

Raphael's Early Work in the National Gallery: Paintings before Rome

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THIS ARTICLE IS INTENDED to complement the National Gallery exhibition catalogue *Raphael: From Urbino to Rome* (October 2004 – January 2005), and in particular the introductory essay by Tom Henry and Carol Plazzotta dealing with Raphael's early artistic development.¹ The aim is to record here, in some detail, the results of recent technical investigations of the early paintings by Raphael in the National Gallery, carried out in the course of cataloguing them for the exhibition. Previous observations, analyses and campaigns of technical photography have been supplemented by new research, including detailed physical examinations, and investigation with infrared reflectography, stereomicroscopy and (where possible) chemical analysis of paint samples. Although a certain amount of technical material on the National Gallery's distinguished group of early paintings by Raphael has been published in the past (including important studies in earlier issues of the *Technical Bulletin*),² there is no single source which draws these accounts together. The first part of this article therefore represents an overview of the young artist's methods and techniques; the second part is a more detailed catalogue of technical data.

Seven paintings from Raphael's pre-Roman period are included in this study: two altarpieces, *The Crucified Christ with the Virgin Mary, Saints and Angels* (*The Mond Crucifixion*) (NG 3943), of c.1502–3 (PLATE 11), and *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari* (*The Ansidei Madonna*) (NG 1171), dated 1505 (PLATE 22); two predella panels, *The Procession to Calvary* (NG 2919, PLATE 19), which is the central scene of the predella of the *Colonna Altarpiece*, of c.1504–5,³ and *Saint John the Baptist Preaching* (NG 6480), the left-hand scene of the predella of the *Ansidei Madonna*, of 1505 (PLATE 31); the tiny jewel-like *Allegory* ('*Vision of a Knight*') (NG 213) of c.1504 (PLATE 13), a small devotional panel, *The Madonna of the Pinks* (*Madonna dei Garofani*) (NG 6596) of c.1506–7 (PLATE 34) and the medium-size *Saint Catherine of Alexandria* (NG 168, c.1507),

Painted shortly before Raphael's departure for Rome in 1508 (PLATE 41).⁴

Technical analyses of Raphael's paintings have been published sporadically since the 1970s, when scientific activity gathered pace in advance of the great series of exhibitions in Europe and America held in 1983 to mark the fifth centenary of Raphael's birth, and many paintings were newly researched and restored. The most important and wide-ranging survey of technical material to emerge was the volume containing the proceedings of the international Raphael Symposium held at Princeton in the centenary year, which was not, however, published until 1990.⁵ Among the sixteen scholarly contributions was a significant survey of Raphael's paintings in the National Gallery by Joyce Plesters, which remains an important source of information today.⁶ However, Plesters was unable to include much material on the *Procession to Calvary*, the *Ansidei Madonna* or *Saint Catherine of Alexandria* because these pictures had not then been sampled and analysed, while the *Madonna of the Pinks* is a recent acquisition. These gaps in the technical narrative have now been filled by the results of our more recent examinations, assisted by improved analytical techniques.

General features of Raphael's early technique

All the works considered here are on wood panel. Where the wood has been sampled, the panels have been identified as poplar (with one exception, those which have not been sampled appear also to be on poplar). There are rare cases of other wood types used by Raphael, for example the *Madonna of the Pinks*, which appears to be on a denser fruit-wood such as cherry,⁷ a support that has been identified also for the large late altarpiece, *The Transfiguration* (Rome, Vatican Museums), left unfinished at Raphael's death in 1520.⁸ The portraits of Agnolo and Maddalena Doni (Florence, Galleria Palatina) are painted on panels identified as limewood, an unusual wood support in Italian painting.⁹ The support of *The Marriage of the Virgin* (Milan,

Brera) is also unusual in that it is a late example of a poplar panel covered with canvas, probably applied to reinforce the eight horizontally planked members.¹⁰ The very early double-sided *gonfalone* (processional banner) representing *The Trinity with Saints Sebastian and Roch* and *The Creation of Eve* (Città di Castello, Pinacoteca Comunale, c.1499) is exceptional among Raphael's pre-Roman works in being on canvas, but the choice of the more light-weight support for this work can be explained by its function as a processional banner to be carried at religious festivals.¹¹ Even in his later career, Raphael rarely chose canvas as a support, the principal exceptions being the *Sistine Madonna* (Dresden), perhaps painted on canvas for ease of transport, and two portraits, *Baldassare Castiglione* of 1514–15 now in Paris (Louvre) and *Portrait of a Lady* ('*La Velata*') in Florence (Palazzo Pitti).¹² Raphael's father, Giovanni Santi, however, produced works on canvas, and they were a common product of the Perugino workshop with which Raphael was familiar in the form of *gonfaloni*, some of which were of considerable size, for example the *Apparition of the Virgin and Child to Saints Bernard and Francis* in Perugia (Galleria Nazionale dell'Umbria, 1496, 218 × 141 cm).¹³

The National Gallery panels are all prepared with layers of gesso, composed of gypsum (calcium sulphate dihydrate), bound in animal glue. In common with many pictures of the period, the gesso had evidently been stirred strongly or overheated during its preparation, as on all of the paintings the dried layer is full of air bubbles. These are visible in the exposed gesso at the edges of the *Ansdei Madonna*, and also register in X-ray images of the other paintings as small randomly scattered white dots (the result of these surface bubbles having become filled with material from the X-ray dense *imprimitura* applied on top, FIG. 1). The gesso was then covered with a very pale *imprimitura* consisting of a thin, off-white oil-bound layer containing lead white, small amounts of lead-tin yellow (less than c.5%) and varying amounts of a colourless material with the particle characteristics and constitution of a manufactured glass (see individual entries below and PLATES 24–30). This type of *imprimitura* has been detected on all of the Raphael panels in this group except the *Vision of a Knight*, which could not be sampled due to its small scale and excellent condition, although the brushstrokes visible in raking light running across forms beneath the surface of the paint are an indication that there is an *imprimitura* here too. It is very probable that the



FIG. 1 Detail from the X-ray of *Saint John the Baptist Preaching* (NG 6480) showing air bubbles in the gesso.

glass was included as a siccative, in spite of the good drying properties of lead white and lead-tin yellow. Perhaps the requirement was for a very rapidly drying *imprimitura* that would not interact with the oil paint to be applied on top. That the *imprimitura* contains lead-tin yellow as well as lead white has been appreciated only relatively recently; in earlier technical studies it has been overlooked, since it is difficult to see in cross-sections under the microscope and requires instrumental analysis for confirmation of its presence. More recent studies have found that an *imprimitura* of this composition is common in paintings of the period from all over Italy, and there are cases of its use beyond Italy.¹⁴ Examples have been reported on several other paintings by Raphael, including paintings from later in his career when he was working in Rome.¹⁵

Raphael was a prolific draughtsman and he characteristically prepared his painted compositions in advance on paper, following traditional central Italian practice. His drawings include rapid preliminary sketches, studies of individual figures and figure groups, as well as smaller details such as heads, limbs, hands, feet, drapery, architecture and landscape, and – as the design began to cohere – more finished compositional drawings.¹⁶ Frequently Raphael would make a cartoon of the finalised design by pricking the outlines of the composition in order to transfer it to the panel by pouncing, a method he favoured in this early period for small and medium-sized pictures.¹⁷ He also used the method of squaring, and several of his compositional drawings are covered with a grid for the purpose of scaling up the design to the prepared support for painting.¹⁸ On some panels, such as the *Madonna of the Pinks*, the drawing revealed by infrared reflectography is freehand in character (see FIG. 6), although in such cases it is likely that Raphael would have been

working from a drawing or model, or perhaps over a design transferred from a cartoon.

In order to anchor his design, Raphael frequently began by marking out the prepared panel with ruled vertical and horizontal lines, a practice he also followed when making drawings. In four of the smaller paintings in our group a vertical and sometimes also a horizontal axis is present. In the *Saint Catherine* Raphael established the position of the perpendicular by making intersecting arcs with a compass from points on the vertical axis. These ruled lines may have been used to help align the cartoon on the panel, but also served as a reminder of the underlying symmetry and divisions of a composition as the painting developed.

These smaller paintings are based on preparatory cartoons, from which the designs were transferred by means of black pouncing. In the case of the two predellas, pounced dots are evident by infrared reflectography, confirming the use of pricked cartoons, although these do not survive.¹⁹ A pricked scale drawing of the *Vision of a Knight*, now in the British Museum, was always assumed to be a preparatory cartoon for the composition until Plesters questioned its function on account of the absence of dots from pouncing on the painting.²⁰ Improved techniques have since confirmed the presence of these dots beneath the underdrawn lines.²¹ It has recently been shown that pounced dots are also present beneath the underdrawn lines of the *Saint Catherine* which correspond to the pricked holes in the related cartoon in the Louvre (earlier examination had failed to find evidence for the direct use of this cartoon).²² In all four pictures, the pounced dots were joined up with lines in a liquid material, most likely applied with a brush (FIG. 2), although in the *Vision of a Knight* these lines appear to have been drawn with a pen, probably because of the almost miniature-like scale of the painting. Once the designs had been transferred by this method, Raphael added some freehand elaboration to the underdrawing, for example areas of hatching for the shadows (chiaroscuro not being easily conveyed in a linear cartoon) and landscape details (for example small bushes in the *Vision of a Knight* and the background hills in *Saint John the Baptist Preaching*). The horses and two of the women supporting the Virgin in the *Procession to Calvary* were drawn in freehand after the cartoon had been transferred.

In larger works Raphael appears to have used a grid, with the specific intention of scaling up a squared design. Thus, on the *Ansidei Madonna* there is an incised grid which is six squares wide and



FIG. 2 Detail from the infrared reflectogram mosaic of *Saint John the Baptist Preaching* (NG 6480), showing fluid drawing joining the pounced dots and hatching in the shadows of the drapery.

nine squares tall (up to the highest point of the arch), with the curve of the arch beginning at the sixth square up. The dimensions of each square are equal to about two-thirds of a Perugian foot or *piede* (36.3 cm.), so that the whole composition is based on a simple geometric construction of a square four *piedi* wide, topped by an arch two *piedi* high.²³ The overall design seems to have been copied from a squared *modello*, but traces of pouncing in the head and hands of the Virgin and Child suggest that certain elements were transferred using a pricked cartoon. No registration lines or squaring have been found in the *Mond Crucifixion*, but Raphael may have adopted similar methods.²⁴ Whatever the transfer process, the manner in which

he painted around the drawn boundaries of the figures left in reserve, without revisions or pentimenti, strongly suggests that he was working from a carefully prepared design.

