁵ The summary below is intended to draw out some particular points and comparisons, as well as more general observations on the whole group of paintings.

All of the paintings in this study are on panel and in all but two cases it was possible to identify the wood. All were found to be walnut, with the only exception being the small altarpiece by the Master of the Pala Sforzesca, which is thought, from the character of the wood grain visible on its reverse, to be some type of softwood such as pine or fir. Leonardo himself used walnut panels for his Lombard paintings, as did many other artists, including those of an earlier generation such as Vincenzo Foppa (active 1456-1515/16).⁶ It seems to have been a typical choice of painting support in Milan in the 1480s and 90s, and was a wood that was also widely used for furniture at that time.7 Leonardo does not in fact mention poplar as a species used for paintings in his Codex A of 1492 (although it was undoubtedly the most common wood used for panels when considering Italy as a whole during this period), but instead lists cypress, walnut, whitebeam and pear wood.8 Cypress is the only type of softwood listed by Leonardo, and although not common, it has been found to have

been used as a support for paintings from the Pollaiuolo workshop. Other softwoods, however, such as fir, pine and spruce, have frequently been identified as supports for works by northern Italian painters.⁹

The small altarpiece by the Master of the Pala Sforzesca (NG 4444) is also an exception among these paintings in another respect, since the paint is bound with egg tempera, while in all the other works oil has been identified as the medium. Although some of the figures, in particular the Virgin, seem to rely on Leonardo's models, suggesting that the painting dates from the early 1490s, in other respects it seems old-fashioned in style, with its extensive gilding not only for details such as haloes and gold embroidery on draperies but also for large areas such as the throne and the dresses or robes of various figures. Although the earlier generation of Lombard artists such as Foppa and Bergognone did employ gold in their paintings, the aesthetic of this small altarpiece seems to have more in common with the gilded and polychromed reliefs by Lombard sculptors such as Giovanni Pietro and Giovanni Ambrogio De Donati.¹⁰ Tempera would have been a convenient medium for the sgrafitto decoration on several of the draperies. It is the only work in which the green pigment is a mineral copper green (a natural mixture consisting mainly of the basic copper carbonate malachite, with other associated green minerals) rather than verdigris, which is also in keeping with the egg tempera binder. The structure of the red draperies vermilion used alone for the mid-tones (which have discoloured as a result), with red lake overlaid for the shadows, and highlights of vermilion mixed with red lead - is also quite unlike the other paintings in this study, but typical of earlier Italian works.¹¹

The panel support of the small altarpiece by the Master of the Pala Sforzesca has been prepared simply with a layer of gesso, as would be expected for a painting in tempera, with no further oil priming layer. Two other paintings in this study also do not have an oil priming layer on the gesso – Boltraffio's *Virgin and Child* (NG 728) and Marco d'Oggiono's late *Virgin and Child* (NG 1149) of about 1520 – although in both cases there is instead a thin unpigmented proteinaceous layer, probably glue, which would have fulfilled a similar function in that it would have reduced the absorbency of the initial ground layer. The survey of preparatory layers in this period carried out in 1998 on around 120 paintings in the National Gallery shows that this method continued to be used well into the sixteenth century.¹²

Two of the panels have no gesso ground and only

a thick oil-based priming. In the Archinto Portrait (NG 1665), thought to have been painted by Marco d'Oggiono early in his career, this priming is pure lead white.¹³ The other panel with no gesso is The Virgin and Child (NG 2496) by a follower of Boltraffio, which has instead a pale orange-pink preparation consisting of lead white, lead-tin yellow and red lead.14 The priming on the Portrait of a Woman in Profile (NG 5752) attributed to Giovanni Ambrogio de Predis has an almost identical composition, but contains a small amount of verdigris in addition and is applied on a gesso ground. The same preparation has been found on the two Angels described in another article in this Bulletin (see pp. 61-2), one of which is attributed to de Predis.15 This particular composition in particular the inclusion of red lead and lead-tin vellow - has resulted in the formation of large lead soap agglomerates that protrude through the paint so that they are visible in the texture of the surface even with the naked eye, particularly in thinner areas such as the flesh.¹⁶

The Master of the Pala Sforzesca does not seem always to have worked in egg tempera, since the small *Saint Paul* (NG 3899) is painted with an oil medium, more specifically walnut oil, which was also identified in all the other paintings in this study. In most cases it was possible to establish that the oil had been heat-bodied, a treatment which would have thickened it and modified the working properties.¹⁷

Many of Leonardo's paintings have suffered from drying defects and wrinkling (discussed in detail in the article by Jill Dunkerton in this Bulletin, pp. 4-31), and the same is true of two of the paintings considered here, Boltraffio's Virgin and Child and Marco d'Oggiono's Archinto Portrait.¹⁸ In the latter the worst-affected area is the bright blue of the doublet, which has drying cracks that must have been the result of the extremely thick application of both the azurite underpaint and the overlying ultramarine, neither of which contain much lead white. The unsound technique is also evident in the wrinkled greenish-blue coat, made up of multiple layers where faster drying lead-white-containing paint overlies dark, slower drying underpaint. Similarly in the Boltraffio Virgin and Child the paint defects are caused by a combination of thick application of poorly drying paint (in the darkest areas of the Virgin's blue cloak), the use of dark underlayers (in the sky and landscape) and multiple layers of paint drying at different rates (in the lighter areas of the Virgin's cloak). Less easy to understand, however, is the reason for the wrinkling in the flesh tones. They do not have the medium-rich dark brown undermodelling which can be cited as a possible cause of the wrinkling seen in flesh paint in paintings by Leonardo,¹⁹ but it may be that the difference in the proportion of lead white in the darker brownish-pink underpaint and the lighter upper layers is sufficient to have resulted in this defect.

The preponderance of dark underlayers as well as upper paint layers containing a significant amount of black pigment has made it difficult to examine the underdrawing in the infrared reflectograms in these paintings. Where it has been possible to see some lines that can be identified as drawing, mainly in areas of flesh where the paint is thinner, the character of the lines seems to indicate that in many of these paintings cartoons have been employed, sometimes with some minor freehand adjustments after transfer of the design to the panel, as in Marco d'Oggiono's late Virgin and Child (see FIG. 42). The use of cartoons does not necessarily imply that these works are copies of other finished paintings; by this period they were commonly being used in artist's workshops as a means of transferring designs from paper to panel.²⁰ The use of partial cartoons, that is separate cartoons for parts of a figure such as the head or hands, has been shown clearly in works by Verrocchio and his workshop, through which Leonardo will have encountered this method.²¹ The survival of many drawings by the artists discussed in this paper and others associated with them, which can be related to these compositions, is testament to the widespread nature of this way of working.

In the early Marco d'Oggiono Archinto Portrait it was not possible to see any underdrawing, not even in the flesh (except a few lines around the hand), partly due to the high proportion of charcoal black in the paint. Several layers of flesh paint of different hues have been fastidiously blended, giving impeccably smooth transitions from light to dark. The artist may have adhered to the principles of Leonardo's ideas on sfumato transitions, but in this case has applied them with a literal understanding of the technique and less attention to the effect it is aiming to achieve, taking the sfumato to a point where the flesh has an almost rubbery appearance that is no longer subtle and realistic. The method by which this is achieved is also slightly different from that used by Leonardo in The Virgin of the Rocks; there is no darker undermodelling that contributes to the tone seen at the surface and the shadows are instead created only by dark grey paint containing charcoal black and red lake applied on the general pink colour for the flesh. The flesh has a distinctive ashen hue also seen in other Leonardeschi paintings, but although this is certainly

due partly to the predominance of charcoal black in the shadows, it may also be the result of fading of the red lake pigment, which would originally have given the paint a slightly warmer, browner tone. The Boltraffio *Virgin and Child* has instead a much warmer skin tone which is rather different in composition; it does contain some red lake but relies more on the opaque red pigment vermilion for the pink flesh colour, and so although the shadows do, in common with the portrait, contain a considerable amount of charcoal black, the cool tone is counteracted by the red pigment, giving the paint an overall warmer, browner tone.

Incorporated into Leonardo's understanding of the depiction of light and shade was his perception that our ability to distinguish colour is reduced at low light levels, and the use of black pigment to darken the shadows of the flesh is consistent with this belief. In the paintings attributed to a follower of Boltraffio, however, and also in the late *Virgin and Child* by Marco d'Oggiono, the darker flesh tones are instead created by increasing the proportion of red and yellow pigment relative to white, so that they keep a high degree of colour saturation even in areas of shadow, a fundamentally different approach to that adopted by Leonardo himself.²²

THE PAINTINGS

NG 4444

Master of the Pala Sforzesca (active *c*.1490–*c*.1500)

The Virgin and Child with Four Saints and Twelve Devotees (FIG. 2)

Probably painted c.1490-5.

Panel (including added strips of wood around all the edges): 57.4 (left) – 57.5 (right) × 50.6 cm, original panel 55.7×48.8 cm, thickness 5 mm (thinned).

Other than revarnishing and retouching of some small old losses and removal of the cradle on the back of the panel in 2010, the painting has not undergone conservation treatment since it was presented to the National Gallery in 1929.

The composition of this painting is monumental in character, despite its small size. The Virgin Mary, who holds an enormous Christ Child, is sitting on a gold throne, topped with a scalloped half dome. She is flanked by four standing saints (on the left Saint James the Great and a deacon – perhaps Saint Stephen; on the right, Saint Bernardino of Siena and a young male saint) and twelve kneeling devotees (on the left the males; on the right the females). This iconographical scheme for altarpieces belongs to a long-standing fifteenth-century Lombard tradition, the archetype being Vincenzo Foppa's Pala Bottigella in the Pinacoteca Malaspina, Pavia, executed nearly three decades earlier. The extensive employment of gold is also typical of the Lombard region, as are the greyish skin tones, which are very similar to those in paintings by Bergognone. However, the artist was clearly familiar with Leonardo's Milanese works, as is evident from the heads of some of the figures, such as that of the Virgin (seemingly a citation in reverse of the head of Leonardo's National Gallery Virgin of the Rocks; FIG.1, p. 33). This 'miniaturised' altarpiece is a precedent of the much larger Pala Sforzesca (Brera, Milan), an important Sforza commission of 1494 executed in about 1495. They are surely by the same hand, but the Pala Sforzesca shows much more developed Leonardesque features.²³

Support and preparatory layers: Wood panel,²⁴ single member, vertical grain. The wood has not been identified but the character of the grain as seen on the reverse suggests that it might be pine or some similar softwood. The panel has a gesso ground.²⁵ In several samples from the edge of the painting there is what appears to be bole immediately over the ground and beneath the paint, perhaps relating to gilding from an engaged frame or moulding that has now been lost.²⁶

Infrared reflectography and X-radiography: All the figures are underdrawn with a liquid medium using a brush. The drawing is simple and stylised; it is followed carefully in most areas and seems to have been based on a cartoon or cartoons. Basic outlines and hair are drawn, with some hatching of the shadows in draperies. There are, however, many minor changes, the most significant of which is that the man nearest the Virgin in the second row was first painted with smaller, clasped hands.

The freehand incisions for the positions of the folds of the Virgin's blue drapery appear white in the X-radiograph image, indicating that they were made before painting began.

Paint binding medium: Analysis of samples from the green of the sleeve of the kneeling male devotee nearest the Virgin and the purple robe of the kneeling devotee at the extreme left edge suggests that the binding medium is egg tempera.²⁷ This is consistent with the characteristic fine network of cracks seen on the painting by examination with a stereomicroscope.

Pigments and layer structure: One striking aspect of this painting is the extensive use of gold leaf to produce highly decorative effects, with what would have been



FIG. 2 Master of the Pala Sforzesca, The Virgin and Child with Four Saints and Twelve Devotees (NG 4444), probably c.1490–5. Egg tempera on panel.

subtle variations in texture and surface, distinctions that are now difficult to see due to the current condition of the work. The Virgin's gold dress, for example, is water gilded on an orange-red bole, with the lines of the main folds defined by black paint over the gold, but otherwise now appearing quite flat. There is, however, some modelling in small hatched strokes with what is probably the same black paint, appearing brown because it is applied more thinly. More extensive modelling consisting of thin washes over areas of shadow was visible in the infrared reflectogram, and careful microscopic examination did reveal thin reddish-brown paint in these areas, now rather patchy, in which some azurite and red lake particles can be seen, suggesting that originally a more colourful effect might have been intended (FIG. 3). There are also some very fine hatched lines indented into the gold in areas of the drapery that were intended to be highlights, which would have caused greater scattering of light and a



 $_{\rm FIG.\,3}$ NG 4444, photomicrograph of the Virgin's gold dress showing the main folds marked with strong black lines and the shadows with thin washy grey modelling.