In addition to the compositional lines mentioned above, Raphael often used ruler and compass to incise the outlines of architectural elements (such as the crucifix in the *Mond Crucifixion*, and the architecture in the *Ansidei Madonna*), as was common practice. Other small-scale linear elements were also incised, such as the swords in the *Procession to Calvary* and the *Vision of a Knight* and the Baptist's cross in the *Saint John the Baptist Preaching*. Compasses were also used for haloes (PLATE 8) and other circular elements, such as the sun and the moon in the *Mond Crucifixion*. There are incised lines around the outlines and along some of the drapery folds of the angels in this painting, which may relate to the method used for transfer of the design. Traces of incisions can also be seen in the outline of the mantle around the shoulders of Saint Nicholas of Bari in the *Ansidei Madonna*. In this case, Raphael had already painted the figure, but wished to extend the contours slightly. The rapidly drawn incisions indicate the position of the new contour.

Raphael characteristically made further changes during the course of painting, generally of a very minor nature, such as the alterations to the neckline in the *Madonna of the Pinks* and to the small group of buildings seen through the window, and the necklines of Virtue and Pleasure in the *Vision of a Knight*. He also added details that were either too small or fiddly to transfer from a cartoon by pouncing, such as the flower held by Pleasure (as well as those in her hair), or features dynamic enough to merit a freehand approach, such as the fluttering pennant in the *Procession to Calvary*. Raphael sometimes made more major changes to the background of his compositions, as has been recently been discovered in the *Ansidei Madonna*, where the entire architectural setting was added after painting had begun (it is incised and painted on top of the first layer of blue sky and parts of the landscape background, PLATE 28). Occasionally he would suppress elements of a design at the painting stage, such as the knot of drapery at Saint Catherine's right shoulder which features both in the cartoon and the underdrawing, but was not included in the finished work, when Raphael must have decided that a purer silhouette was preferable against the blue sky.

The binding medium of the paint in the works discussed here is predominantly drying oil.

Instrumental analysis (Gas-Chromatography–Mass Spectrometry, GC–MS) of the *Mond Crucifixion*²⁵ and *Saint Catherine* has demonstrated the use of both linseed and walnut oils in separate passages of the paintings, and FTIR analysis has shown that drying oil is also the binder of the *imprimitura*. In samples analysed from the *Ansidei Madonna*, only walnut oil was detected as the paint binder; in some areas it was heat-bodied, in others the walnut oil had not been pre-heated. Three samples from the *Madonna of the Pinks* were found to contain heat-bodied walnut oil. Walnut oil appears to be the preferred medium in this period in Italy, particularly in central Italy, although linseed oil was certainly also used, and there are other cases of paintings in which it has been established by analysis that walnut oil occurs in one area of a composition and linseed in another.²⁶

Recent examination of the *Vision of a Knight* suggests a more extensive use of oil medium than had been assumed previously (see PLATE 15); solubility tests in 1957 on a single sample had indicated that the paint binder was egg tempera (see entry below). The two National Gallery predella panels had also been thought to have been painted mainly with egg tempera, although the central panels of the altarpieces to which they belong are painted wholly in oil. Again, only three samples of paint had been analysed from each predella (although by GC and GC–MS, which are far more reliable than heating tests).²⁷ Recent analysis of a broader range of samples by FTIR microscopy, however, suggests that these paintings were executed principally or entirely in an oil medium (see entries below). The earlier analyses identified drying oils and pine resin in areas of green on both predellas, but suggested that tempera had been used in sky paint and for the red lake paint of Saint John the Baptist's drapery. This last result is surprising since often, where oil has been used on a painting for translucent verdigris-containing greens, it has also been used for translucent reds. The recent examination has revealed, however, that the paint in these areas contains powdered glass, which interferes with interpretation of the results of analysis, and as a consequence the earlier results require reassessment (see entries). Although there is strong evidence to suggest that the predellas are in fact predominantly in oil, the possibility that egg tempera has been used cannot be dismissed lightly since its use for predella panels, with oil for the central panel, is a familiar method of the Perugino workshop. Similarly in Raphael's *Oddi Altarpiece* in the Vatican, the predella has most recently been described as

tempera grassa, although at least some parts of the predella – notably the thickly painted blue draperies – have the appearance of oil paint.²⁸ Other roughly contemporary altarpieces, however, such as those by Signorelli, seem to have been executed entirely in oil, including the predella scenes.

It is not known to what extent Raphael received practical training from his father, Giovanni Santi, and the latter's paintings have not been the subject of much technical analysis. The single example of Santi's work in the National Gallery, a *Virgin and Child* (NG 751) on panel (1480s), has been shown to have been painted partly in walnut oil and partly in egg tempera.²⁹ However, Raphael must have been exposed to a considerable range of technical practices, first through Santi's workshop and then from contact with the Perugino enterprise, which was producing paintings on panel and canvas of various sizes and in a range of media: egg tempera, oil and combinations of egg and oil, as well as glue tempera (on canvas) and *buon fresco*.³⁰ The National Gallery panels from Perugino's Certosa di Pavia altarpiece (NG 288) of around 1496–1500, for example, are painted largely in walnut oil, but include passages, such as the Archangel Raphael's pale blue drapery, in which a final glaze of ultramarine in oil was laid over an off-white underpaint bound in egg.³¹ There seems to have been considerable experimentation with combinations of egg and oil on panel in the last decades of the fifteenth century. Examples include the use of egg combined with small amounts of drying oil (*tempera grassa*), the deployment of oil glazes over underlayers in egg for red lakes, copper-based greens and ultramarine blue, in order to achieve saturation and transparency, and the use of egg for certain passages and pigments, and drying oil for others.³²

The manner in which Raphael applied his paint can be judged from close examination of the paint surfaces, and both infrared photographs and X-radiographs are helpful in confirming interpretations made visually. Comparison of the smaller scale predella paintings with the larger scale works reveals a consistent pattern. The foregrounds, backgrounds and sky paints were laid in with broadly horizontal strokes, often leaving a brushmarked, slightly textured surface (see PLATES 1 and 8). The main elements of the compositions, including the figures, were left in reserve and the background paints were later brought around their outlines, sometimes by extending the horizontal brushwork up to a junction and sometimes by painting around the contour. Occasionally, as in the junction of the top of Saint



PLATE 1 *The Mond Crucifixion* (NG 3943). Detail showing hatching in the paint of the dark grey-mauve drapery around the Virgin's head.



PLATE 2 *Saint John the Baptist Preaching* (NG 6480). Detail showing the figure group in the centre of the painting.

Jerome's head with the surrounding landscape in the *Mond Crucifixion*, the paint of neither part fully covers the ground, and the *imprimitura* can be seen at this point; a similar area is visible to the right of Saint John the Evangelist's shoulder. In the large works, fairly substantial passages were brushed out fluidly and freely in single layers of oil paint. The draperies tend to be more thickly painted, because specific colour and saturation effects were sought, or the use of particular pigments dictated a multilayered

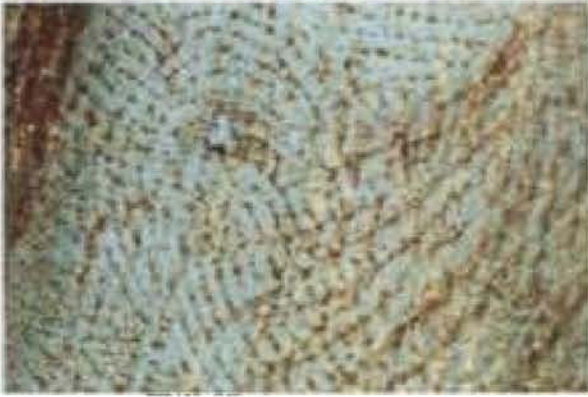


PLATE 3 *The Mond Crucifixion* (NG 3943).
Macrophotograph from the area in PLATE 1 showing
fingerprints in the purple glaze.



PLATE 4 *Saint John the Baptist Preaching* (NG 6480).
Macrophotograph showing the hatching in the shadows of
the purple drapery of the figure seen from behind in PLATE 2.

technique, as, for example, in the deep green, red and greyish-mauve draperies in the *Mond Crucifixion*, all essentially based on glaze-like surface paints over solid underlayers of an equivalent colour. Similarly, the paint is thickly applied in the deep green sleeve and the yellow folded-over lining of the red cloak in *Saint Catherine*. The build-up of Raphael's paint in the saturated greens often involved the use of copper green glazes over opaque underlayers containing verdigris with white or lead-tin yellow, and the translucent reds relied on red lake glazes over vermilion, vermilion with white, red earth or vermilion mixed with lake. Where ultramarine is used as a surface paint, it was often applied over a layer of azurite, or azurite and white, leading to a thicker paint layer structure than elsewhere, and this is evident in the dark blue drapery of the enthroned Virgin in the *Ansidei Madonna* and, on a small scale, in the Virgin's drapery of the *Madonna of the Pinks*.

In this period, Raphael commonly applied a final layer of modelling to draperies, and sometimes also to flesh paint, by using dark hatched brushstrokes to

reinforce an area of shadow, a method derived from Perugino.³³ This technique is particularly noticeable in the draperies in the *Mond Crucifixion*, for example in Saint Jerome's muted greyish-mauve robe, Saint John the Evangelist's red and green draperies, the Virgin's dark grey-mauve cloak (PLATE 1), and Christ's loincloth. Similar hatched strokes are also clearly visible in the red lake drapery of Saint John the Baptist in the *Ansidei Madonna* and in the shadows of the red cloak in *Saint Catherine*, as well as in the modelling of the flesh of her cheek, neck, chest and hand. This technique of surface hatching also occurs, on a small scale, in the draperies of the *Procession to Calvary* and *Saint John the Baptist Preaching* (PLATES 2 and 4).

Raphael also used his hands and fingers to blot and model wet surface paint so as to blend brushstrokes and efface transitions between mid-tones and shadow. On close examination, fingerprints and palm prints are clearly visible in the shadows of the heads in the *Mond Crucifixion*, particularly in Christ's hair, face and beard, and in the necks of Saint John the Evangelist and Mary Magdalene. Palm prints occur in the landscape background behind Saint Jerome's head, although these may be in underlayers or in the *imprimitura*, and the mid-tone paint of the Virgin's dark grey-mauve hood, covered with closely spaced fingerprints (PLATE 3), was also blended manually.

Raphael's method of modelling the flesh paints of his subjects in this early period followed closely the way in which the Perugino workshop painted and had its basis in the technique practised by Verrocchio and his followers. The consistent use of a faintly greenish-brown underpaint may well have been a development of the traditional method of underpainting flesh with *terra verde*, and modelling with brownish-green *verdaccio* based on mixtures of translucent yellow pigments combined with black.³⁴ The method that developed was evidently widespread and can be seen also in the works of the Ghirlandaio studio, of Fra Bartolommeo and in other Florentine paintings. The flesh colour is applied in thin, spare layers and the highlights are then developed by pulling an opaque layer of pinkish or brownish-pink paint over the semi-translucent undermodelling, which was generally of a rather golden greenish-brown tone. This lower layer was allowed to stand exposed for the shadows. The character of undermodelling in the flesh can be judged very well in the small unfinished panel in Budapest (Museum of Fine Arts), *The Esterházy Madonna*, usually dated to c.1507, in which the



PLATE 5 *The Mond Crucifixion* (NG 3943). Detail of the Magdalen.



PLATE 7 *Saint John the Baptist Preaching* (NG 6480). Detail showing the babies.



PLATE 6 *Saint Catherine of Alexandria* (NG 168). Detail of Saint Catherine's head showing hatching in the shadows.



FIG. 3 *Saint Catherine of Alexandria* (NG 168). X-ray detail.

flesh paints were abandoned at this preliminary stage.³⁵ Frequently, the strongest shadows were then reinforced with a thin final brownish-grey glaze, dabbed with the fingers or stippled with a stiff brush, or, alternatively, with hatched strokes of dark colour on top of the lighter paint. The former technique can be seen in the *Mond Crucifixion* (PLATE 5) and the latter hatched method in the *Saint Catherine* (PLATE 6). Even for the small-scale figures in the predella paintings, the method and sequence

of painting the flesh tones was the same (PLATE 7).

In all the pictures discussed here, and in many others from about 1502–3 onwards (the moment when Raphael was absorbing Perugino's style and practice most fully), the flesh layers are generally very thinly applied in comparison with the paints of the landscape backgrounds, sky, draperies and other elements, so that they generally appear as strikingly dark areas in X-ray images of the paintings, an effect which can be seen very clearly in the

X-radiograph of the head of Saint Catherine (FIG. 3). In spite of the alabaster appearance of the flesh tones and a more extensive use of the light pink mid-tone than usual, the overall thickness of the flesh layer is minimal. Raphael's technique closely mirrors that of Perugino, and the radiographic images of their paintings are remarkably similar in this respect. It has been argued, based on examination of Raphael's *Canigiani Holy Family* in Munich (Alte Pinakothek, c.1507), that the painting of the flesh areas was a late stage of the development of the composition and this reflects Raphael's general practice throughout this time.³⁶ This is corroborated by the degree of completion of the figures in the large altarpiece, the *Madonna del Baldacchino* (Florence, Palazzo Pitti), left incomplete on Raphael's departure for Rome in 1508.³⁷

Raphael's paintings in this period include many materials that are familiar from the traditions of Quattrocento painting, often employed in a similar manner as, for example, the use of ultramarine over azurite for the most intense blues of skies and draperies. He also employs standard mixtures to create the greens and blues of landscapes, including azurite, lead white, lead-tin yellow, earth pigments and verdigris, in a variety of combinations. Paint was applied in multiple layers in order to achieve the intense red and green glazed draperies: final translucent glazes of lake pigments for the reds, and glazes containing copper-based pigments for the saturated greens. All the pictures described here contain drapery passages ranging from greyish mauve to an aubergine colour made up of varying proportions of red lake and azurite mixed with white and black pigment to either lighten or darken the hue, a combination of which Raphael was particularly fond.

The core palette for this group of pictures consists of azurite, ultramarine, verdigris and copper green glazes (probably derived from verdigris), lead-tin yellow ('type I'), vermilion, red lake pigments, yellow lake pigments, earth pigments, carbon blacks and lead white. However, more detailed re-examination of older samples, and analysis of a limited number of new samples from the National Gallery pictures, has revealed that Raphael employed materials outside the standard canon of later Quattrocento and early Cinquecento painting, although these were previously undetected, or uncharacterised. They include red lead (lead tetroxide), orpiment (mineral arsenic trisulphide) and an unusual dark warm grey pigment composed of metallic bismuth. Only a few occurrences of this last pigment on easel paintings have been published, on paintings by Fra

Bartolommeo and Francesco Granacci. Raphael appears to have used it where he required a grey pigment rather than a true black.³⁸

Another new finding is the presence of colourless glass in the paint, which has been detected in the *imprimature* of the paintings and also in other paint layers, particularly those consisting of red lake (see PLATES 24–8). As mentioned above, the glass appears to have been added as a siccativ (discussed in more detail in the entry for the *Ansidei Madonna*). The characterisation of this glass material, which will be published elsewhere,³⁹ has shown that, in every sample where it was analysed, it contains manganese and is therefore capable of acting as a siccativ. The addition of glass is not confined to paintings by Raphael, and appears to be relatively common in sixteenth-century paintings.⁴⁰ However, Raphael seems to have used it particularly extensively. Inevitably, the glass would increase the translucency of the paint when mixed with opaque pigments, and indeed translucency does appear to be a feature of Raphael's paint. Advances in the application of HPLC to dyestuffs analysis⁴¹ has enabled the sources of the red dyes in the red lake pigments to be determined, and it is now known that Raphael used kermes, madder and brazilwood lakes. Other developments in organic analytical methods, particularly GC–MS, have exposed his occasional use of translucent brown glazes composed of softwood pitch.⁴² The entries for each painting describe more fully the use and location of these and the more standard materials in the individual pictures.

The very last stage of the painting would have been the application of shell gold or mordant gilding as, for example, in the gold thread patterns and arabesque decoration in the necklines and borders of many of the figures' draperies. Other fine details, such as the haloes, often appear to have



PLATE 8 *The Procession to Calvary* (NG 2919). Detail of Christ showing the incised circle for the shell gold halo.



PLATE 9 *The Ansidei Madonna* (NG 1171). Detail of Saint John's robe showing the silver and gold pattern.

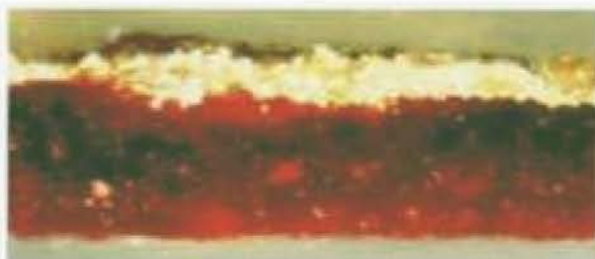


PLATE 10 *The Ansidei Madonna* (NG 1171). Cross-section from the shell gold decoration on Saint John's robe. Original magnification 400×; actual magnification 350×.

been executed in shell gold (PLATE 8). In the *Ansidei Madonna*, a band of shell gold decoration on the hem of Saint John the Baptist's deep red cloak was further enlivened with a second band of metallic silver (PLATES 9 and 10), although degeneration of the metal has reduced the impact of this part of the design. Where mordants are used for gilding, they are sometimes thick enough to be X-ray absorbent in radiographs (that is, they appear as a light feature); others are less substantial. Forceful passages of mordant gilding occur in the *Ansidei Madonna* – in the inscription over the throne

(PLATE 23), for the bands of gilded Greek key decoration in the canopy and plinth, and for the golden balls at Saint Nicholas of Bari's feet, while the inscription on the cross – 'INRI' – in the *Mond Crucifixion* is also mordant gilded directly on to the *imprimitura*, and the paint carefully worked around the gilded characters. Unusually, Raphael's signature at the foot of the cross appears to be a type of sgraffito in which the letters were formed by scraping through the brown paint, while it was still soft, to a small patch of silver leaf applied beneath. Silver leaf,⁴³ now tarnished, was used for the moon at the top right of the *Crucifixion*, while gold leaf stands for the sun; in these cases the layers of metal leaf were applied over a layer of red-brown bole, and are therefore in the old-fashioned technique of water gilding.

Analysis of Raphael's painting technique during the period of his early career in The Marches, Umbria and Tuscany shows that it was thoroughly grounded in the traditions of central Italy and followed many of the practices that had been developed there in the second half of the fifteenth century. This technique had its roots in much earlier Italian practice, the principal later developments in the last two or three decades of the fifteenth century being the increasing application of oil as the essential paint medium, the concomitant use of a thin oil-based *imprimitura* over the gesso ground on panel, as well as changes in the construction of altarpieces, with the tendency to move away from compartmentalised Gothic constructions to the more modern single *pala* format, and a reduction in the role of decorative gold, particularly gold leaf.