FIG. 4 NG 4444, photomicrograph of the Virgin's gold dress showing small indented parallel lines that mark the highlight.

brighter appearance in a rather subtle manner (FIG. 4).

Several other figures also wear garments depicted using decorated water gilding, for example the female devotee at the extreme right edge whose underdress is similar to the Virgin's dress, with brownish-black lines marking the main folds, and shadows modelled with an extremely thin greyish paint or wash that, again, is more evident in the infrared image than under normal viewing conditions. The female devotee nearest the Virgin wears a gold underdress of a more elaborate fabric, where a foliate off-white pattern (painted with white mixed with a little red pigment) was applied after the modelling of the sleeve had been indicated in the same way as in the sleeve of the devotee at the extreme right. The pattern on the water-gilded cope of the deacon saint is made with green malachite-containing paint that has darkened due to discoloration of the egg tempera binding medium. For the foliate pattern on the square panel on his chest, however, a sgrafitto technique was used instead. The azurite-containing paint, now darkened, was scraped away exposing the gold beneath; the slight incision made by the tool can be seen in the centre of the lines created (FIG. 5). The same technique was used for the red collar, the cuffs and the border along the edge of the cope, with a red lake-containing paint which has now faded and also flaked from the gold leaf in many places. Only fragments remain of the black lines that indicated the tassels on the corner of the collar.

The throne is also water gilded, with brownish-black lines marking the main features of the architecture, brownish-grey washes in which a little blue pigment can be seen in the shadows (now hardly visible) and some hatched parallel incisions in areas of highlight. The pinnacles on the throne, however, are instead mordant gilding. Water gilding would have been carried out first, before painting began, and mordant-gilded details then applied at a later stage. The fact that these are mordant gilded, and are applied on top of the paint of the sky, might suggest that they were not originally planned, but this cannot be the case since they were underdrawn.

Mordant gilding was also used for finer patterns on draperies and smaller areas of gold such as the lacing on the bodice of the female devotee nearest the Virgin and the cuffs of the woman behind her. A sample from



FIG. 5 NG 4444, photomicrograph of the blue *sgrafitto*-decorated panel on the Bishop Saint's cope.



FIG. 6 NG 4444, cross-section of the mordant gilding on the blue dress of the woman at the right edge showing the thick translucent orange mordant layer (the gold leaf is missing), which lies on top of the blue paint of the dress (lead white and azurite).

the gold pattern on the discoloured blue overdress of the woman at the far right shows that the red-brown mordant is relatively thick and has a translucency that indicates that it is mainly organic in character. Attenuated total reflectance Fourier transform infrared imaging (ATR–FTIR) on the cross-section identified gum ammoniac in this layer, which also contains some vermilion, lead white and perhaps some red lake (FIG. 6).²⁸ Shell gold was used instead, however, for the very fine pattern on the purple overdress of the woman second from the right, depicting watered silk.

The only blue pigment in the painting is azurite, generally of very large particle size. It was used in the blue cloak of the Virgin (perhaps on a grey underpaint), the sky, the overdress of the woman at the far right edge (mixed with some red lake in the shadows) and the robe of the male devotee second from the left (which has hatched darker and lighter blue lines to indicate both the modelling and the texture of the fabric). The blue draperies appear quite dull, but the samples showed that while there may be some slight darkening of the paint, this is mainly due to the numerous layers of discoloured varnish and dirt on the surface. Paint has, however, certainly darkened due to discoloration of the binder in the *sgrafitto* panel on the chest of the deacon, where very little white has been mixed with the azurite.

Azurite is also used mixed with white and red lake (of large particle size) in all the purple draperies, including the lining of the Virgin's cloak, the overdress of the woman second from the right, the cloak of Saint James and the robe of the male devotee at the far left edge. As with the blues, these appear rather grey, but in crosssection the paint beneath the surface coatings can be seen to be intense in colour and well preserved.

All the green areas are painted with a green copper mineral pigment consisting of a natural combination of malachite (basic copper carbonate) and other minerals



FIG. 7 NG 4444, paint cross-section of the deep green sleeve of the male devotee nearest the Virgin. The green copper mineral pigment, of variable particle shape and hue, consists of malachite (basic copper carbonate) and also other copper minerals such as copper sulphate.

such as copper sulphates and carbonates, either with small amounts of zinc in addition to copper, or with small amounts of chloride (FIG. 7).²⁹ In all the other paintings discussed here, the green pigment was verdigris, but use of the mineral copper pigment in this painting instead is consistent with the fact that it is also the only work in this group that has an egg tempera binding medium.³⁰ It is of large particle size, as is evident from the thick application and coarse surface texture of the paint. It was used, sometimes mixed with lead-tin yellow and lead white, for the sleeves and collar of the male devotee nearest the Virgin, the pattern on the deacon saint's cope, the bodice of the underdress of the female devotee at the far right, the sleeves of the female devotee in the second row wearing a gold cap and the watered silk robe of the unidentified saint at the far right.

A little of this same copper mineral pigment was also mixed into black paint in the hose of the male devotee nearest the Virgin and the bodice of the female devotee nearest the Virgin, as well as the hose of the male devotee at the extreme left edge.

Several of the red draperies have suffered from discoloration of the mercury sulphide pigment vermilion. This deterioration is most noticeable in the dress of the female devotee nearest the Virgin and the robe of the male devotee at the extreme left, where it has become a purplish grey colour. The vermilion has not darkened in the shadows of the drapery, where it is glazed with red lake, or in the brightest highlights, where the paint has a more orange colour, suggesting that it is mixed with red lead.³¹ This is a rather old-fashioned method of painting red drapery quite different from that used in the other paintings in this study, but exactly equivalent to the traditional practice in Italian tempera paintings.³²

The red lake pigment has an intense raspberry pink colour that derives from the kermes insect, *Kermes vermilio* (Planch.).³³ When examining with a stereomicroscope



 $_{\rm FIG.\,8}~$ NG 4444, photomicrograph of the face of the old man second from the left on the front row of devotees.

the surface of the pink robe of the male devotee nearest the Virgin and the Virgin's flesh paint – both areas where this pigment has been used – red fibres were seen, an indication that the dyestuff was extracted from red textile shearings, a very common practice at this time.³⁴

The flesh paint consists of the same pigment mixture in all the figures: lead white, red lake, opaque red (probably red lead), black and distinctive large agglomerates of warm yellow earth. A thin, browner wash was used to model the shadows, and some of the figures have brown outlining. The highlights are more strongly textured, particularly in the wrinkled face of the older devotee second from the left, where the features have been emphasised with yellow earth in and around the eyes (FIG. 8).

NG 3899

Master of the Pala Sforzesca (active *c*.1490– *c*.1500) *Saint Paul* (FIG. 9)

Painted c.1490-5.

Panel: 24.4 (left) – 24.3 (right) × 14.9 cm, thickness of original panel about 7 mm, total thickness including attached nonoriginal secondary panel about 12 mm. Painted area 23.6 (left) – 23.5 (right) × 13.5 cm. Other than surface cleaning and revarnishing, the painting has not undergone conservation treatment since it entered the National Gallery in 1924.

This small panel may once have been part of an altarpiece; another panel, representing Saint John the Evangelist, which is probably from the same altarpiece, was recently donated to the Pinacoteca di Brera, Milan (FIG. 10). The two saints stand inside identical niches, characterised by a scalloped half-dome. The Saint John has lost its parapet, so the panel has probably been trimmed at the lower edge. The Saint Paul panel has sometimes been associated with the series of five small Apostles in the Museo d'Arte Antica, Castello Sforzesco, Milan. This connection seems unlikely, however, since there are slight differences in the forms of the niches, and also since the Saint Paul has a more archaic and somehow less Leonardesque character, which in its spatial illusionism is still highly indebted to the local tradition of, for example, Vincenzo Foppa and Bernardino Butinone. This tradition is not dismissed in the Pala Sforzesca, but there Leonardo's lesson on chiaroscuro seems to have been fully absorbed by the Master. A very similar figure of Saint Paul appears in a cycle of frescoes in the church of San Giorgio, Annone Brianza. This has been rightly attributed to the Master of the Pala Sforzesca, and is datable to the early 1490s.³⁵

Support and preparatory layers: Wood panel, single member, horizontal grain, attached to a walnut panel with a vertical grain.³⁶ The paint and ground stop short of the edges (although the unpainted wood is now heavily overpainted), except along the bottom, where the panel seems to have been cut. The pronounced barb where the ground and paint finish indicates that the panel originally had an engaged frame or mouldings. The ground is gesso, over which an off-white priming has been applied.

Infrared reflectography and X-radiography: There is underdrawing in a liquid medium applied with a brush in both the figure and the architecture. In the figure it is quite stylised, with many short, overlapping strokes where a continuous line would be expected (see especially the hand on the book), which could be the result of fixing a design transferred from a cartoon. In addition to the outlines, there is some parallel hatching for shadows. There are some differences between the underdrawing and the painted figure; most significantly, the hand – which now appears disproportionately large – was drawn smaller and at a different angle and the book has also been enlarged at the painting stage.

There is no underdrawing for the sword, although the centre line of the blade and position of the hilt have



FIG. 9 Master of the Pala Sforzesca, *Saint Paul* (NG 3899), *c*.1490–5. Oil on panel.



FIG. 10 Master of the Pala Sforzesca, *Saint John the Evangelist*, c.1490-5. Oil on panel, 21.7×16.2 cm. Milan, Pinacoteca di Brera, Gift of the Associazione Amici di Brera, 2011.

been incised into the paint with the help of a straight edge. Incisions were also made with compasses for the circles in the top corners and the arcs of the niche, and using a straight edge for the ledge at the bottom of the painting; these show white in the X-radiograph and must therefore lie beneath the paint.

Paint binding medium: Analysis of the paint of the grey stone of the niche at the left edge indicated that the binding medium is heat-bodied walnut oil.³⁷

Pigments and layer structure:³⁸ The saint wears a red cloak which is painted with mixtures of vermilion, red lead and a coarse black pigment which has the appearance of coal,³⁹ with more translucent paint used for modelling of the shadows. Large lead soap agglomerates are visible in the cloak and also in the paint of the yellow line running along the border of the cloak. The warm yellow tone of this line suggests that it is composed of a mixture of lead-tin yellow with a darker yellow pigment such as yellow earth.

The saint's robe now appears brownish in colour, but the paint beneath the varnish and repaint is probably a warm grey, since a few scattered blue and green particles are visible, mixed with white and black. The cover of his book, which is now rather dull in colour, is painted with azurite, much of it applied over the red drapery, as are the open pages and parts of the book cover and clasp. The sword is also painted over the cloak, the blade of which consists of white mixed with a coarse black pigment rather similar to that in the red paint. The flesh paint consists of white, a little red lake and vermilion, with some black added for the shadows. Large lead soap agglomerates that originate either in the thin flesh paint itself, or are protruding through from the priming, are easily visible.

All of the gilding, on the arch and the saint's halo, is on a thick reddish-brown mordant similar in overall tone to that on NG 4444, but more translucent. It therefore appears to be predominantly organic in nature, with only a scattering of opaque red pigment particles visible in the cross-section, together with some larger white inclusions. There is some brownish translucent toning over the gold on the arch to indicate some of the modelling of the architecture. The blue paint of the arch, worked wet-in-wet, consists of azurite mixed with varying amounts of white. The marbling on the ledge is carried out with pink paint based on red lake, and green based on verdigris, on a grey stone colour. It is applied wet-in-wet, as is the marbling on the roundels at the top corners, where azurite-containing blue is also used. The black spandrels behind these roundels are both completely repainted and it is impossible to speculate as to their original appearance.

NG 1665

Marco d'Oggiono (documented from 1487; died 1524) *Portrait of a Man aged 20 ('The Archinto Portrait')* (FIG. 11)

Dated 1494.

Panel: 54.2 (left) – 54.4 (right) \times 38.4 cm, thickness about 5 mm (thinned).