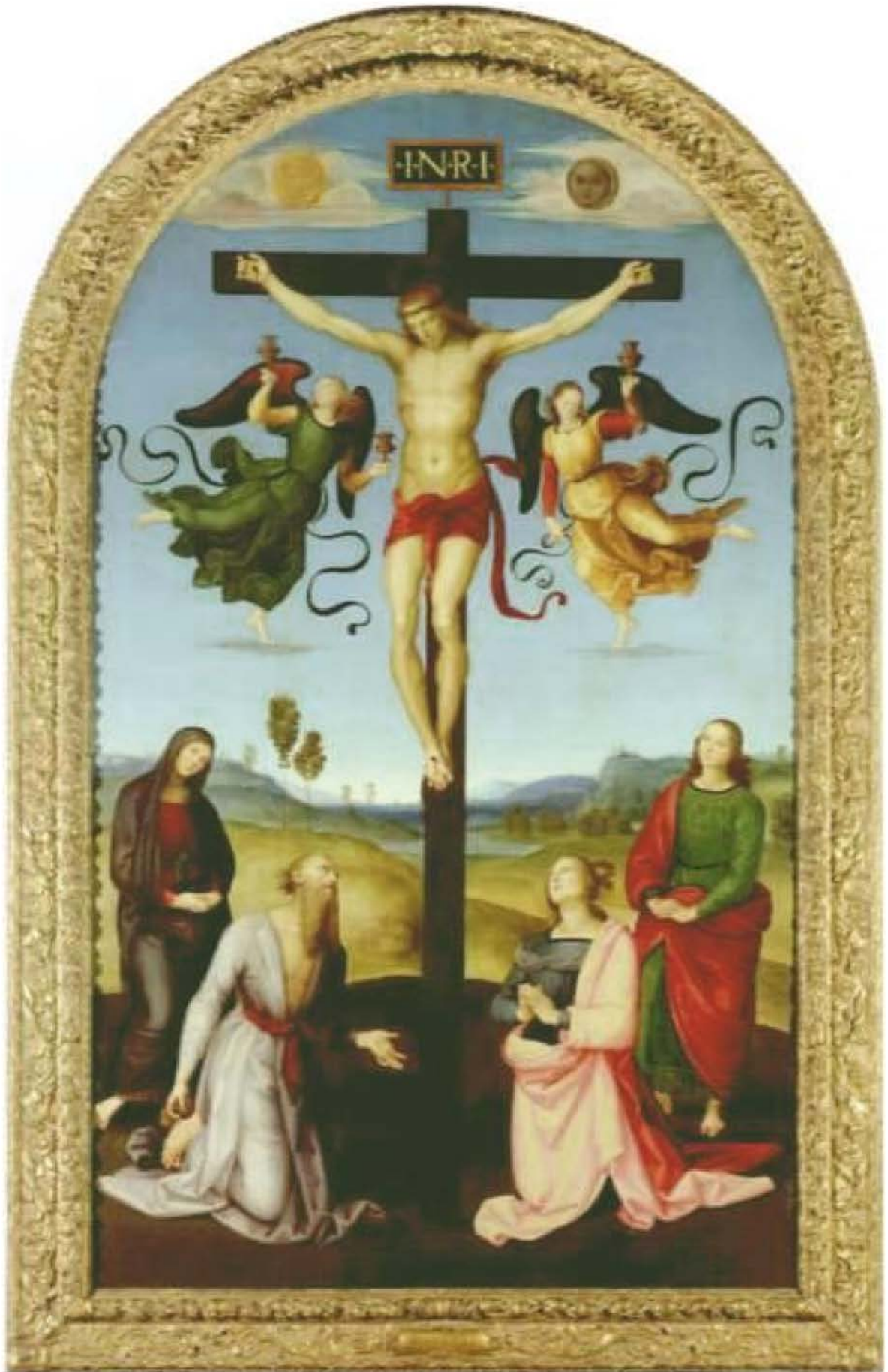
The Paintings

The Crucified Christ with the Virgin Mary, Saints and Angels (*The Mond Crucifixion*) PLATE 11 (NG 3943)

Painted c.1502–3. Panel, 283.3 × 167.3 cm. Painted area inside incised line around edge, 281 × 164.5 cm. Cleaned and restored at the National Gallery, 1966–7.

Support and preparatory layers: poplar panel, composed of six vertical members, with a gesso ground, identified by XRD as gypsum (calcium sulphate dihydrate). Over the gesso there is a thin *imprimitura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a low concentration of lead-tin yellow.

OPPOSITE: PLATE 11 (NG 3943)



Underdrawing: fluid black underdrawing for the figures, directly on the gesso. Drawing apparently freehand, no sign of pouncing or other mechanical transfer, simple and linear, no hatching. Incisions for the straight lines of the crucifix, rays from the sun and moon, and the outlines of the angels as well as some folds of their drapery; circles drawn with compasses.

Paint binding medium: early analysis by GC and later analyses by GC–MS indicated the use of both linseed and walnut oils in separate passages of the painting. The GC results show that the paint of the brown foreground and Saint John's green drapery are bound in linseed oil, and the sky in walnut oil; GC–MS showed that the oil binder for the sky had been heat-bodied and that the same medium was present in Christ's flesh. Heat-bodied linseed oil was used for the translucent brown sash of the angel on the left.

Pigments and layer structure: the sky consists of natural ultramarine with white over azurite and white. The Virgin's drapery, which appears at first sight dark grey, in fact has a purplish cast. It has a bluish underpaint that consists largely of azurite with a little red lake pigment, vermillion and some white, the surface of which is modelled with a dark brownish purple made from red lake, azurite and a significant amount of black. This was applied in hatched strokes in the shadows and has been blotted with a finger in the highlights to give a thin translucent layer through which the lighter coloured underpaint can be seen (PLATES 1 and 4). Although the mixture of azurite and red lake is likely to have darkened to some extent, Raphael evidently intended that this drapery should be muted in colour since he also included black in the paint. Saint Jerome's robe, which is a very pale greyish lilac, consists of azurite, red lake and white. The paint in the shadows, again applied in hatched strokes, contains only azurite and red lake. This has darkened to a reddish-brown colour, which contrasts with the better-preserved lilac mid-tones.

Saint John the Evangelist's red cloak is a particularly striking deep saturated colour. The most intense shadows consist of thick layers of red lake glaze over a deep red underpaint of vermillion mixed with red lake (PLATE 12). The darkest areas contain black in addition. The fluorescence of samples in ultraviolet (UV) light under the microscope suggested the presence of two distinct types of red lake pigment: these were identified by HPLC as derived from kermes and madder (the latter having a characteristic orange UV fluorescence). UV light examination of



PLATE 12 *The Mond Crucifixion* (NG 3943). Detail of Saint John the Evangelist.

samples also reveals that these red glazes contain considerable quantities of powdered glass, and in fact this material has been added to many of the paints, not just the reds.⁴⁴ The other areas of saturated red in the draperies also make use of red lake, for example the shadows of the Magdalen's pink

and yellow *cangiante* drapery. The contrast between the shadows and the pink mid-tones has almost certainly become more marked as a result of fading of the red lake.

Lead-tin yellow ('type I') has been identified by XRD in the drapery of the Magdalen and of the angel on the right, which also contains yellow earth pigment in the warmer tones. Lead-tin yellow occurs extensively in the mixed browns and greens of the landscape and has been identified by XRD in the Virgin's green sash. The brownish-gold rays of the sun at the upper left contain orpiment (mineral arsenic trisulphide; EDX), now rather deteriorated. The deep brown paint of the cross is based on vermilion, black and earth pigments.

To contrast with the saturated red cloak, Saint John's robe is a deep saturated green. This is also thickly painted and multilayered, consisting of translucent deep green verdigris glazes, virtually undiscoloured, over a more solid dark green underlayer, also containing verdigris with some lead-tin yellow and white. The dark translucent brown ribbons hanging from the waist of the angel dressed in green have the appearance of darkened copper green glazes, but in fact are painted in verdigris mixed with red lake and are therefore, presumably, an intentional choice of colour. The angels' dark-toned wings are painted in the same way.

There is both gold and silver on the picture, applied in several different ways. The sun on the top left is water gilded – gold leaf applied to red bole – and the silver moon on the top right is made in the same way. There are more delicate touches of gold on Christ's loincloth, the angels' wings, Saint Jerome's belt and the borders of the robes of the Virgin and Saint John. It is not certain how the gold was applied in these areas, but the lack of a pigmented mordant and the character of the line suggest that it is probably shell gold, even though it appears more solid than is usual for shell gold.⁴⁵ A reserve was left for the relatively large letters of the inscription above the cross. This has been confirmed by a recent cross-section in which a comparatively thick orange-brown oil mordant layer for the gold leaf is present directly on the *imprimitura*. The mordant contains the strongly drying pigments red lead (lead tetroxide) and verdigris. The silver inscription at the bottom of the cross is also mordant gilded, but is unusual in that the brown paint of the cross was brought over the silver and then scratched away to form the letters in a type of sgraffito technique.

An Allegory ('Vision of a Knight') PLATE 13 (NG 213)

Painted c.1504. Panel, 17.5 × 17.5 cm, painted area now 17.1 × 17.3 cm. Cleaned and restored at the National Gallery in 1985.

Because of the small size of the picture, and its excellent state of preservation, no samples were taken during the present examination; the painting was studied under the stereomicroscope at magnifications up to 80×.

Support and preparatory layers: poplar panel, single member, vertical grain, with a gesso ground. Brushstrokes running across forms beneath the surface of the paint can be seen in raking light, which suggests that there is an *imprimitura*, although its composition is not known as the painting has not been sampled.

Underdrawing: vertical centre line, incised. Fluid underdrawing (pen?) over traces of pouncing, from a surviving pricked cartoon. Some freehand elaboration adding hatching and small details such as bushes in the background. Ruled straight lines (for example, for swords) are incised.

Paint binding medium: an earlier report based on solubility tests on a single sample suggested the use of egg tempera;⁴⁶ however, the presence of lead-soap inclusions in passages containing lead-tin yellow (including much of the landscape) strongly suggests the use of an oil binding medium (PLATE 15). The nature of the brushwork is also indicative of an oil medium (PLATES 15 and 17).

Pigments and layer structure: the surface paint of the sky consists of natural ultramarine mixed with white. The distant mountains are also painted in ultramarine. The greener parts of the landscape contain lead-tin yellow, a green pigment, probably verdigris, and some ultramarine; the strongest greens in the middle distance contain verdigris and some black. The central tree is painted directly over the sky; the greenish-blue foliage contains azurite, verdigris and a yellow pigment; the highlights contain lead-tin yellow as the principal pigment. The middle-ground rocks are painted in lead white with some ultramarine, black and yellow; the light greenish-grey foreground is similar and contains a little azurite in addition.

The blue dress of the figure of Virtue, at the left, consists of a layer of ultramarine with varying



PLATE 13 (NG 213)

amounts of white over a purplish underlayer containing ultramarine, red lake and white (PLATE 14). The yellow and pale pink parts of the sleeves are modelled with red lake and red earth mixed with white over a lead-tin yellow underpaint, while the browner yellow upper part of the sleeves contains orpiment and red earth pigment with lead-tin yellow highlights.⁴⁷ The green sash of the dress is painted in verdigris and lead-tin yellow. The headdress contains white, ultramarine and a trace of red lake.

The tunic worn by the sleeping knight is painted in high-quality ultramarine (PLATE 18). The cool grey of the armour is painted with white and black; ultramarine is added to this mixture for the bluer highlights. The green cloak is lead-tin yellow mixed

with verdigris with a green glaze. The orange hose have a modelled pink underlayer of red lake and white partially covered with a layer of yellow containing orpiment and yellow earth; a similar technique is used for the shoes, which have a grey-mauve underlayer. The leather parts of the armour also contain orpiment. The shield consists of a modelled underlayer based on orange-red vermilion with a red lake glaze; its duller red reflection in the armour is represented in red earth mixed with some black.

The figure of Pleasure's red underdress has a mauve undermodelling which tends towards pure blue (ultramarine and lead white) in the shadows; the upper glaze is red lake with some vermilion in



PLATE 14 *Vision of a Knight* (NG 213). Macrophotograph of the neckline of the figure on the left.



PLATE 16 *Vision of a Knight* (NG 213). Macrophotograph showing Pleasure's face.

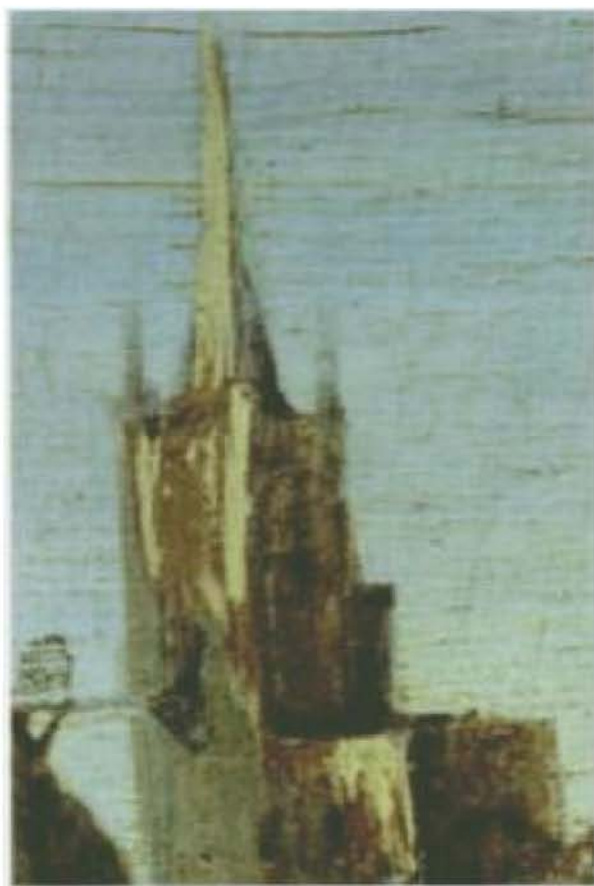


PLATE 15 *Vision of a Knight* (NG 213). Macrophotograph of the tower, showing the texture of the lead-tin yellow highlights. Translucent inclusions of lead soaps are just visible.

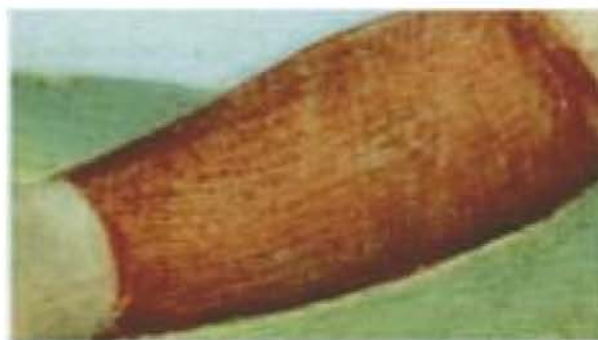


PLATE 17 *Vision of a Knight* (NG 213). Macrophotograph of the sleeve of Pleasure, showing the red lake glaze, which has been blotted with a finger.



PLATE 18 *Vision of a Knight* (NG 213). Macrophotograph of the knight's breastplate.

the shadows. On the sleeve, the red lake glaze shows evidence of blotting with a finger (PLATE 17). Her pink and blue *cangiante* drapery consists of a pinkish-mauve combination of white, red lake (faded) and some ultramarine, with an ultramarine glaze to represent the bluest areas. There is a thin fragmentary

line of gilding following the hem. The string of coral beads is pure vermilion.

The flesh paints are quite solidly worked (PLATE 16), given the small scale of the painting, and are modelled with lead white, red lake and a little vermilion.



PLATE 19 (NG 2919)

The Procession to Calvary PLATE 19 (NG 2919)

Painted c.1504–5. Predella panel, 24.4 × 85.5 cm. Cleaned and restored at the National Gallery, 1992–5.

Support and preparatory layers: poplar panel, single member, horizontal grain, almost certainly part of a longer plank. Gesso ground, identified by XRD as gypsum (calcium sulphate dihydrate). Over the gesso there is a thin *imprimatura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a low concentration of lead-tin yellow in an oil binding medium (EDX and FTIR).

Underdrawing: bisected horizontally and vertically with very fine ruled lines in what appears to be a dry black material, probably metalpoint. Fluid black underdrawing over traces of pouncing transferred from a pricked cartoon (on top of the *imprimatura*) with freehand elaboration – hatching for shadows. Changes to composition added freehand using finer, more sketchy lines, possibly in a dry material. Straight lines incised, for example the cross and the soldier's staff; circular haloes incised with compasses.

Paint binding medium: FTIR analysis of samples from six different areas of the painting suggests that the binding medium is oil.⁴⁸ In areas containing lead-tin yellow (such as the light green paint of the landscape, the pale yellow tunic of the foot soldier dragging Christ and the golden-yellow robe of the first mounted horseman), relatively large translucent agglomerations are visible in cross-sections which have been identified as lead soaps. Recent work has demonstrated that these lead soaps form by reaction between certain lead pigments and oil.⁴⁹ Their presence is therefore consistent with the identification of an oil binding medium. Previous analysis by GC–MS and FTIR, published in 1995, identified walnut oil with some pine resin in the translucent dark green armband of the second mounted figure. The results from a sample from the blue distant mountain and the pink drapery of Saint John the Evangelist, however, suggested that the medium here was egg tempera.⁵⁰ Recent FTIR examination of another sample from this pink drapery, where each layer was analysed individually, presents a more complicated picture. The priming clearly contains oil. Since the analysis in 1995, the cream underpaint has been shown (by EDX) to contain a faded red lake and a substantial amount of powdered glass, as



well as lead white. The FTIR spectra of powdered glass (and deteriorated glass) contain peaks in the region where the amide bands of proteins are normally found. The presence of glass in this layer thus interferes with the interpretation of the infrared spectra and it is not therefore possible to determine the nature of the binding medium. In fact the glass content of this layer is so substantial that it dominates the spectrum. The results of the earlier analysis should be reassessed in the light of this finding.⁵¹

Pigments and layer structure: the sky consists of natural ultramarine with white over azurite and white. Christ's robe is a dull blue with slightly purplish shadows (PLATE 8); the principal pigment is azurite with some red lake, a mixture that often becomes duller and darker with time. In contrast, the draperies and hose of the surrounding figures contain ultramarine. The Virgin's cloak is a sombre purplish grey in the mid-tones and aubergine in the shadows. A sample from a mid-tone has a blue underpaint of azurite and white, which is covered with a dark brownish-red paint containing black, lead white, a tiny amount of vermillion and rather pale brownish-red lake. Where the red lake is used on its own in Saint John's cloak (PLATE 20), the

drapery of the figure supporting the cross and that of the horseman, it is also rather dull and brownish red in tone. PLATE 21 shows the layer structure in Saint John's drapery: first a cream underpaint and then a much thinner layer of vermillion and a pure red lake glaze. The surface glaze is pale in colour and must have faded. The cream underlayer contains lead white and colourless particles of glass, as well as transparent yellow particles in which aluminium, calcium and sulphur were detected by EDX; these elements are often found in lake pigment substrates. Although these particles now appear pale yellow, they are likely to be the remnants of a faded red lake (see also under the *Ansidei Madonna* below).

The pigment in the pale yellow tunic worn by the foot soldier dragging Christ has been identified as lead-tin yellow mixed with lead white, while the golden-yellow robe of the mounted horseman leading the procession is based on lead-tin yellow combined with a strongly coloured yellow earth rich in iron oxide. The foreground also contains this pigment with some azurite and lead-tin yellow.

The most unusual pigment used in the painting is a warm dark grey, the particles of which have a distinctive metallic lustre under the microscope.



PLATE 20 *The Procession to Calvary* (NG 2919). Detail showing Saint John's pale pink cloak.



PLATE 21 *The Procession to Calvary* (NG 2919). Cross-section of Saint John's pale pink cloak. The thin uppermost red layers contain faded kermes red lake and vermilion. Beneath is a cream layer consisting of lead white, powdered glass and rounded translucent yellow particles that contain Al and Ca, and which are therefore very likely to be faded red lake (see PLATE 24). Below the cream layer is some black underdrawing, which lies on top of the pale yellow priming (lead white and lead-tin yellow). Original magnification 480x; actual magnification 420x.

This same material occurs in the architecture of the *Ansidei Madonna* where it has been identified positively (XRD and EDX) as powdered bismuth metal. In the *Procession to Calvary* it occurs in Simon of Cyrene's hose and in the body of the grey horse. The shadows of the grey horse appear unusually dark in infrared images in spite of the relatively

light grey colour of the paint, which is characteristic of this metallic pigment, and distinguishes it from stibnite (antimony sulphide), which has a similar microscopic appearance.⁵²

It is not clear whether the haloes of Christ and the figure group at the left are mordant gilded or employ shell gold. They do not register in the X-ray image as light lines and, if mordant gilding was used, the mordant must be very thin and radiotransparent. There are also traces of gold on Saint John's robe, on the cuffs and the border at the bottom, and on the hood of the halberdier dressed in yellow and red.

In many of the cross-sections, transparent colourless angular particles are visible in the paint under the microscope. This material is a glass of the same composition as in the *imprimitura*; its presence has been confirmed by EDX analysis in the greenish paint of the foreground, the orange-yellow tunic of the man on the brown horse and the cream underpaint of the pink robe of Saint John.

The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansidei Madonna) PLATE 22 (NG 1171)

Dated 1505. Panel, 245 × 157 cm, painted area 216.8 × 147.6 cm. Cleaned and restored at the National Gallery in 1956.