Inscribed on the scroll he holds: $\cdot 1494 \cdot / \cdot M \land R F \cdot$ [in monogram] / [A]ETA[TIS] S[VAE] $\cdot \land N[N]O \cdot 20 \cdot$ Cleaned and restored at the National Gallery in 1984–5.

The attribution of this painting is critical for a whole group of works, which have often been given to an artist named as the 'Master of the Archinto Portrait'. This artist is here believed to be the young Marco d'Oggiono,⁴⁰ mainly on stylistic grounds but also partly on the basis of a new interpretation of the monogram. The letters M and R are certainly included in the monogram (FIG. 12). Horizontal strokes seem to indicate that there is also an 'A' and an 'F', but they are in a black paint which is different from that of the letters 'M' and 'R' and therefore need to be interpreted with caution, as they may not have been painted at the same time as the 'M' and the 'R', although it is not impossible that they reinforce remnants of similar strokes



FIG. 11 Marco d'Oggiono, Portrait of a Man aged 20 ('The Archinto Portrait') (NG 1665), 1494. Oil on walnut panel.



FIG. 12 NG 1665, photomicrograph of the monogram on the scroll.



FIG. 13 NG 1665, paint cross-section of the greyish pink flesh on the sitter's chin, showing that it is the uppermost layer, rather than dark underlayers, that is the cause of the cool tone. Two layers of flesh paint (lead white, charcoal black, red lake, a little yellow earth, vermilion and lead-tin yellow) lie on the thick lead white ground.

beneath.⁴¹ Marco was recorded in Leonardo's studio in 1490, but his activity later in the 1490s is almost entirely obscure. His late career, which is characterised by a monotonous and easily recognisable style, is better understood (see, for example, the National Gallery *Virgin and Child*, NG 1149).⁴² This painting is also important because it bears a date, 1494, which provides a fixed point around which to base our understanding of the development of Leonardism in Milan. Marco d'Oggiono's skilful – yet slightly exaggerated – employment of *sfumato* closely follows Leonardo's ideas as expressed both in his paintings (for instance the London *Virgin of the Rocks*, NG 1093) and in the notes for his treatise (the *Trattato della pittura*).

Support and preparatory layers: Walnut panel,⁴³ single member, vertical grain. There is no gesso ground and instead the panel has been prepared with a thick application of lead white in oil (FIG. 13). This layer dominates the X-ray image, making marks from finishing the front of the panel with a hand tool very visible.

There are traces of a raised barb along the bottom and right edges, and a tiny fragment of wood adhered to the very edge of the paint at the bottom right, indicating that the painting once had an engaged frame; the lack of unpainted edges suggests the panel has been trimmed.

Infrared reflectography and X-radiography: Nothing that could be firmly identified as underdrawing could be seen in the head, clothes or the ledge at the bottom of the painting in the infrared reflectogram, due to poor penetration of the paint. A few drawn lines are just visible where the paint is thinner in the hand and the scroll. The clearest are those following the shape of the index finger, starting across the knuckle and running down the middle of the finger, and those in the area now occupied by the thumb. The hand seems first to have been drawn slightly to our left of its final position and was perhaps smaller and/or more tightly clenched. The scroll and inscription seem to have been painted after the ledge and hand were completed.

Paint binding medium: Analysis of samples from the blue doublet and the greenish-blue mantle identified the binding medium as walnut oil.⁴⁴

Pigments and layer structure: A striking aspect of this portrait is the greyish, pearly, almost sepulchral tone of the flesh, especially the lips. This effect is not created by using dark undermodelling, but instead by the use of considerable quantities of charcoal black in the upper paint layers, especially in the shadows, which are applied on a lighter pink mid-tone. The charcoal is mixed with lead white, red lake, distinctive agglomerates of a warm yellow earth pigment and a very small amount of vermilion and lead-tin yellow (FIG. 13).⁴⁵ Areas that are more pink in colour, such as the lips and cheeks, contain a slightly higher amount of vermilion, but the painter seems to have relied on red lake to give the pink tone of the flesh, and it seems likely that the appearance has been affected by fading and is not entirely intentional.

Charcoal black was also used for the black background and for the collar of the coat, where the black spots are feathered wet-in-wet into the grey base colour to convey the texture of the fur.

The intense blue of the doublet is achieved with a thickly applied paint of natural ultramarine mixed with lead white, on an underpaint of azurite and lead white. In cross-section, the upper part of the ultramarine paint has a lighter appearance than the lower part due to the blanching that is often associated with this pigment (FIG. 14);⁴⁶ it may be this deterioration that is responsible for the flat unmodelled appearance of this drapery, since it tends to be more marked in the shadows, where the ultramarine is not mixed with white and the lightening



FIG. 14 NG 1665, paint cross-section of the blue doublet showing a thick layer of ultramarine, slightly blanched in the upper part, lying over an equally thick layer of azurite.



FIG. 15 NG 1665, paint cross-section from the greenish-blue cloak, showing multiple blue, red and purple layers of paint based on azurite, red lake, lead white and a little black.

of the paint results in the distinction between the shadows and mid-tones being lost. The wrinkling and drying cracks evident in many areas of the painting are particularly severe in the blue doublet, probably because the paint (which does not contain much lead white) is so thickly applied that it appears raised relative to the adjacent draperies. These defects were perhaps exacerbated by the use of walnut oil as a binder.

There is a striking colour difference between the bright blue of the doublet and the coat; the predominant pigment in the surface paint of the coat is azurite, but it now appears a rather dull greenish colour. The azurite is of the same small particle size and slightly greenish colour as that in the underpaint for the doublet, which, together with discoloration of the oil binder over time, could be responsible for this effect. The deepest shadows are modelled in black, but there is some red lake pigment of large particle size mixed with the azurite in some areas, and also an underpaint containing red lake, visible with a stereomicroscope through cracks in the upper layers, suggesting perhaps that a purple-blue colour was intended. Deeper in the structure there seems to be a lighter beige paint layer. The multiple layers making up the coat are fully revealed in a cross-section from just above the point of the slit in the sitter's proper right sleeve (FIG. 15). A purple layer of azurite, red lake and white



 $_{\rm FIG.\,16}$ NG 1665, photomicrograph of the sitter's hair.



FIG. 17 NG 1665, photomicrograph of the sitter's hair at higher magnification than in FIG. 16, showing the bubbly texture caused by the formation of lead soaps in the lead-tin yellow-containing paint.

lies on the ground layer, followed by a thick brownish-red layer of red lake in a translucent yellow matrix; a layer containing only azurite; the beige-coloured paint; another very thin layer of red lake and finally the uppermost layer of azurite and white. The wrinkling that can be seen in the paint at the surface of the coat is perhaps caused by the thick medium-rich layers lower down in the structure which contain no lead white, such as that which contains only red lake.

The coat can never have had, however, the rich deep purple colour of the hat. This is painted with a mixture of red lake, azurite and lead white on a similar lighter underpaint. Red fibres in the paint were visible with a stereomicroscope, both here and in the pinker areas of the flesh, suggesting that the source of the dyestuff for the red lake pigment was red textile shearings. These would usually be removed during manufacture by filtering, once the dyestuff had been extracted into solution, but the method used here has resulted in them remaining in the pigment.⁴⁷

Lively and delicate pale yellow and dull orange strands of the sitter's reddish-blond hair escape around the hat and onto the black background (FIG. 16). The hair is painted with a mixture of earth pigments, lead white and a little black, but lead-tin yellow alone for the lightest highlights, which has caused extensive lead soap formation in the paint, creating small visible translucent white agglomerates which give the paint a frothy appearance (FIG. 17).

NG 5752 Attributed to Ambrogio de Predis (c.1455–1510)

Portrait of a Woman in Profile (FIG. 18)

Probably painted c.1495-9.

Panel: 53.6 (left) -53.9 (right) $\times 38.3$ (top) -38.0 cm (bottom), thickness 7 mm (centre top). Painted surface: 52.5×37.3 cm. Inscribed on the buckle of the belt: 'L' and 'O', with a Moor's head in between.

Cleaned and restored at the National Gallery in 2003-4.

This brown-haired and elegantly dressed woman is shown in profile, which is the only known typology among the surviving portraits by Ambrogio de Predis. One of the most famous among them is the *Portrait of Bianca Maria Sforza* in the National Gallery of Art, Washington,⁴⁸ and the only one that is signed – and dated 1502 – is the portrait of Bianca Maria's husband, the *Emperor Maximilian I*, in the Kunsthistorisches Museum, Vienna.

After Leonardo's innovations in portraiture, as can be seen in his Cecilia Gallerani,49 the profile type became rather obsolete, but it was still generally preferred by rulers and their families for their official portraits. It is not impossible that NG 5752 represents a woman who was related to the Milanese court, since the Moor's head between 'L' and 'O' on the buckle of her belt may refer to Ludovico 'il Moro' ('the Moor'), who became Duke of Milan in 1494 and remained as such until his downfall in 1499. It has sometimes been argued that the sitter is Lucrezia Crivelli, who was one of Ludovico's mistresses at about that time. Ambrogio de Predis was nearly the same age as Leonardo, and he had already received his artistic training by the time of Leonardo's arrival in Milan. Partly for this reason, and unlike - for example - Boltraffio and Marco d'Oggiono, or the Master of the Pala Sforzesca, he never became a fully Leonardesque painter, although this work shows him at his most Leonardesque (suggesting that a cautious 'attributed to' is appropriate here).⁵⁰

Support and preparatory layers: Walnut panel,⁵¹ single member, vertical grain. The remains of a barb are particularly clear at the top edge, but are present all round the edges of the panel, indicating that either a frame or mouldings were in place when the gesso ground was applied. The unpainted edge is 8–10 mm wide along the bottom edge. On top of the gesso is a relatively thick orange-pink priming layer consisting of lead white, a little lead-tin yellow, red lead and a small amount of verdigris.⁵² Large lead soap agglomerates have formed in the priming and protrude into the paint layers above.

Infrared reflectography and X-radiography: Interpretation of the infrared images is complicated by the condition of the painting, particularly in the background, and also because the panel was first used (the other way up) for a different portrait, a profile of a young man.⁵³ The drawing for this first portrait consists of outlines painted with relatively broad brushstrokes, the most visible of which are those running across the sleeve of the second female portrait, marking the position of his hat. More careful study of the area above these lines (or below the male portrait's hat, bearing in mind that the first portrait is upside down relative to the second) reveals his eye, nose and some hair, while in the lower part are some lines which may relate to the young man's body (FIG. 19). There is no indication in the reflectogram that the male portrait was completely painted, but the face at least does show in the X-ray image, so painting must have begun; the forehead, nose and eye are relatively clear, as is the bottom edge of the hat.



FIG. 18 Attributed to Ambrogio de Predis, Portrait of a Woman in Profile (NG 5752), c.1495–9. Oil on panel.

Underdrawing is also visible, in the face, for the *Portrait of a Woman*. It consists of simple outlines of a different character from the drawing for the young man, in that the lines are relatively fine, short and overlapping, of the type usually associated with the use of a cartoon or tracing. The drawing was followed quite closely during painting, apart from a slight change to the forehead.

Pigments and layer structure: The head is in general well preserved, but clumsy cleaning and restoration undertaken just before the painting entered the National Gallery collection have significantly affected the condition of the dress, particularly the sleeve, making it difficult to interpret the original appearance. The dress is painted with an opaque green mixture of verdigris, lead white, lead-tin yellow and yellow earth on a dark grey modelled underpaint that is quite substantial in thickness. In darker areas the green also contains coarse charcoal black and the deepest shadows seem to be a brownish, more translucent combination of red lake and verdigris. The paint of the sleeve appears to have been a similar mixture, but with a higher proportion of red lake in relation to verdigris. This combination of translucent red and green has been encountered in the work of other painters such



FIG. 19 NG 5752, infrared reflectogram, upside down, with blue lines indicating the location of the drawing for the first male portrait.

as Pietro Perugino, Raphael and Cima da Conegliano. A closer comparison, however, is perhaps the decorated green belt or scarf around the Christ Child in Boltraffio's *Virgin and Child* (NG 728, see below), painted with a translucent green based on verdigris over a subdued red consisting of red lake and black.

Charcoal has been extensively used in the painting, not only in the underlayer for the green dress, but also in the shadows of the flesh and the brown hair. Near the bottom of the hair where it meets the neck there is a fingerprint-like texture in the lighter flesh paint, which seems to have been brought over the darker brown of the hair to soften the transition.