Support and preparatory layers: poplar panel, six members, vertical grain, with a gesso ground, identified by FTIR as gypsum (calcium sulphate dihydrate). Over the gesso there is a thin *imprimitura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a low concentration of lead-tin yellow.

Underdrawing: lines forming a square grid (each square corresponding to roughly two-thirds of a Perugian foot or *piede*) lightly incised; fluid black freehand underdrawing, with some hatching for the shadows of the draperies. Traces of pouncing found in the head and hands of the Virgin and Child. Numerous incisions for straight lines, often not very careful – the lines are frequently longer than necessary in the architecture, or have slipped and have had to be redrawn. Some straight lines in the architecture are ruled using a dry material, but not incised (they show in infrared but not in the X-radiograph). Circles and arcs are incised with compasses. The freehand incision around the figure

OPPOSITE: PLATE 22 (NG 1171)



of Saint Nicholas of Bari apparently indicates a change during painting.

Paint binding medium: analysis of a number of samples by GC–MS indicated general use of heat-bodied walnut oil, other than in the Madonna's blue cloak, where there was no evidence for heat pre-treatment of the walnut oil binder.

Pigments and layer structure: the sky consists of a layer of natural ultramarine over a layer of azurite, in both cases mixed with white. The Madonna's dark blue cloak is painted as a thin glaze of virtually pure ultramarine over a layer of azurite, with a little lead white in the lighter areas of the drapery for the modelling. Both the ultramarine and azurite paint layers are medium rich and have probably darkened markedly as a result. The deepest shadows are finished with hatched strokes of very dark paint containing only ultramarine. The blackish strip of paint on which the gold inscription at the top of the Madonna's throne is painted contains azurite, and was also originally a brighter blue.

The underside of the roof of the canopy over the throne (PLATE 23) is made up of a red lake glaze over an underlayer that is now brown but which, from its constitution, may well have altered in colour. The underlayer contains red lake, a little vermilion, black, powdered glass and a translucent yellow pigment (PLATES 24 and 25). Aluminium, calcium and sulphur were detected by EDX in this yellow pigment, and it appears to be similar to that seen in the underpaint of Saint John's red drapery in the *Procession to Calvary*. As mentioned above, these elements are characteristic of a typical lake pigment



PLATE 23 *The Ansidei Madonna* (NG 1171). Detail of the canopy of the throne showing the mordant-gilded pattern.



PLATE 24 *The Ansidei Madonna* (NG 1171). Cross-section from the dark purplish paint of the underside of the roof of the canopy. The gesso ground is missing; the lowest layer is the pale yellow *imprimitura* containing lead white, lead-tin yellow and angular translucent particles of colourless glass. The thick translucent yellow layer above the *imprimitura* contains faded brazilwood lake, powdered glass and black. There is a thin kermes red lake glaze on the surface. Original magnification 220x; actual magnification 200x.



PLATE 25 *The Ansidei Madonna* (NG 1171). Cross-section in PLATE 24 in ultraviolet light. The layer structure and the angular particles of glass are more visible than in normal light. The rounded particles in the yellow layer, and those with a faint pink fluorescence, are the faded red lake pigment. Original magnification 220x; actual magnification 200x.

substrate, and so HPLC analysis was carried out to attempt to identify the dyestuff in both this pigment and the translucent red that is present in the sample. Kermes was found to be present (presumably in the red particles) as well as a constituent that has been observed in samples of brazilwood.⁵³ This suggests that the paint contains a brazilwood lake, which has deteriorated to a yellow colour, mixed with a kermes lake which has retained its red colour.⁵⁴ The dark paint of the roof of the canopy, which appears similar in tone to the underside, but a shade lighter, is a purple mixture of azurite and red lake painted over a greenish-blue underlayer. In a cross-section, azurite, lead white and translucent yellow particles are visible in this layer. As in the darker areas of the canopy, the yellow particles are likely to be faded brazilwood red lake pigment, so that the underpaint was originally purple rather than greenish blue. The intended original colour was probably a deep translucent purplish red, perhaps representing a velvet textile.



PLATE 26 *The Ansidei Madonna* (NG 1171). Cross-section from a mid-tone of Saint John's red drapery. The pale yellow *imprimatura* contains lead white, lead-tin yellow and powdered glass. Above are several red paint layers containing red lake, vermillion and powdered glass. Original magnification 480x; actual magnification 420x.



PLATE 27 *The Ansidei Madonna* (NG 1171). Cross-section in PLATE 26 under ultraviolet light. The angular particles of colourless glass in the paint layer, which are particularly large in this sample, are visible. The difference in the colour of the fluorescence of the red lake particles is due to the presence of two red lake pigments prepared from different dyestuffs (kermes and madder). The madder lake has an orange fluorescence. Original magnification 480x; actual magnification 420x.



PLATE 28 *The Ansidei Madonna* (NG 1171). Cross-section from the grey paint of the architecture. Particles of bismuth with a metallic lustre are visible in the layer of grey paint, as well as angular translucent particles of colourless glass. The green paint of the landscape, now covered by the architecture, lies beneath. Particles of glass are visible in the pale yellow *imprimatura*. Original magnification 500x; actual magnification 440x.

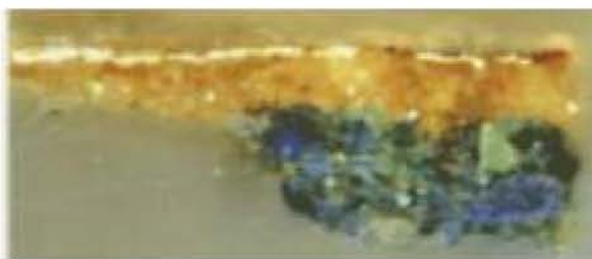


PLATE 29 *The Ansidei Madonna* (NG 1171). Cross-section of the mordant-gilded inscription on the throne. Beneath the gold leaf is a relatively thick translucent yellow mordant layer containing powdered colourless glass. This lies on azurite-containing paint which has darkened so that it appears almost black at the surface (see PLATE 23). Original magnification 250x; actual magnification 220x.



PLATE 30 *The Ansidei Madonna* (NG 1171). Cross-section in PLATE 29 under ultraviolet light. The glass particles in the mordant layer are visible. Original magnification 250x; actual magnification 220x.

Saint John the Baptist's intense red drapery is a fairly elaborate passage of painting, involving several layers varying in composition and tone (PLATES 26 and 27). For example, the mid-tones are underpainted with a combination of vermillion and red lake pigment, whereas in the darkest shadows the underlayer contains black in addition (and registers as dark in infrared photographs). In two samples from the shadow of the drapery there is a dark yellow-brown underlayer containing translucent yellow and black beneath the red paint. As in the transparent yellow pigment in the paint of the canopy, elements characteristic of lake pigments were detected by EDX analysis, and it appears that here again Raphael has used an unstable brazilwood red lake pigment. The final glazes have been identified by HPLC as containing red lake based on the dyestuff from the kermes insect. Certain areas of half shadow on the red drapery are reinforced by hatching at the surface in red lake; it is particularly clear in the folds on the saint's shoulder. The solid opaque orange-red lining of Saint Nicholas of Bari's cope is painted quite

differently and is made up of vermilion mixed with red lead (lead tetroxide).

The paint of Saint Nicholas's dark green cope contains verdigris mixed with lead-tin yellow, with white and black incorporated according to the modelling of the drapery. The final deep green glazes contain only verdigris. The green paint of the scalloped fringe around the canopy is similar in constitution. The mid-greens of the background landscape are based on verdigris and lead-tin yellow, some of them are rather translucent strong greens with a high proportion of verdigris.

The translucent brown background colour of the broad gold-embroidered borders of Saint Nicholas's cope comprises vermilion, black, white, orange earth and a little verdigris with a final mid-brown organic glaze, identified by GC-MS as a softwood pitch in heat-bodied walnut oil. The embroidery is represented by a pattern of mordant gilding on top. The more solid, flat lighter yellow-brown colours of the throne are worked in lead-tin yellow and earth pigments, with almost pure lead-tin yellow in the lightest areas.

The light grey colours of the architectural setting have a lilac tinge and contain lead white with powdered metallic bismuth (XRD) used as a pigment (PLATE 28). Elsewhere, a different black pigment which is rich in sulphur (EDX) is used; this has been shown to be a form of coal.⁵⁵ This occurs, for example, in the darkest shadows of Saint John the Baptist's red drapery and in the underpaint for the canopy.

There is gold and silver on the painting, applied in several different ways. The gold decoration on the draperies is shell gold (powdered gold applied with a medium, confirmed from examination of a cross-section, PLATE 10). The haloes, and the fine flecks of gold within the Virgin's halo, are, from their appearance, probably also shell gold. The inscription over the throne and the golden balls at Saint Nicholas's feet are in mordant gilding with an oil-based adhesive. The mordant layer for the golden balls consists of a light brown oil paint containing vermilion, black, white and some earth. The mordant layer for the inscription, however, is of a different composition, consisting of colourless manganese-containing powdered glass in oil (PLATES 23, 29 and 30). This observation is significant in understanding the function of the glass, which has been found to be widespread in Raphael's paint. The most likely explanation for its use in this mordant is as a siccativ (manganese acts as a drier for oil paint); in this context it cannot have been incorporated for optical properties such as translucency.



PLATE 31 (NG 6480)

Powdered glass was also found in the *imprimatura*, the red lake glazes (PLATES 26 and 27), the grey of the architecture, the dark brown of the canopy and the yellow-brown of the throne. It is likely that its function here too is primarily as a drier and not for its optical properties. It is unlikely to be an extender or bulking agent since it has been found in paint layers based on cheap earth pigments.



Saint John the Baptist Preaching PLATE 31 (NG 6480)

Painted 1505. Scene from the predella of the *Ansidei Madonna* (see above), 29.2 × 54 cm, painted area 26.2 × 52 cm (within vertical black-painted borders). Cleaned and restored at the National Gallery in 1983.

Support and preparatory layers: poplar panel, single member, horizontal grain, with a gesso ground, identified as gypsum (calcium sulphate dihydrate) by XRD. Over the gesso there is a thin *imprimitura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a low concentration of lead-tin yellow.