NG 728

Giovanni Antonio Boltraffio (c.1467–1516) *The Virgin and Child* (FIG. 20)

Probably painted c.1493-9.

Panel: 92.7×67.3 cm, thickness about 5 mm. Cleaned and restored at the National Gallery in 1994.

This Virgin and Child has been believed in the past to be a fragment of a larger composition, perhaps part of an altarpiece, but it is in fact in its original size and shape. It can therefore be considered as the largest and most monumental of Boltraffio's surviving independent Virgin and Child paintings, slightly larger than the Budapest Virgin and Child.54 This painting belongs to a phase in Boltraffio's career very close to his Casio Altarpiece (Paris, Louvre), executed in 1500. It may just precede it, since it still retains – unlike his post-1500 works – some of the qualities of his metalpoint studies of the 1490s, such as the Williamstown Head of a Young Woman.55 The setting, with a green curtain in the middle behind the Virgin, and two vertical strips of landscape, is not very Leonardesque, and is more typical of Venetian Virgin and Child compositions of the late fifteenth century, such as those by Giovanni Bellini, with which Marco d'Oggiono also experimented in the same years.⁵⁶ A rather odd (although probably early) copy - in reverse - of this painting (FIG. 21) was in the collection of Mrs Charles Frederick Moulton, New York, in the 1960s, perhaps providing further evidence that the National Gallery painting has always had its current format.57

Support and preparatory layers: Walnut panel,⁵⁸ vertical grain. The panel is prepared with a gesso ground, probably bound in glue.⁵⁹ A thin unpigmented layer which may be glue has been applied on top of the gesso.



FIG. 20 Giovanni Antonio Boltraffio, *The Virgin and Child* (NG 728), probably *c*.1493–9. Oil panel.



FIG. 21 Black and white archive print of the painting *Madonna and Child* (copy of NG 728). New York, Frick Art Reference Library, inv. 3766 (707-8a).



FIG.22 NG 728, X-radiograph detail showing the changes in the position of the child's legs.

Infrared reflectography and X-radiography: Due to poor penetration of the paint it is difficult to identify any features in the infrared reflectogram that can definitely be said to be underdrawing. The curtain, rocks and sky, the Virgin's cloak and dress, and the child's wrap all appear dark in the infrared image because the paint contains black pigment, particularly in the underpaint. Some changes made at the painting stage can, however, be seen. The child's left leg has been lowered slightly and his right leg lowered more significantly - it seems first to have been painted in a position in which the leg was bent much more, so that the knee was level with his left hand. This change is even more clearly visible in the X-radiograph (FIG. 22). The Virgin's right arm was painted when the composition still had the child's leg in this position, so the leg in its final version had to be painted over the Virgin's sleeve, which in turn had to be extended to the left over the paint of the background. It is less easy to follow the changes to the Virgin's left hand, but it has certainly been moved; it is possible that it was first painted lower down, with the thumb just above where the index finger is now and at more of an angle.

Paint binding medium: Several samples from various areas of the painting were analysed and found to contain walnut oil as the binding medium.⁶⁰ An earlier study reported that the dark underpaint beneath the green hanging contains egg tempera, but new analyses using ATR–FTIR imaging directly on a paint cross-section did not detect any protein in this layer, suggesting that the old analyses need to be reinterpreted and that the dark underpaint may instead have an oil binder.⁶¹

Pigments and layer structure: The technique of this painting has already been discussed in an earlier article, which noted in particular Boltraffio's assimilation of apparently Leonardesque features, such as the use of dark underpaint, and the paint defects, especially drying cracks and wrinkling caused in part by the layer structure but also perhaps by the use of walnut oil as a binder.⁶² Here, further observations from the recent study, as well as a more detailed description of the materials, are presented.

The very substantial dark underpaint beneath the green hanging (FIG. 23), which also extends beneath the sky and landscape, consists of charcoal black mixed with azurite and only a very small amount of lead white. It is now visible through the extensive drying cracks in the wrinkled sky paint; these defects are probably caused not only by the dark underpaint but also by the application of a first blue layer of azurite with only a very small amount of lead white on to which a faster drying, lighter



FIG. 23 NG 728, paint cross-section from the green hanging behind the Virgin showing several layers containing verdigris, lead white, lead-tin yellow and yellow earth, lying on top of a dark underpaint consisting of black and a little azurite with a very small proportion of lead white.

blue has been applied, containing a high proportion of lead white relative to azurite. The green paint of the hanging comprises multiple layers of verdigris mixed with varying proportions of yellow earth, charcoal black and lead-tin yellow (FIG. 23). As in the other paintings in this study, the green paint does not have the translucency and bottle green hue that is often seen where verdigris has reacted with the oil binder and 'dissolved' so that it is difficult to see individual particles. Instead, large particles that have a cold bluish-green colour are visible in the cross-section in a warmer green matrix where smaller particles may have reacted with the oil, a supposition supported by the detection of copper carboxylates in this layer by ATR–FTIR imaging.⁶³

Christ's green garment is painted with a similar mixture, but has an unusual layer structure in that the green lies on a dull red underpaint of red lake mixed with some black. This combination of red and green is also found in the de Predis portrait discussed above (pp. 92–4) and was perhaps chosen to create a subtly different tone from the green of the hanging. The free brushy application of the gold decoration on the garment indicates that it is shell gold (FIG. 24), as is Christ's halo. Shell gold has also been used for the delicate motifs on the green curtain, including the thin trailing lines and the gold circles, which have cracked and reticulated into small islands in conjunction with the green paint beneath.

There is dark underpaint in the Virgin's red dress, although it is not a flat monochrome layer, as it is under the background, but is instead modelled according to the folds of the drapery, and is dark red-brown rather than black, consisting of a mixture of red earth and black. The upper paint layers are based on various mixtures of red lake, vermilion and black, although the current appearance is considerably affected by thin muddy layers of the



FIG. 24 NG 728, photomicrograph of the shell gold decoration on the Christ Child's green belt.

overpaint that was discovered during the most recent cleaning but mostly left in place, as there was little to be gained by removing it. It was not therefore possible to identify the type of red lake pigment that was used, but, as in two other paintings in this study, red fibres were visible on the painting, associated with the lake pigment, indicating that the source of the dyestuff was coloured textile shearings.

The Virgin's dark blue cloak has also suffered from extensive drying cracks, most noticeable in the deepest shadows, as well as blanching in the final glazes. It is modelled first in an underpaint containing azurite, black and lead white (FIG. 25); this is quite dark in much of the drapery but is far lighter in the highlights. This is followed by further modelling in various shades, including azurite used alone, azurite mixed with white, and a purplish paint of azurite mixed with red lake. In some areas, there is also further final modelling based on ultramarine, again either mixed with white, used alone or mixed with red lake. It is these final



FIG. 25 NG 728, paint cross-section of a mid-blue fold of the Virgin's cloak where it hangs off her knee. The underpaint contains a considerable amount of black pigment, mixed with azurite and lead white. There is a further dark blue layer of azurite and white followed by a lighter paint containing lead white and ultramarine.



FIG. 26 NG 728, paint cross-section of the shadow of the Christ Child's calf. The paint contains lead white, charcoal black, vermilion, a little red lake and a small amount of yellow earth. The underpaint is greyer in hue than the upper layers.



 $_{\rm FIG.\,27}\,$ NG 728, photomicrograph of the fingerprint where locks of the child's hair run over his temple.

ultramarine-containing glazes that are responsible for the blanched appearance. This multi-layered structure, interspersing layers containing a substantial amount of lead white, which would have dried well, with slower drying layers containing poorly drying pigments such as ultramarine and red lake, together with the use of walnut oil as the binder, must have contributed to the paint defects that are now so evident.

The flesh paint is based on mixtures of lead white, charcoal black, a substantial amount of vermilion in the form of large, highly refracting columnar particles, some red lake and a little intensely coloured yellow earth. A cross-section from the child's calf shows that there is an initial darker layer marking out the area of shadow, but while it contains black pigment it is a relatively substantial dark pinkish-brown paint rather than the type of thin greyish modelling seen on some unfinished works by Leonardo (FIG. 26). Where the locks of Christ's hair run over his forehead, the artist has used his finger to blend and spread the paint, leaving his fingerprint visible at the child's temple (FIG. 27).

NG 3916 Giovanni Antonio Boltraffio (c.1467–1516) *Portrait of a Man in Profile* (FIG. 28)

Probably painted c.1500.

Panel: 57.5×43.0 cm.

The painting has not undergone conservation treatment since it was bequeathed to the National Gallery in 1924.

This is the only surviving independent profile portrait in Boltraffio's oeuvre. Another portrait exists - this time showing a man set frontally – in the Uffizi, Florence (FIG. 29), which has often been argued to show the same sitter. Moreover, the Uffizi Portrait is painted on a panel nearly identical in size to NG 3916 and, interestingly, has the same nineteenth-century provenance. This may indicate that the two pictures could have been conceived as pendants, in order to show the sitter from two different viewpoints, perhaps explaining why Boltraffio in this case departed from his usual practice and painted a profile portrait. It has sometimes been argued that the two Portraits show the Bolognese poet Girolamo Casio, who was Boltraffio's close friend and patron.⁶⁴ The only indisputable and realistic portrait of Casio by Boltraffio is that showing him in profile kneeling on the right in the 'Pala Casio', now in the Louvre but painted in 1500 for the Bolognese church of the Misericordia (FIG. 30). The possibility that the two independent portraits show Casio is excluded by comparison with the 'Pala Casio'. There is, however, a close resemblance in terms of style with the Louvre altarpiece where, in common with NG 3916, the man has a rather fleshy chin indicative of the naturalistic tendencies that Boltraffio displays around 1500, by which time he had abandoned the genre of the idealised portrait, more typical of his work in the early 1490s.65

Support and preparatory layers: Walnut panel,⁶⁶ single member, vertical grain. Marks on the back from finishing with a hand tool suggest that the panel has not been thinned. The panel has been prepared with a gesso ground. There are traces of unpainted wood along the top, bottom and right edges, and possibly also the left edge. This suggests that an integral frame or moulding of some sort was present when the gesso was applied and that the panel has been cut along all the edges.

Infrared reflectography and X-radiography: Much overpaint is evident in the infrared reflectogram, especially in the background, black draperies and hair. The black folds visible in the clothes, especially on his right sleeve, are repaint from a restoration. The infrared image



FIG. 28 Giovanni Antonio Boltraffio, Portrait of a Man in Profile (NG 3916), probably c.1500. Oil on panel.





FIG. 30 Giovanni Antonio Boltraffio, *Virgin and Child with Saint John the Baptist, Saint Sebastian and Two Donors, known as the Pala Casio,* 1500, detail of Girolamo Casio at the right of the painting. Oil on poplar, 186×184 cm. Paris, Musée du Louvre, inv. 103.

FIG. 29 Giovanni Antonio Boltraffio, *Portrait of a Man*, probably c.1500. Oil on panel, 51.5×37 cm. Florence, Galleria degli Uffizi, inv. Contini Bonacossi n.28.

does, however, give some idea of the original modelling, and what appear to be changes to the line of his arm against the background. There also seem to be changes (made during painting) at the back of the figure and in the hat, which has been made larger. Lines to the left of where the profile of the face is painted are probably underdrawing for the head, and there is clear drawing for an eye, slightly lower than the painted position. The drawing found consists of the bare minimum by way of outlines, with no hatching.

Paint binding medium: A heat-bodied oil binding medium, probably walnut, was identified in two samples from the greenish-blue background paint.⁶⁷

Pigments and layer structure: The background of the portrait now appears green due to the thick layers of varnish and overpaint. Beneath these surface coatings, however, is blue paint containing azurite applied in two layers; the pigment in the upper layer is of higher quality, with a more intense colour and larger particle size than that in the lower layer.

Overpaint has changed the contours of the hat, extending it at the top edge and creating an indentation

at the junction between the hair and the hat on the right which is not original. The original paint consists of black mixed with white, some of which is in the form of large particles that are easily visible with a stereomicroscope.

The eye is brown, with darker paint for the pupil and paler grey-brown paint for the white of the eye. The paint of the greyer parts of the shadows of the flesh seems to have been applied in one layer; the grey appearance is due to black having been mixed into the surface paint rather than being a result of dark undermodelling.

There is an azurite blue tassel at the man's neck, with dark grey detailing which again contains large white particles mixed with black. The golden toggles on the end of the lacing have lead-tin yellow highlights.