Underdrawing: a very fine ruled line in what appears to be a dry dark material, probably metalpoint, bisects the composition vertically. Extensive fluid black underdrawing over traces of pouncing, transferred from a pricked cartoon (FIG. 2). Some freehand elaboration, which is also fluid. The straight lines of Saint John's cross are incised.

Paint binding medium: recent FTIR analysis of three samples, from the blue sky, the grey hose of the man on the left and the brown mound on which Saint John stands, suggests that the binding medium is oil. Previous analyses, by GC-MS, confirmed the presence of oil in the green foliage of the trees and



PLATE 32 *Saint John the Baptist Preaching* (NG 6480).
Macrophotograph of the red lake glaze on Saint John's
drapery, which has been blotted with a piece of textile.



PLATE 33 *Saint John the Baptist Preaching* (NG 6480).
Macrophotograph of the tree in the centre of the painting.

identified the oil as walnut. A small amount of pine resin was also found in the sample.⁵⁶

Pigments and layer structure: the sky is painted with a layer of natural ultramarine mixed with white, over azurite mixed with white. The mid-blue drapery of the figure at the far left also consists of ultramarine painted over azurite. The mauve hose of the figure in the red cloak, on the left, consists of red lake, ultramarine and lead white, in two layers. The red cloak, also in several layers, contains red lake pigment mixed with a little vermilion in the shadows and some white in the highlights. The red glaze on Saint John's red cloak has been blotted with a textile (PLATE 32).

The deep green draperies contain verdigris⁵⁷ and are simply painted. The landscape varies in colour from strong pure greens to greenish and yellowish browns and is underpainted with a layer of yellowish green made up of azurite, lead-tin yellow, yellow earth and lead white. The upper layers, forming the contours of the landscape, contain verdigris and

lead-tin yellow and, in some parts, yellow earth. The browner areas, such as the detail in the bare lower part of the tussock on which the Baptist stands, are finished with thin translucent yellow glazes.

The foliage of the small delicate tree towards the centre of the composition is painted over both layers of the sky, while the trees on the left lie only on the underpaint. All the trees have an opaque yellowish-green underpaint of lead-tin yellow, yellow earth and a little verdigris. The final layers of dark green paint are mainly verdigris, with details in lighter opaque green (PLATE 33). There is some superficial discoloration of the deepest green paint.⁵⁸

There is gold on Saint John's halo and cross, around the neckline of the man nearest Saint John, and in the pattern on the chest and around the neckline of the man in a yellow tunic.

The paint generally contains particles of powdered glass of the composition found in the other pictures discussed here. Its presence has been confirmed by EDX analysis in the *imprimitura*, the grey hose of the figure fourth from the left and the brown foreground.

The Madonna of the Pinks (Madonna dei Garofani)

PLATE 34 (NG 6596)

Painted 1506–7. Panel, 28.8 × 22.9 cm. Painted area, 27.9 × 22.4 cm. Cleaned in 1991.⁵⁹

Because of the small size of the picture, and its beautiful state of preservation, it was only possible to take a very limited number of samples from the extreme edge of the painted surface under the frame. For the same reason the wood of the panel could not be sampled for positive identification. The painting was also studied under the stereomicroscope at magnifications of up to 80× and on the stage of the Leitz Aristomet research microscope at magnifications up to 400×.

Support and preparatory layers: a dense hardwood panel of a single plank, possibly cherry wood, with a gesso ground (FIGS 4 and 5). Over the gesso there is a thin *imprimitura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a small proportion of lead-tin yellow (EDX).

Underdrawing: full freehand underdrawing, over the *imprimitura*, in a very fine greyish-black line, identified by EDX as metalpoint composed of an alloy of lead and tin (PLATE 35).⁶⁰ Many exploratory passages and details, with some shading (FIG. 6) and



PLATE 34 (NG 6596)



FIG. 4 X-ray photograph of the *Madonna of the Pinks* (NG 6596). The erratic grain of the panel is particularly visible at the lower left, and the thin, but solid, modelling of the flesh paints is evident.

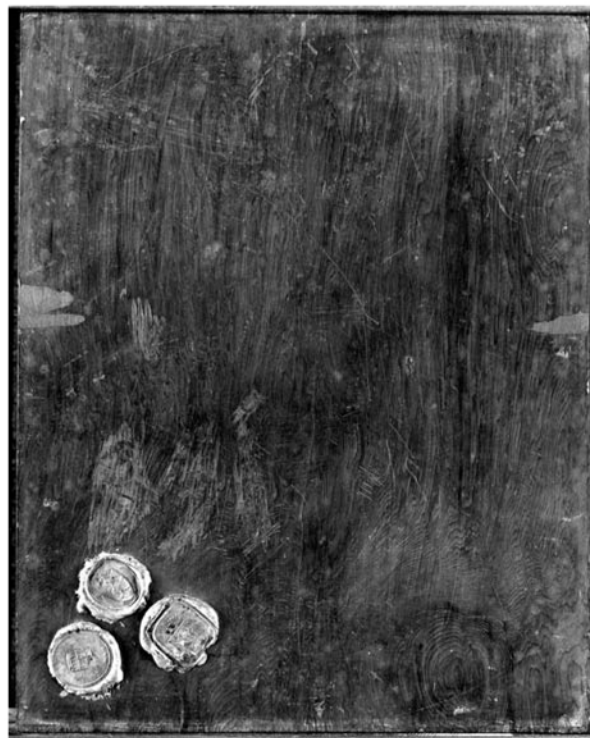


FIG. 5 Reverse of the *Madonna of the Pinks* (NG 6596). The back of the panel has a number of incised arcs of unknown function. Three red wax seals are evident, applied when the picture was in the Camuccini collection.

changes in design between the underdrawing and the painted image. There is no visible evidence from the infrared reflectogram mosaic for the use of a pricked cartoon (that is, pouncing), although it cannot be excluded that one was used.⁶¹

Paint binding medium: GC–MS analysis of samples from the yellowish-brown bench on which the Virgin sits, the blue sky and the off-white *imprimatura* identified the binding medium as heat-bodied walnut oil. The paint of the *imprimatura* was found to be lean in medium relative to the other areas analysed.

Pigments and layer structure: the small patch of blue sky to the right is painted in natural ultramarine (lapis lazuli) mixed with white (PLATE 37), and the same pigment forms the deepest blue surface paint of the Virgin's blue drapery, painted over an underlayer containing mineral azurite (PLATE 38). The rather greenish-blue azurite underlayer is left exposed in the shadows of the drapery. Azurite mixed with red lake pigment, white and a little black, in varying proportions, forms the range of mauvish-grey tones of the Virgin's dress; in the deepest shadows the proportions of red lake and

black pigment are at their greatest. A mauve colour, consisting of red lake and azurite, lies beneath the deep green curtain at the left, and can be glimpsed under magnification through small losses and cracks in the upper green paint layer; this is not underpainting but represents a notable change to the colour of the curtain made by Raphael in the course of painting.

The bench on which the Virgin sits contains lead-tin yellow (EDX). The same pigment has been identified microscopically in the Virgin's yellow sleeve and golden yellow drapery, where it has reacted with the oil medium to form lead soap inclusions. Again from microscopical examination, lead-tin yellow occurs in the paler yellow greens of the distant patch of landscape, combined with mineral malachite and verdigris, as well as in the green curtain to the left (where it is mixed with verdigris).

The sleeve of the Virgin's chemise cast into shadow, the tie on her sleeve and her belt contain a variety of pigments mixed with an unusual dark grey pigment, with a distinctive shiny, sparkling metallic lustre (PLATES 36 and 39). A pigment with the same microscopical appearance occurs in the *Procession to Calvary*, and in the *Ansidei Madonna*



FIG. 6 *The Madonna of the Pinks* (NG 6596). Infrared reflectogram mosaic revealing Raphael's detailed metalpoint underdrawing.



PLATE 35 *The Madonna of the Pinks* (NG 6596).
Macrophotograph of a line of metalpoint underdrawing (lead and tin alloy) over the *imprimatura* at the extreme left-hand unpainted edge.



PLATE 36 *The Madonna of the Pinks* (NG 6596).
Macrophotograph of the grey sleeve of the Virgin's chemise and the dark grey tie on the sleeve.



37 *The Madonna of the Pinks* (NG 6596).
micrograph of the surface of the sky paint with
and natural ultramarine, 160x.



PLATE 38 *The Madonna of the Pinks* (NG 6596).
Photomicrograph of the surface of the Virgin's deep blue
robe, showing ultramarine over a greenish-blue layer
containing azurite, 160x.



PLATE 39 *The Madonna of the Pinks* (NG 6596).
Photomicrograph of the right edge of the dark grey tie of
the chemise in PLATE 36, showing a pigment with a metallic
lustre which has the characteristics of bismuth, 160x.

where it was identified by EDX and XRD as powdered metallic bismuth (see above). A characteristic of this material is that it absorbs infrared light strongly. Even the light grey areas of the sleeve of the chemise appear dark in the infrared reflectogram mosaic (FIG. 6), which provides further evidence for the presence of bismuth.⁶²

There is a delicate and refined use of shell gold (powdered metallic gold pigment) in the haloes of the Virgin and the Child, and touches on the Virgin's belt.

The flesh paints are quite solidly modelled, in spite of their thinness, using lead-white and vermilion. The technique is comparable with the flesh painting in *An Allegory* ('*Vision of a Knight*') and, on a larger scale, *Saint Catherine of Alexandria*.

Saint Catherine of Alexandria PLATE 41 (NG 168)

Painted c.1507. Panel, 72.2 × 55.7 cm. Cleaned and restored at the National Gallery in 1967.

Support and preparatory layers: poplar panel, two members, vertical grain. Gesso ground, identified as gypsum (calcium sulphate dihydrate) by FTIR. Over the gesso there is a thin *imprimitura* composed of lead white, powdered glass (manganese-containing soda-lime type) and a low concentration of lead-tin yellow.

Underdrawing: very fine vertical and horizontal incised ruled axes. The position of the latter has been constructed using compasses. Traces of pouncing due to transfer of the design from a surviving pricked cartoon. The pounced design has been reinforced with black drawing; it is not possible to deduce from the character of the line whether the drawing was carried out with a dry or fluid material. There is also a great deal of freehand adjusting of contours (in the saint's face for example) and drapery folds. Ruled straight lines of rays of light from the sun are incised, as is her elliptical halo.