NG 2673

Follower of Giovanni Antonio Boltraffio (conventionally called 'Pseudo-Boltraffio', active *c*.1500) *Narcissus* (FIG. 31)

Probably painted c.1500.

 $\begin{array}{l} \mbox{Panel: } 24.0 \ (left) - 23.9 \ (right) \times 26.1 \ (top) - 26.5 \ cm \ (bottom), \\ \mbox{including a non-original addition about } 1.5 \ cm \ wide \ on the \\ \mbox{right. Painted surface: } 23.1 \ (left) - 23.2 \ (right) \times 26.1 \ (top) \\ \ - 26.5 \ cm \ (bottom), \ thickness 5 \ mm \ (thinned). \end{array}$

Cleaned and restored at the National Gallery in 1983–4.

Narcissus, a young boy elegantly dressed and crowned with leaves, stands in a rocky and wild landscape behind an oddly elevated and reflecting pool, and looks at himself in it. This painting is also known in another version at the Uffizi (FIG. 32), which has differences in the format and also in the composition, mainly in the landscape. They have both been attributed to Boltraffio in the past, but they are of lower quality than any of his works, especially those of the 1490s. They both appear to have been executed by the same artist, who followed Boltraffio's ideas closely; it does seem to have been common practice in Leonardo's studio for artists to paint variants of their own works (this is also the case for the *Virgin and Child*, NG 2496).⁶⁸ The typology of this picture is typical of the Milanese court of the 1490s, where images of idealised, strictly androgynous beauty were highly desired by cultivated patrons. Boltraffio expressed this ideal, developed probably by Leonardo himself, mainly in his metalpoint drawings of the early 1490s, such as the Uffizi *Head of a Youth with an Ivy Wreath*.⁶⁹



FIG. 31 Follower of Giovanni Antonio Boltraffio (conventionally called 'Pseudo-Boltraffio'), Narcissus (NG 2673), c.1500. Oil on panel.



FIG. 32 Follower of Giovanni Antonio Boltraffio (conventionally called 'Pseudo-Boltraffio'), *Narcissus*, *c*.1500. Oil on panel, 19 × 31 cm. Florence, Galleria degli Uffizi, inv. no. 2184.

Support and preparatory layers:⁷⁰ Walnut panel,⁷¹ single member, vertical grain. An original unpainted edge is present along the top, but not along the other three sides. The paint is therefore complete at the top, but at least some has been lost from the other three sides. The panel appears to be in good condition apart from an area about 2 cm wide towards the left (as seen from the back) which is extensively worm damaged up to the junction with the addition; this raises the possibility that worm-eaten wood was cut from the original panel along this edge.

Infrared reflectography and X-radiography: Very little that can definitely be identified as underdrawing can be seen in the infrared reflectogram. There are some fine lines around the nose and defining the neck and chin. Similar fine lines suggest approximate outlines for the darker green parts of the landscape on the left (although no such lines could be found for the distant hills or horizon).

During painting the position of the head was slightly altered – a larger reserve was left for the back of the head, and changes in the paint of the rocks above the collar, as well as some curved lines, suggest either that more hair was planned or that the collar was higher and the fur was longer. The profile of the face has also been slightly modified – the forehead has been moved to our left of its first position and the nose, lips and chin to our right (pivoting the angle slightly, which matches the change made at the back of the head). The infrared image shows that reserves were left in the paint of the hair for some of the leaves of the wreath, although these have not been followed exactly. Some of the leaves did not have a reserve and are painted over the hair.

Paint binding medium: The binding medium of the blue azurite-containing paint of the sky was identified as a drying oil, probably walnut.⁷²

Pigments and layer structure⁷³ The blue paint in the sky and its reflection in the bowl is azurite of relatively fine particle size, mixed with white. In the distant land-scape and the leaves of the wreath, verdigris of unusually large particle size has been used.⁷⁴ It has been mixed with white, lead-tin yellow and yellow earth for the lighter tones, and in the wreath there are traces of a green glaze over the lighter base colour. The grass on the rock, at the top of the painting, is painted with similar mixtures – distinctive agglomerates of the yellow earth pigment are visible with the stereomicroscope.

The paint texture and method of modelling of the leaves of the wreath is very similar to the leaves of the plant held by the Virgin in NG 2946 (see FIGS 33 and 39). There are also similarities in the manner of painting the curling strands of hair and the facial features. The paint of Narcissus' brown hair is composed of yellow earth, an opaque red (probably vermilion), charcoal black and some white. Some of the paler hairs contain more red and white in the mix and appear quite pink as a result. The warm pink flesh is painted with mixtures of white, red lake and a fine opaque red (probably vermilion), a little yellow earth and charcoal black. The shadows are achieved by adding more black to the surface paint rather than by the use of dark undermodelling.

The paint of the red sleeves of the cloak worn by Narcissus includes red lake pigment of large particle size mixed with vermilion, with black added in the shadows. The cloth-of-gold robe has a pattern made up of black lines and pale yellow spots painted onto an orange-brown base colour made from mixtures of the same pigments used for the hair but in different proportions. Many translucent whitish lead soap inclusions can be seen in the yellow spots due to reaction of the yellow lead-containing pigment with the binding medium.



 ${\tt FIG.33}~NG~2673,$ photomicrograph of a leaf on the wreath worn by Narcissus.

NG 2496

Follower of Giovanni Antonio Boltraffio (conventionally called 'Pseudo-Boltraffio', active *c*.1500) *The Virgin and Child* (FIG. 34)

Probably painted c.1500.

Panel (including additions): 52.6 (left) – 52.8 (right) \times 39.8 (top) – 39.6 (bottom) cm. Size of original panel and painted surface 50.7 (left) – 50.9 (right) \times 37.8 (top) – 37.6 (bottom), thickness about 6 mm (thinned and cradled).

The painting has not undergone conservation treatment since it was bequeathed to the National Gallery in 1910.

The Virgin stands in a room with two rectangular windows, with the Christ Child in front of her, resting on a parapet. She rests her right hand on a red book, while with her left hand she offers a flower to the child, who already carries an apple. The colour scheme of her clothes is very simple: blue, green and red. This composition, which ultimately derives its general scheme from the Madonna Litta,75 is known in many variants, each of them showing slight differences. Most of them are today ascribed to an anonymous imitator of Boltraffio (thus called 'Pseudo-Boltraffio' by Wilhelm Suida), who also appears to have been responsible for the Narcissus (NG 2673). He seems to have been in the habit of creating collages of preparatory drawings made mainly by other artists. For example, the head of the Virgin is inspired by a metalpoint, wash and black chalk drawing, the *Head of a Young Woman looking Down* at the Royal Library in Windsor, which is also by a follower of Boltraffio (FIG. 35). The twisting body of the child seems inspired by Boltraffio's own Headless Body of a Child, turning to the Right in the Louvre,⁷⁶ whereas the head of the child seems to be derived from a famous cartoon, also in the Louvre.⁷⁷ The only area of the painting in which this artist seems to express his own personality is in the landscape, with its charming small details such as the tiny female figure by a river, seen through the window at the left, and the man walking through the fields in the window on the right.78

Support and preparatory layers: Wood panel,⁷⁹ single member, vertical grain. There does not appear to be a gesso ground. Instead the panel has been prepared with a thick layer of pale orange-pink oil paint consisting of lead white mixed with a little red lead and lead-tin yellow. This has caused extensive formation of large lead soap agglomerates that protrude through the surface paint in all areas.

Infrared reflectography and X-radiography: Infrared reflectography clearly shows the underdrawing in the

figures. This consists of simple, stylised outlines applied in short overlapping strokes, probably based on a cartoon or cartoons. In the fingers of the right hand of the Virgin there may be some traces of pouncing (although there are no signs of it elsewhere). In the child there seem to be two types of underdrawing, with some broader and more fluid lines apparently drawn over thinner lines more similar to those elsewhere (FIG. 36). The drawing in the Virgin's face is finer and more delicate than that in the child, but has the same character, in that it appears to be based on a cartoon. The drawing is generally followed quite carefully, but there are slight alterations to the Virgin's profile and the chin and ear of the Christ Child. The most significant change is in the fruit held by the child, which is painted over his painted hand and was not underdrawn.

The pattern of light and shade of the folds and modelling of the Virgin's blue drapery in the infrared reflectogram does not exactly match that seen at the surface, suggesting that there may be a modelled underpaint containing black pigment. No underdrawing is visible in the distant landscapes, but the greener areas are more absorbing of infrared than the distant blue hills and sky. The larger round trees, especially, appear quite dark in the infrared reflectogram due to the significant amount of black mixed with the green pigment in the paint.

Paint binding medium: Analysis of a sample from the brown parapet taken from the left edge of the painting identified the binding medium as heat-bodied walnut oil.⁸⁰

Pigments and layer structure:⁸¹ The flesh is thinly painted directly over the pale pinkish priming and there is no sign of a dark undermodelling. The pigments, mixed in varying proportions depending on the shade needed, include white, red lake, a fine opaque red (perhaps vermilion), large splinters of charcoal black and in places some yellow earth pigment. Details such as the Christ Child's toenails are outlined with thin reddish-brown lines (FIG. 37).

The only blue pigment in the painting is azurite. It was used for the Virgin's cloak, the sky, the hills and the river in the distant landscape, as well as the costume of the man visible in the landscape at the right. The small trees are painted with a base colour of verdigris mixed with white and yellow, according to the modelling, over which are darker, bluer strokes which in addition contain some azurite, and highlights containing a high proportion of lead-tin yellow (FIG. 38).



FIG. 34 Follower of Giovanni Antonio Boltraffio (conventionally called 'Pseudo-Boltraffio'), *The Virgin and Child* (NG 2496), *c*.1500. Oil on panel.



FIG. 35 Follower of Giovanni Antonio Boltraffio, *The Head* of a Young Woman looking Down, c.1500. Metalpoint and wash on pale blue prepared paper, 18.0×16.9 cm. Windsor Castle, Royal Library, inv. no. RL 12509.



FIG. 36 NG 2496, detail from the infrared reflectogram showing the Christ Child.



FIG. 37 NG 2496, photomicrograph showing the child's foot.



FIG. 38 NG 2496, photomicrograph of one of the small trees seen through the window at the right, just below the church.



FIG. 39 NG 2496, photomicrograph of one of the leaves of the plant held by the Virgin.

A cross-section from one of the larger trees shows that they were painted using the same principles as the smaller trees, but there is bluish-grey paint under the green, which contains charcoal black, azurite and lead white. The green paint also contains some charcoal (explaining the dark appearance in infrared), together with verdigris, lead white, azurite, lead-tin yellow and similar agglomerates of yellow earth seen in many of the paintings in this study. There is an even higher proportion of charcoal black mixed with verdigris in the darkest green paint layer at the surface of the sample, which forms the shadowed part of the tree.

The leaves of the plant that the Virgin holds are painted in a similar way to the trees, but the underpaint is darker and more translucent, containing distinctive large particles of verdigris (FIG. 39). Interestingly, the paint build-up and texture, as well as the manner in which the leaves are modelled, is similar to that of the leaves in the wreath on the head of Narcissus in NG 2673 (see p. 102). There are also similarities in the way that the hair and the facial features, particularly the eyes, are painted.

NG 1149

Marco d'Oggiono (documented from 1487; died 1524) *The Virgin and Child* (FIG. 40)

Probably painted *c*.1520.

Panel, 66.6 (left) – 67.0 (right) \times 52.9 (top) – 53.3 (bottom) cm, thickness 6 mm (thinned).

Other than removal of surface dirt and revarnishing, and treatment of the panel support, the painting has not undergone conservation treatment since it entered the National Gallery in 1883.

The Virgin, with the Christ Child on her knees, is seated on the ground, thus representing the type of the Madonna of Humility, surrounded by a rocky landscape. They are both contemplating a flower, which she has just picked from the plant on the left. The awkwardness of some anatomical details, such as the hands, has led scholars to doubt the attribution to Marco d'Oggiono, but throughout his career he is an artist who never really mastered the naturalistic depiction of anatomy. This can be seen, for example, in the hand in The Archinto Portrait (NG 1665), here attributed to him, which would stand as an early (1494) example of his style, reflecting Leonardo's works of his first Milanese period. This Virgin was painted considerably later, when Marco was repeating models that he had learned during his youth. One of the visual sources for this type of composition is Leonardo's Virgin and Child with Saint Anne in the Louvre, which may indeed belong to Leonardo's second Milanese period, of about 1508-13. Therefore, the technical and stylistic differences between the Archinto Portrait and this Virgin are explicable in the light of a gap of about 25 years between them. There is a pricked drawing of a woman's head at the Victoria and Albert Museum (FIG. 41), which has been reasonably connected with the head of the Virgin in NG 1149, and is indeed very similar in scale. The drawing is of slightly higher quality than the painting.⁸²

Support and preparatory layers: Wood panel,⁸³ single member, vertical grain. The panel has been prepared with a gesso ground, over which is a thin unpigmented layer that is probably glue, perhaps applied to reduce the absorbency of the gesso.⁸⁴

Underdrawing: No underdrawing is visible in the infrared reflectogram in the background, as the paint is

not penetrated due to the significant amount of black pigment it contains. The Virgin's blue drapery also appears very dark, but here this is because of the modelled purple-grey underpaint, which could be seen in a paint cross-section and also during examination of the paint surface with a stereomicroscope. Even so, underdrawing is just visible – simple lines for folds and some scribbled hatching in deep shadows. Elsewhere in the figures it is easier to see. In the Christ Child it consists of simple, stylised outlines applied in short overlapping strokes, probably based on a cartoon (FIG. 42). There are, however, quite a few lines, possibly freehand, that relate to some changes in the drawing: the ear has been moved and his left arm made fatter.

More significant changes seem to have been made to the Virgin. There is drawing for a face roughly where it is painted, but there are also lines – one of which is especially visible in the nose – which seems to be drawing for a head in a position lower down the painting (and perhaps also smaller), with the tip of the nose roughly where the upper lip now is, and lips where the dimple above the chin is in the final painted version. There is also a line across her left hand which may be a (lower) first position of the hand. The first drawn head does not appear to derive from the pricked drawing in the Victoria and Albert Museum. The second head, in the position where it was finally painted, does, however, seem to have a close relationship with the drawing, although there are no clear signs of pouncing in the infrared reflectogram.⁸⁵

Paint binding medium: The binding medium was identified as heat-bodied walnut oil in samples from the blue sky, mid-green foliage and flesh paint of the Christ Child.⁸⁶

Pigments and layer structure: A rather greenish-blue azurite pigment was used, mixed with white, for the Virgin's cloak. The cloak has an undermodelling that varies in tone from a very dark grey consisting mainly of charcoal black to a light purplish-grey made with lead white and only a little charcoal black, azurite and red lake in the highlights. Her dress is an intense red colour. It is painted with vermilion, mixed with some black in the shadows, glazed with a thin layer of madder red lake pigment.⁸⁷

The flesh in this painting does not have the ashen tone of the portrait attributed to Marco d'Oggiono early in his career, but instead has a warm orange-pink tone consisting of lead white, vermilion, red lake, yellow earth, brown and some charcoal black, but not in the quantity seen in the shadows of the flesh of the portrait.⁸⁸ Here,



 $_{\rm FIG.\,40}~$ Marco d'Oggiono, The Virgin and Child (NG 1149), probably c.1520. Oil on panel.



FIG. 41 Marco d'Oggiono (?), *Head of the Virgin*, early 16th century. Black chalk on paper, pricked for transfer, 16×14 cm. London, Victoria and Albert Museum, London, inv. no. DYCE.222.



FIG. 42 NG 1149, detail from the infrared reflectogram showing the Christ Child.

instead, the deepest tones of the modelling are made by including a higher proportion of red and yellow pigments (FIG. 43).

The sky also consists of azurite and white; it extends beneath the grey rocks as far as the right edge of the painting, indicating that there has been a significant change in the composition of the background landscape. The bank on which the Virgin sits and the foliage around her appear very dark in the infrared image, and a crosssection of a sample from one of the leaves shows a



FIG. 43 NG 1149, paint cross-section of the flesh paint from the shadow of the Virgin's arm (lead white, red lake, vermilion, yellow earth, lead white, black). The uppermost layer contains more red lake and yellow earth than the lower layer.



FIG. 44 NG 1149, paint cross-section of one of the green leaves of the foliage to the left of the Virgin; the paint contains verdigris, agglomerates of an intensely yellow earth pigment and black, as well as brown lenticular particles, one of which is visible in the middle of the lowest green layer.



FIG. 45 NG 1149, photomicrograph of one of the leaves of the foliage to the left of the Virgin; distinctive lenticular brown particles are visible embedded in the green paint.

multi-layered structure with black pigment in almost every layer (FIG. 44). It may be that the lowest layers are the brownish-mauve and dark grey paint of the bank rather than underpaint specifically for the green. The green is a mixture of verdigris, black and agglomerates of an intensely yellow earth pigment similar to that seen in the other paintings in this study. Rather unusual brown lenticular-shaped particles were also visible both with the stereomicroscope on the surface of the painting and in paint samples (FIGS 44 and 45).⁸⁹

Acknowledgements

The authors would like to thank Barbara Berrie, National Gallery of Art, Washington DC, for her helpful comments and suggestions, and Luke Syson, Curator of Italian Paintings before 1500 at the National Gallery, for reading the text and engaging in valuable discussions on its content. We are also grateful to Satoko Tanimoto and Sergei Kazarian, Imperial College, London, for the ATR–FTIR imaging analyses.

This article is available for download at: http://www.nationalgallery.org.uk/technical-bulletin/ spring_mazzotta_roy_billinge_peggie2011

Notes

- L. Keith and A. Roy, 'Giampetrino, Boltraffio and the influence of Leonardo', National Gallery Technical Bulletin, 17, 1996, pp. 4–19.
- 2 See 'Representing the Divine: The Virgin of the Rocks' in L. Syson et al., *Leonardo da Vinci: Painter at the Court of Milan*, exh. cat., National Gallery, London 2011, pp. 160–211.
- 3 See fig. 98 in Syson et al. 2011 (cited in note 2), p. 240.
- 4 See cat. 65 in Syson et al. 2011 (cited in note 2), pp. 240–41.
- 5 The exact dimensions of the panel and painted surface were recorded and the structure of the panel was examined in conjunction with the X-radiographs. Infrared reflectography was carried out using the OSIRIS camera (InGaAs sensor). A stereobinocular operating microscope at magnifications between 6x and 40x was used to examine the surface and for macro photography using a Zeiss Axiocam HrC camera. Where paint samples were taken they were examined using optical microscopy, variable pressure scanning electron microscopy with a large area (80 mm²) energy-dispersive X-ray detector, FTIR microscopy (transmission mode using a diamond compression cell), gas chromatography–mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC).
- 6 R. Bruzzone and M.C. Galassi, 'Wood species in Italian panel paintings of the fifteenth and sixteenth centuries; historical investigation and microscopical wood identification', in *Studying Old Master Paintings, Technology and Practice, The National Gallery Technical Bulletin 30th Anniversary Conference Postprints, M. Spring (ed.), with H. Howard, J. Kirby, J. Padfield, D. Peggie, A. Roy and A. Stephenson-Wright, Archetype Publications in association with the National Gallery, London 2011, pp. 253–9. Other paintings in the National Gallery that are on a walnut panel are mentioned in Keith and Roy 1996 (cited in note 1).*
- 7 Bruzzone and Galassi 2011 (cited in note 6), provide a recent summary of paintings of this period where the support has been found to be walnut and consider this from a statistical point of view in relation to the types of wood found as painting supports over Italy as a whole. The use of walnut in relation to Leonardo and Leonardeschi paintings in Milan in this period is discussed in L. Keith, 'The Pursuit of Perfection: Leonardo's Painting Technique', in Syson et al. 2011 (cited in note 2), pp. 54–77. See also J. Marette, Connaissance des primitives par l'étude du bois du XIIe au XVIe siècle, Paris 1961.
- 8 Bruzzone and Galassi 2011 (cited in note 6).
- 9 Bruzzone and Galassi 2011 (cited in note 6) discuss the use of softwoods as a support in Italian paintings of this period, particularly among Northern Italian painters. They also mention some examples of the use of pine by Tuscan and Roman painters. Klein and Bauch also report identification of softwood panels in Italian paintings, including cypress, fir and spruce. See P. Klein and

J. Bauch, 'Analyses of wood from Italian paintings with special reference to Raphael', *The Princeton Raphael Symposium, Science in the Service of Art History,* J. Shearman and M.B. Hall (eds), Princeton, New Jersey, 1990, pp. 85–92. For identification of cypress as a support for paintings from the Pollaiuolo workshop see also A. Cecchi, 'The Conservation of Antonio and Piero del Pollaiuolo's Altar-Piece for the Cardinal of Portugal's Chapel', *The Burlington Magazine,* CXLI, 1154, May 1999, pp. 81–8, and an appendix to this article, S. Freschi and N. MacGregor, 'Conservation report', pp. 86–8.

- 10 See, for example, Colloquio mistico di san Pietro con le sante Agnese, Caterina e Cecilia, a gilded and polychromed relief by Giovanni Pietro and Giovanni Ambrogio De Donati in Opava (Silesian Museum), Czech Republic. This is illustrated in Giovanni Pietro e Giovanni Ambrogio De Donati, scultori e imprenditori del legno nella Lombardia del Rinascimento, Rassegna di Studi e di Notizie, vol. XXXII, Castello Sforzesco, Milan 2009, p. 165.
- 11 See M. Spring and R. Grout, "The blackening of vermilion: an analytical study of the process in paintings', *National Gallery Technical Bulletin*, 23, 2002, pp. 50–61.
- 12 J. Dunkerton and M. Spring, "The development of painting on coloured surfaces in sixteenth-century Italy', in *Painting Techniques: History, Materials and Studio Practice, Contributions to the Dublin IIC Congress, 7–11 September 1998, A. Roy and P. Smith (eds), London* 1998, pp. 120–30.
- 13 The Pollaiuolo brothers used a panel prepared in this way, with only a lead white priming and no gesso, for their altarpiece for the Cardinal of Portugal's chapel. See Cecchi 1999 (cited in note 9). Two other examples are known of sixteenth-century Italian paintings that have a lead white priming (with no gesso): Paris Bordone's *Pair of Lovers* (NG 637), 1535–50, and Federico Barocci's *Madonna of the Cat ('La Madonna del Gatto')* (NG 29), about 1575, but these are both much later in date and are on canvas rather than panel. See Dunkerton and Spring 1998 (cited in note 12). One Netherlandish painting in the National Gallery has been found to have this type of preparation on a wooden panel of oak; the Netherlandish School Virgin and Child with Saints and Angels in a Garden (NG 1085), about 1500.
- 14 Giovanni Battista Armenini states the following in the 1586 edition of his treatise: 'But among the tinted primings, one that is held to be good is that which tends towards the colour of very light flesh and has a certain brilliant quality due to the fact that there is more varnish in it than in the others.' See E.J. Olszewski (ed. and trans.), *Giovanni Battista Armenini on the True Precepts of the Art of Painting*, New York 1977, p. 192. These primings of lead white, red lead and lead-tin yellow seem to conform to this description.
- 15 A priming of very similar composition has also been found on Boltraffio's Virgin and Child in the Museum of Fine Arts, Budapest. Cross-section analysis was carried out by Alan Phenix, J. Paul Getty Museum, while the Budapest painting was undergoing conservation treatment at the Getty Museum. We are very grateful to him for making his report available to us. The priming on the Budapest painting contains a higher proportion of red lead, although this is ascribed by Alan Phenix to remineralisation following lead soap formation. A slightly later example of a priming of this type of composition (but without any verdigris), applied on gesso, is Giovanni Girolamo Savoldo's *Saint Jerome* (NG 3092), perhaps 1527, although this is on canvas and not on panel; see Dunkerton and Spring 1998 (cited in note 12).
- 16 All three of these pigments are known often to react with fatty acids in the oil binding medium to form lead carboxylates, or lead soaps, which agglomerate and migrate to form large pustules. See C. Higgitt, M. Spring and D. Saunders, 'Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow', *National Gallery Technical Bulletin*, 24, 2003, pp. 75–95; J.J. Boon, J. van der Weerd, K. Keune, P. Noble and J. Wadum, 'Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings', *ICOM-CC 13th Triennial Meeting, Rio de Janeiro*, London 2002, pp. 401–6; J. van der Weerd, J.J. Boon, M. Geldof, R.M.A. Heeren and P. Noble, 'Chemical Changes in Old Master Paintings: Dissolution,

Metal Soap Formation and Remineralisation Processes in Lead Pigmented Paint Layers of 17th Century Paintings', Zeitschrift für Kunsttechnologie und Konservierung, 2002, 16, pp. 36-51. Lead soaps are always found in oil paint containing lead-tin yellow, but lead-tin yellow itself $(Pb_{3}SnO_{4})$ is less reactive than red lead $(Pb_{3}O_{4})$ and lead white, and it is probably PbO that is present in the pigment from incomplete conversion during preparation that is reacting with the oil. Red lead can also contain PbO, depending on how long it was roasted during preparation. See D. Saunders, M. Spring and C. Higgitt, 'Colour change in red lead containing paint films', ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, London 2002, pp. 455-63. Lead white is often cited as the cause of lead soap agglomerates, but although it does certainly react with the oil, it is to a lesser extent than these other lead pigments: here, for example, there are no lead soap agglomerates in the priming of NG 1665, which contains only lead white.

- 17 Heat-bodying would also have improved the drying properties, which would have been an advantage for the relatively slow-drying walnut oil. Despite this, several of the paintings in this study suffer from drying defects, probably mainly due to unsound technique as explained below, but perhaps also exacerbated by the use of walnut oil.
- 18 Leonardo, Boltraffio and Marco d'Oggiono are not the only artists to suffer from these paint defects – see the discussion in the article by Jill Dunkerton in this *Bulletin*, pp. 4–31, and also Keith 2011 (cited in note 7).
- 19 J. Dunkerton in this *Bulletin* discusses the possible causes of wrinkling and other paint defects in paintings by Leonardo and other artists. See also Keith 2011 (cited in note 7).
- 20 Designs were indeed also sometimes transferred from paper to paper during the design process. For cartoon use see C. Bambach, *Drawing and Painting in the Italian Renaissance Workshop; Theory and Practice, 1300–1600,* Cambridge 1999.
- 21 See J. Dunkerton and L. Syson, 'In Search of Verrocchio the Painter: The Cleaning and Examination of *The Virgin and Child with Two Angels'*, *National Gallery Technical Bulletin*, 31, 2010, pp. 4–41, especially pp. 21–5. See also J. Dunkerton in this *Bulletin*, p. 17.
- 22 For a complete discussion on this point see Keith 2011 (cited in note 7).
- 23 For general bibliography see M. Davies, National Gallery Catalogues. The Earlier Italian Schools, 2nd edn (rev.), London 1961 (1st edn 1951), p. 369 (which provides a general bibliography up to 1961); G. Romano, 'La Pala Sforzesca', in Il Maestro della Pala Sforzesca: Quaderni di Brera 4, G. Romano, M.T. Binaghi Olivari and D. Collura (eds), Florence 1978, pp. 7–23; esp. p. 13, fig. 3 and pp. 15–16, note 1; P.C. Marani, 'Master of the Pala Sforzesca: Milan, active c.1490–1520', in The Legacy of Leonardo: Painters in Lombardy 1490–1530, Milan 1998, pp. 179–98, esp. 186–7; C. Baker and T. Henry, The National Gallery Complete Illustrated Catalogue: With a supplement of new acquisitions and loans 1995–2000, London 2001, p. 34.
- 24 Strips of wood have been attached to all the edges, so it was not possible to make a firm identification of the wood of the original panel.
- 25 FTIR analysis confirmed that the gesso consists of gypsum, the dihydrate form of calcium sulphate.
- 26 SEM-EDX mapping of the cross-sections showed that this pale orange layer contains aluminium silicon and iron, and can therefore be identified as 'bole', a clay-like earth pigment.
- 27 When analysed using FTIR spectroscopy, absorbance bands consistent with the use of a proteinaceous binder were observed in both samples. This was confirmed by GC–MS analysis, which indicated a very low proportion of di-acid methyl esters, suggesting the absence of an oil binding medium. In addition, the proportions of the saturated fatty acid methyl esters palmitate and stearate were in the range expected for egg tempera: green of sleeve [A/P 0.2; P/S 2.2], purple robe [A/P 0.2; P/S 2.4].
- 28 The gum resins from ammoniacum, asafoetida and galbanum, produced by Dorema and Ferula (Umbelliferae, now Apiaceae) have a long tradition of use and would have been available in fifteenth-century Italy. They are collected from stems and roots and are predominantly esters of aromatic phenols (see J.H. Langenheim,

Plant Resins: Chemistry, evolution, ecology and ethnobotany, Portland, Oregon 2003, pp. 412–17). The FTIR spectra obtained from such resins are therefore quite characteristic and distinct from those obtained from other organic materials that might be found in mordants and that are mentioned in documentary sources, such as oils, proteins or polysaccharides. However, it is extremely difficult to distinguish between these closely related gum resins by FTIR spectroscopy alone, so the more general term 'gum resin' has been used here. The analysis was carried out on the cross-section by ATR-FTIR imaging by Satoko Tanimoto, Imperial College, London. For details of this analytical technique see M. Spring, C. Ricci, D. Peggie and S. Kazarian, 'ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London', Analytical and Bioanalytical Chemistry, 392 (1-2), 2008, pp. 37-45. Other examples of the use of gum ammoniac as a mordant are cited in C. Higgitt, A. Reeve, M. Spring and L. Syson, 'Working with Perugino: the technique of an Annunciation attributed to Giannicola di Paolo', National Gallery Technical Bulletin, 27, 2006, pp. 96–110, esp. note 12. EDX analysis confirmed that the mordant was mainly organic in nature, but that some vermilion and lead white was also included. There are, in addition, some copper-containing particles, although they do not appear green and so it is not clear exactly what material is present. Fibrous particles are also visible in the cross-section which under normal light appear a warm brownish yellow, but are surprisingly highly scattering in the backscattered image in the SEM. Some lead was detected more generally in the mordant.

- 29 The green pigment was analysed by SEM-EDX on a cross-section. In addition to particles that contain only Cu. C and O (and which are therefore probably the basic copper carbonate malachite), others contain a small amount of zinc in addition to copper, but not enough to be able to characterise the mineral as rosasite or some other copper zinc carbonate. Other particles contain a little chloride, again not enough to suggest a copper chloride mineral, but instead a copper carbonate with a small amount of chloride included. Some other particles also contain small amounts of antimony or arsenic. Copper mineral pigments containing these types of associated minerals have been found in other fifteenthcentury paintings; see G. Heydenreich, M. Spring, M. Stillhammerova and C.M. Pina, 'Malachite pigment of spherical particle form', ICOM Committee for Conservation 14th Triennial Meeting, The Hague, Preprints, Vol. 1, 2005, pp. 480-9.
- 30 Botticelli is known to have used a mineral copper green pigment when working in egg tempera and verdigris in paintings where he used an oil medium. See C. Higgitt and R. White, 'Analyses of Paint Media: New studies of Italian Paintings of the Fifteenth and Sixteenth Centuries', *National Gallery Technical Bulletin*, 26, 2005, pp. 88–104.
- 31 The phenomenon seen here, where only the mid-tone of the red drapery (in which vermilion was used alone) has suffered from discoloration, is common. The degradation involves reaction of the mercury sulphide pigment with chloride, most likely from environmental pollutants and, in particular, dirt that has settled on the surface of the painting, to form, among other compounds, a white mercury chloride degradation product as well as a black product which is as yet unidentified. The shadows are protected because the vermilion is covered with a glaze containing red lake. The highlights here may be painted instead with red lead, or perhaps a mixture of red lead and vermilion, which has also been observed to protect the vermilion. See Spring and Grout 2002 (cited in note 11).
- 32 For other examples see Spring and Grout 2002 (cited in note 11).
- 33 HPLC analysis identified kermesic acid as the principal constituent by its retention time and UV-visible spectrum.
- 34 See J. Kirby, M. Spring and C. Higgitt, 'Insight into the Technology of Red Lake Pigment Manufacture through Study of the Dyestuff Substrate', *National Gallery Technical Bulletin*, 26, 2005, pp. 71–87. Ellagic acid is sometimes detected in lake pigments by HPLC, and it is thought likely that it indicates that the dyestuff was extracted from silk fibres, as it was used to weight silk. None was detected in this case. Although this does not exclude the possibility that the fibres are silk, it may be that they are instead wool. It is more

common to find madder lake pigments where the dyestuff has been extracted from wool fibres, but kermes was sometimes used to dye wool if it was of the highest quality. Often an indicator of wool is a high sulphur content in the pigment detected by SEM– EDX (as was confirmed here) and detection of protein by FTIR spectroscopy.

- 35 For general bibliography and information referred to in this introduction see Davies 1961 (cited in note 23) pp. 368–89; Marani 1998 (cited in note 23), p. 191, fig. 69, p. 183; Baker and Henry 2001 (cited in note 23), p. 435.
- 36 Davies 1961 (cited in note 23), pp. 368–9, states that the painting is on a walnut panel, identified as such by the Forest Products Research Laboratory. However, the recent re-examination of this painting indicated that the sample was taken from the secondary panel. It has not been possible to identify the wood of the original panel. The X-radiograph shows that there are horizontal splits in the original panel which have been mended with nails that are modern in character. These are now hidden by the secondary panel, which must therefore be a later addition. Their location in the original panel was confirmed by a CAT scan. See research.ng-london.org.uk/wiki/index.php/CAT_scanning
- 37 GC–MS analysis of the methylated sample found a large proportion of di-acid methyl esters, clearly indicating the use of an oil binding medium. The ratio of the saturated fatty-acid methyl esters palmitate and stearate, and the relative proportion of the di-acids azelate and suberate, indicated that the binder was a heat-bodied walnut oil: grey architecture [A/P 1.2; P/S 3.4; A/Sub 2.9].
- 38 Since the painting is small, only two samples were taken from the edge for pigment and layer structure examination and most of the description is based on stereomicroscopic examination, hindered to some extent by the heavily discoloured varnish on the surface of the painting, as well as dirt and repaints.
- 39 EDX analysis confirmed that the paint contains mainly vermilion, with some red lead (and large lead soap agglomerates), a little red earth and black. The black pigment is rich in sulphur (in addition to carbon) suggesting coal black.
- 40 For a comprehensive discussion see cat. 19 in Syson et al. 2011 (cited in note 2), pp. 130–33.
- 41 The difference in the black paint of the horizontal strokes that seem to indicate an 'A' and an 'F' is evident under the stereomicroscope and also in the infrared reflectogram. They are abraded, and therefore old, but not as abraded as the strokes of the 'M' and 'R' immediately around them, and they have not disrupted the wet paint of the strokes that they that they cross (unlike the '4's of the date), perhaps suggesting that the 'M' and the 'R' were already dry when the horizontal strokes making the 'A' and 'F' were painted. Although they could simply be overpaint reinforcing the remnants of original horizontal strokes (rather than an attempt to introduce the letters 'A' and 'F' into the monogram), it seems strange that only these two crucial strokes are reinforced rather than any of the other letters. The monogram might relate to the artist but could also indicate the name of the sitter.
- 42 Davies 1961 (cited in note 23), pp. 448–9 (as by Ambrogio de Predis; with provenance); S. Farrow, 'An examination of the *Archinto Portrait* in the National Gallery of London', *Raccolta Vinciana*, XXIX, 2001, pp. 65–102 (as by the 'Master of the Archinto Portrait'); Baker and Henry 2001 (cited in note 23), p. 344 (as 'Italian, Milanese'); A. Mazzotta in Syson et al. 2011 (cited in note 2), pp. 130–33 (as by Marco d'Oggiono; with previous bibliography and a full discussion of the interpretation of the monogram).
- 43 A thin transverse section of the end grain of the panel showed microscopic features indicating that the wood is a species of walnut. See summary report by Ashok Roy in the Scientific Department file, dated 5 July 1985.
- 44 J. Mills and R. White, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 9, 1985, pp. 70–2. The two samples were analysed by gas chromatography (GC). In both cases the ratios of the saturated fatty-acid methyl esters, palmitate and stearate, indicated the use of walnut oil. Due to the relatively early date of these analyses, they do not give information on the proportions of the di-acids, so the extent of heat-bodying cannot be determined: blue doublet [P/S 3.0], 'green' mantle [P/S 3.3].

- 45 EDX analysis of the cross-section of the flesh paint identified lead white, vermilion, yellow earth, red lake on an alumina substrate and a small amount of lead-tin yellow. Black is also present.
- 46 EDX analysis confirmed that the lower layer in the cross-section contains azurite, while the upper layer contains ultramarine. In addition to blue particles of lazurite, and a small amount of pale blue sodalite, the natural ultramarine pigment includes numerous colourless associated minerals. The combinations of elements detected suggest these include a high proportion of a potassium aluminium silicate such as orthoclase or microcline (Si, Al, K), and smaller proportions of biotite or phlogopite (Si, Mg, Al, K, Ti). The appearance of the ultramarine layer in the backscattered image and also in EDX maps confirmed that the lighter appearance of the upper part is due to blanching and not to a greater lead white content.
- 47 For a discussion of preparation of red lake pigments from textile shearings see Kirby et al. 2005 (cited in note 34).
- 48 See cat. 8 in Syson et al. 2011 (cited in note 2), pp. 106–7.
- 49 See cat. 10 in Syson et al. 2011 (cited in note 2), pp. 110–13.
- 50 Davies 1961 (cited in note 23), pp. 449–50 (with provenance); Baker and Henry 2001 (cited in note 23), p. 548.
- 51 Davies 1961 (cited in note 23), p. 449, letter from B.J. Rendle, Forest Products Research Laboratory.
- 52 See note 15 for references to other examples of primings with this composition.
- 53 There is a drawing attributed to Ambrogio de Predis of a similar male profile portrait, with mid-length hair and a hat, in the British Museum (inv. no. 1895,0915.614). See British Museum collection database online, http://www.britishmuseum.org/research/search_ the_collection_database.aspx, for an image of the drawing.
- 54 See cat. 53 in Syson et al. 2011 (cited in note 2), pp. 210–11.
- 55 See cat. 52 in Syson et al. 2011 (cited in note 2), pp. 208–9.
- 56 See cat. 67 in Syson et al. 2011 (cited in note 2), pp. 244–5.
- 57 Davies 1961 (cited in note 23), pp. 88–9; Keith and Roy 1996 (cited in note 1), pp. 14–16; M.T. Fiorio, *Giovanni Antonio Boltraffio: Un pittore milanese nel lume di Leonardo*, Milan–Rome 2000, pp. 105–6, n. A13 (with previous bibliography); Baker and Henry 2001 (cited in note 23), p. 45.
- 58 Walnut was identified from microscopic examination of a transverse thin section from the end grain of the wood. Keith and Roy 1996 (cited in note 1).
- 59 Gypsum, $CaSO_4 \cdot 2H_2O$, was identified by FTIR microscopy, and the presence of amide bands at 1547 cm⁻¹ and 1660 cm⁻¹ suggests a proteinaceous binding medium such as glue.
- 60 R. White and J. Pilc, 'Analyses of Paint Media', National Gallery Technical Bulletin, 17, 1996, pp. 91–103.
- 61 The earlier analyses by FTIR microscopy in transmission mode in a diamond compression cell and GC–MS suggested that the dark undermodelling in this painting was executed in egg tempera with a little oil and the paint layers executed mainly in walnut oil (White and Pilc 1996, cited in note 60). However, recent studies using ATR–FTIR on cross-sections (performed at Imperial College, London by Satoko Tanimoto) found no evidence for proteinaceous material within these layers.
- 62 Keith and Roy 1996 (cited in note 1).
- The production, chemistry and analysis of the copper acetates 63 are described in detail in D.A. Scott, Copper and Bronze in Art: Corrosion, colorants, conservation, Getty Publications, Los Angeles 2002, pp. 270-316. See also M. San Andrés, J.M. de la Roja, V.G. Baonza and N. Sancho, 'Verdigris pigment: a mixture of compounds. Input from Raman spectroscopy', Journal of Raman Spectroscopy, 41, 2010, pp. 1178-1186. In their detailed spectroscopic investigation of different verdigris pigments they found that the Cu(CH₃COO)₂/Cu(OH)₂ ratio had a strong influence on the colour of the pigment, with the greenish colour becoming deeper as the Cu(CH₂COO), content increased, regardless of the water content. The neutral copper (II) acetate monohydrate, which has a distinctive blue-green colour, was also studied. ATR-FTIR imaging was carried out on a cross-section of the green curtain in NG 728 by Satoko Tanimoto at Imperial College, London. The green pigment could be identified from the FTIR spectra as verdigris. It seems to be a variety with a more opaque and cooler

(more blue-green) appearance than is generally seen. Determining the exact type of verdigris present, degree of basicity and hydration is not straightforward, however, and will require further investigation.

- 64 See Davies 1961 (cited in note 23), pp. 89–90; Fiorio 2000 (cited in note 57), pp. 122–3, n. A19 (with previous bibliography); Baker and Henry 2001 (cited in note 23), p. 46.
- 65 See for example cat. 18 in Syson et al. 2011 (cited in note 2), pp. 128–9.
- 66 Walnut was identified from a transverse thin section of sample taken from the end grain. Very thin fillets of wood that are slightly lighter in colour than the original panel are attached to the top and bottom, but care was taken to ensure that the sample was from the original wood.
- 67 Two samples were analysed from the background at the right edge of the painting, approximately level with the bottom of the hat. The amount and proportion of azelate and suberate, the di-acid methyl esters, clearly indicate the use of a heat-bodied oil binding medium in both samples. However, the ratios of palmitate to stearate, the saturated fatty-acid methyl esters generally used to gain an indication of the type of oil, are more ambiguous, being on the low side for walnut oil but too high for linseed oil alone. Although the majority of surface material was mechanically removed before sampling, the thick layers of varnish, possibly containing a little linseed oil, may have contributed to the results. On balance, the binding medium of the paint is therefore likely to be walnut oil; Background sample 1 [A/P 1.3; P/S 2.0; A/Sub 2.5], Background sample 2 [A/P 1.1; P/S 2.2; A/Sub 2.7].
- 68 Davies 1961 (cited in note 23), pp. 91–2; Fiorio 2000 (cited in note 57), pp. 166–7, n. C4 (with previous bibliography); Baker and Henry 2001 (cited in note 23), p. 375.
- 69 See cat. 50 in Syson et al. 2011 (cited in note 2), pp. 204–5.
- 70 No samples were taken for examination of the layer structure and so the method of preparation of the panel for painting is not known.
- 71 A thin transverse section of the end grain of the panel showed microscopic features indicating that the wood is a species of walnut. See notes in the National Gallery Scientific Department file by Joyce Plesters, dated 13 January 1983.
- 72 The sample was obtained from the top edge of the painting and analysed by GC–MS. The small uncertainty over the type of oil arises from the presence of a trace amount of beeswax. Although every effort was made to obtain a 'clean' sample, this seems to indicate contamination from a surface coating.
- 73 The information in this section is based mainly on examination of the surface of the painting with a stereomicroscope, as no samples were taken for pigment analysis. Some of the results from FTIR analysis of samples taken for organic analysis are included here.
- 74 The presence of both copper acetate (verdigris) and copper soap (produced by reaction of the oil binding medium with the pigment) was confirmed by FTIR microscopy in a sample from the green landscape at the left edge.
- 75 See cat. 57 in Syson et al. 2011 (cited in note 2), pp. 222–5.
- $76 \quad \text{See cat. 51 in Syson et al. 2011 (cited in note 2), pp. 206-7.}$
- 77 See cat. 41 in Syson et al. 2011 (cited in note 2), pp. 186–7.
- 78 This introduction is based on recent considerations during the research carried out for this study, combined with information from the literature, including Davies 1961 (cited in note 23), pp. 90–1; Fiorio 2000 (cited in note 57), pp. 184–5, n. D10 (with previous bibliography); Baker and Henry 2001 (cited in note 23), p. 46.
- 79 There are strips of wood attached to the panel around all the edges, so it was not possible to identify the wood of the original panel. However, in the X-radiograph the grain shows as a dense pattern of flecks which is typical of walnut.
- 80 The paint was analysed by GC–MS. The ratios of palmitate to stearate, the saturated fatty-acid methyl esters, clearly indicate the use of a walnut oil binding medium, while the amount and proportion of azelate and suberate, the di-acid methyl esters, suggest the oil is heat-bodied: brown of parapet [A/P 1.7; P/S 3.1; A/Sub 2.6].
- 81 The painting has a rather dirty and discoloured varnish. It has also suffered from flaking of the paint, so has a significant amount of retouching associated with this. Most of the information in this

section comes from stereomicroscope examination as only a limited number of samples were taken.

- 82 For general bibliography see Davies 1961 (cited in note 23), pp. 342–3; D. Sedini, *Marco d'Oggiono: tradizione e rinnovamento in Lombardia tra Quattrocento e Cinquecento*, Milan–Rome 1989, pp. 201–2, n. 105 (with previous bibliography); Baker and Henry 2001 (cited in note 23), p. 410.
- 83 The back of the panel is covered with polyester sailcloth, so it was not possible to identify the type of wood.
- 84 The cross-section was analysed by ATR–FTIR microspectroscopy by Satoko Tanimoto at Imperial College, London. Absorbance bands that can be assigned to amide groups indicated that the thin layer on top of the gesso ground contains a proteinaceous material, which in this context is most likely to be glue of some type.
- 85 An overlay was made of the Victoria and Albert Museum drawing, the infrared reflectogram and the painting. The lines of the drawing match well with those of the painted head, although it is more difficult to say whether they also coincide with the underdrawing for the head in the second position, as it is not easy to see it in the infrared reflectogram. Likewise, although dark spots that might be pouncing can be seen in some areas in the infrared reflectogram, similar dark spots are certainly connected with blister laying, and so it is not possible to determine whether or not pouncing is present. However, the Virgin's head was extended up and to the left after the sky had been painted (leaving a reserve for the head), and the underdrawn line relating to the upper contour of the head before this change matches that in the Victoria and Albert Museum drawing.
- 86 GC–MS analysis of the methylated samples found a large proportion of di-acid methyl esters, clearly indicating the use of an oil binding medium. The ratio of the saturated fatty-acid methyl esters palmitate and stearate and the relative proportion of the di-acids azelate and suberate indicated that the binder was a heat-bodied walnut oil in all cases: blue sky [A/P 1.8; P/S 3.0; A/Sub 3.1], mid-green foliage [A/P 0.9; P/S 3.1; A/Sub 4.0], flesh [A/P 1.5; P/S 2.2; A/Sub 2.9].
- 87 HPLC analysis of the red lake pigment indicated that it contains dyestuff extracted from madder root. However, although at least some alizarin would be expected to be present, only pseudopurpurin and purpurin were detected. It is very unusual to find so little trace of any other components in a lake pigment derived from a natural dyestuff, with the only other comparable sample being from The Virgin and Child with Saints Jerome and Nicholas of Tolentino by Lorenzo Lotto (NG 2281), where the red lake also contains pseudopurpurin as the principal component. The absence of alizarin or any of the other minor components usually associated with lake pigments prepared with madder would usually suggest a nineteenth-century Rose Madder. However, the area from which the sample was taken was inspected carefully with a stereomicroscope and did not seem to be retouched or overpainted. A second sample taken from a different area confirmed the result.

EDX analysis of the cross-section from the shadow of the Virgin's 88 arm confirmed the presence of lead white, red lake (on an alumina substrate), vermilion, yellow earth and black. In addition there is a translucent inhomogeneous brown earth pigment containing elements consistent with an aluminosilicate (Al, Si, K, and a small amount of Ti and Mg), as well as Fe and an exceptionally large amount of Mn (relative to Fe), concentrated in darker inclusions within individual brown particles. This seems to be a brown umber type pigment unusually rich in Mn. Interestingly, what appears to be a similar pigment (although detected by the non-invasive method of XRF and as a result interpreted as separate umber and black manganese dioxide pigments) has been found in later paintings by Leonardo. See L. de Viguerie, P. Walter, E. Laval, B. Mottin and V. Solé, 'Revealing the sfumato Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy', Angewandte Chemie International Edition, 49, 2010, pp. 6125-8, doi: 10.1002/ anie.201001116 and V.A. Solé, P. Walter, L. de Viguerie, 'Analyse de tableaux de Léonard de Vinci par spectrométrie de fluorescence des rayons X', Techniques de L'ingénieur, 3, 2011, Référence RE200.

89 Some of these particles were identified as silicates by EDX analysis of a cross-section but others seem to be organic in nature.