PLATE 40 *Saint Catherine of Alexandria* (NG 168). Detail of the landscape on the left of the painting.



PLATE 41 (NG 168)

Paint binding medium: analysis of samples by GC-MS showed the use of walnut oil in the sunlit sky, upper left; heat-bodied linseed oil with some pine resin in the red glazes on Saint Catherine's cloak and in the brownish-green shadows of the rock, lower left.

Pigments and layer structure: the purest blue of the sky consists of a single layer of natural ultramarine with white over the *imprimitura*. The more greenish-blue areas of the clouds contain some azurite mixed with ultramarine.

Saint Catherine's red drapery has final glazes of red lake pigment, with madder lake mainly in the lower layers (there is a characteristic fluorescence in UV light under the microscope) and kermes lake on top. The dyestuffs in the lakes have been identified by HPLC analysis. No vermilion has been used in the underlayers, which in the shadows contain only a small amount of lead white together with red lake. In lighter areas, more lead white is present in the underpaint and there is a little azurite, presumably to shift the colour subtly to a more purplish tone. The band of shadow along the outer edge of Saint Catherine's arm is reinforced in hatched strokes of red lake at the surface, which also accentuate the volume of the drapery.

Saint Catherine's wheel is simply painted in a single layer composed of lead-tin yellow, lead white, a yellow earth of intense colour, umber (manganese detected by EDX), vermilion, black and a little azurite. The greenish browns of the landscape make use of the same pigment mixture as the wheel, varying in their proportions according to the colour (PLATE 40). In the dark brown foliage of the small tree at the left edge, no discoloured copper green glazes are present, and the paint is composed of red and brown earth pigments, azurite and a little lead-tin yellow.

The paint generally contains particles of powdered glass of the composition found in the other pictures discussed here. EDX analysis has confirmed the presence of glass particles in samples from the red lake drapery, the yellow-brown paint of the wheel and the background landscape.

The rays of the sun and the saint's halo are lightly incised and the gold lines that follow the incisions appear to be shell gold. There is also gold on her neckline, belt, and around the cuff of her right sleeve.

Conclusion

The recent re-examination of the early paintings by Raphael in the National Gallery has brought to light further information on how Raphael transferred his designs for these works to the panel, for example the discovery of traces of a grid on the *Ansidei Madonna*, and of dots from the transfer of a pricked cartoon on the *Vision of a Knight*, *Saint John the Baptist Preaching* and *Saint Catherine*. Some new findings on the materials he employed in the course of preparing and painting the pictures have also emerged, such as the use of the rare dark grey metallic pigment bismuth, the presence of lead-tin yellow in the off-white *imprimitura* and the addition of powdered glass as a siccative for the oil. These last two technical features are not unique to Raphael, as recent comparative studies of sixteenth-century pictures at the National Gallery have begun to demonstrate, but they contribute to a fuller understanding of his specific technique and of technical developments in Italy and beyond.

Acknowledgements

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Notes and references

- 1 Chapman, Henry and Plazzotta, et al., *Raphael: From Urbino to Rome*, exh. cat., National Gallery, London 2004.
- 2 See J. Plesters, 'Technical Aspects of Some Paintings by Raphael in the National Gallery, London', in *The Princeton Raphael Symposium: Science in the Service of Art History*, Princeton Monographs in Art and Archaeology XLVII, eds J. Shearman and M.B. Hall, Princeton, New Jersey 1990, pp. 15–37 and figs 1–29; A. Braham and M. Wyld, 'Raphael's "S. John the Baptist Preaching"', *National Gallery Technical Bulletin*, 8, 1984, pp. 15–23. For accounts of the underdrawings of the *Procession to Calvary* and the *Garvagh Madonna*, see entries by C. Plazzotta in *Art in the Making: Underdrawings in Renaissance Paintings*, ed. D. Bomford, exh. cat., National Gallery, London 2002, pp. 122–35. For a description of the underdrawing and X-ray of the *Madonna of the Pinks*, see N. Penny, 'Raphael's "Madonna dei garofani" rediscovered', *Burlington Magazine*, CXXXIV, 1992, pp. 66–81. The latter painting had been on loan to the National Gallery from the Trustees of the 10th Duke of Northumberland's Wills Trust. It was acquired for the National Gallery in March 2004 with assistance from the Heritage Lottery Fund, the National Art Collections Fund, the American Friends of the National Gallery London, many private donors (including Sir Christopher Ondaatje) and members of the public. The *Mackintosh Madonna* (NG 2069, c.1509–11) was excluded because of its completely ruined condition. For the two Roman paintings in the National Gallery, the *Garvagh Madonna* (NG 744, c.1509–10) and *Pope Julius II* (NG 27, mid-1511), see J. Dunkerton and N. Penny, 'The Infra-red Examination of Raphael's "Garvagh Madonna"', *National Gallery Technical Bulletin*, 14, 1993, pp. 6–21, and C. Gould, *Raphael's "Portrait of Pope Julius". The Re-emergence of the Original*, London 1971. A full technical account of the latter is in preparation for future publication.
- 3 *The Madonna and Child Enthroned with Saints* (the *Colonna Altarpiece*), c.1504–5, New York, Metropolitan Museum, inv.16.30ab.
- 4 The history of these pictures and the circumstances of their commission are described by Cecil Gould in his *Catalogue of the Sixteenth Century Italian Schools*, and more recently in entries by C. Plazzotta in London 2004 (cited in note 1).
- 5 Shearman and Hall 1990 (cited in note 2).
- 6 Plesters in Shearman and Hall 1990 (cited in note 2), pp. 15–37 and figs 1–29.
- 7 Penny 1992 (cited in note 2), p. 67.
- 8 F. Mancinelli, 'La Trasfigurazione e la Pala di Monteluce: Considerazioni sulla loro tecnica esecutiva alla luce dei recenti restauri' in Shearman and Hall (cited in note 2), pp. 149–50.
- 9 *Raffaello a Firenze: Dipinti, e disegni delle collezioni fiorentine*, exh. cat., Palazzo Pitti, Florence 1984, p. 252. Limewood is more frequently found as a support in German paintings.
- 10 Entry by C. Bertelli (cat. no. 79, pp. 192–9), in *Pinacoteca di Brera. Scuole dell'Italia centrale e meridionale*, ed. C. Pirovano, Milan 1992, p. 193.
- 11 *Raffaello giovane e Città di Castello*, exh. cat., Pinacoteca Comunale, Città di Castello 1983–4, pp. 195–7; London 2004 (cited in note 1).
- 12 A considerable number of Raphael's works that are now on canvas are in fact transfers from their original panels undertaken in the eighteenth and nineteenth centuries, one of the most famous being *Saint Cecilia* (Bologna, Pinacoteca), which was transferred to canvas in France in 1805. R.R. Manaresi, 'A Technical examination of Raphael's *Santa Cecilia* with Reference to the *Transfiguration* and the *Madonna di Foligno*' in Shearman and Hall 1990 (cited in note 2), p. 126.
- 13 See, for example, V. Garibaldi, *Perugino: Catalogo completo*, Florence 1999, cat. no. 44, p. 42. See also Giovanni Santi's canvas painting of *Saint Jerome Enthroned* in the Vatican Museum Collection (Rome), no. 326 (231).
- 14 The use of an *imprimatura* containing lead white and a little lead-tin yellow is discussed in M. Spring, 'Perugino's painting materials: analysis and context within sixteenth-century easel painting', *Postprints of the workshop on the painting technique of Pietro Vannucci, called il Perugino*, organised by INSTM and LabS-TECH, Perugia, 14–15 April 2003, in *Quaderni di Kermes*, 2004, pp. 17–24. Examples on paintings from the period from all over Europe are reported, including paintings by Perugino.
- 15 An *imprimatura* containing lead white and traces of lead-tin yellow has been reported on Raphael's *Madonna del Cardellino* of around 1506 (Florence, Uffizi). See P. Riitano, 'Anticipazioni sulla pulitura della Madonna del Cardellino di Raffaello', *Restauri e Ricerche: Dipinti su tela e tavola*, eds M. Ciatti and C. Frosinini, Florence 2003, p. 71. Lead-tin yellow was also detected by XRF analysis in the *imprimatura* of the *Fornarina* (Rome, Palazzo Barberini), see R. Bellucci, M. Cetica, R. Coppola, P. Moio, P. Poggi, C. Silvestri and C. Seccaroni, 'Indagini su Raffaello: La Fornarina', *Kermes*, 49, Anno XVI, 2003, p. 66. In note 7 of the article it is stated that this type of priming is common on paintings of the period from Tuscany and Umbria and further examples are given. It has also been found on the *Garvagh Madonna* (NG 744), which was most likely painted in Rome.
- 16 For a general overview of Raphael's drawing practice, see P. Joannides, *The Drawings of Raphael*, Oxford 1983, pp. 11–31, and further F. Ames-Lewis, *The Draftsman Raphael*, New Haven and London 1986.
- 17 Raphael's use of cartoons is discussed in C. Bambach, *Drawing and Painting in the Italian Renaissance Workshop. Theory and Practice, 1300–1600*, Cambridge 1999, pp. 14–15 (where she notes that about one-sixth of Raphael's surviving drawings are either pricked for transfer or drawn on *spolvero* marks), and *passim*. Raphael later employed cartoons for large-scale projects in the Vatican, notably the frescoes in the Stanze and the tapestries for the Sistine Chapel.
- 18 Many worked-up composition drawings by Raphael are squared but do not correspond exactly to the finished painting, suggesting further intermediary stages in which the design was perfected. See, for example, the *modello* for the Baglioni *Entombment* discussed, *inter alia*, by Ames-Lewis 1986 (cited in note 16), p. 59, and Bambach 1999 (cited in note 17), p. 122.
- 19 A new infrared reflectogram mosaic of *Saint John the Baptist Preaching* has revealed the presence of previously undetected dots from pouncing. Infrared reflectogram mosaic details of the *Procession to Calvary* showing the use of pouncing first appeared in J. Meyer zur Capellen, *Raphael. A Critical Catalogue of His Paintings. Vol. 1. The Beginnings in Umbria and Florence, ca. 1500–1508*, Landshut 2001, pp. 180–1, but were extensively analysed by C. Plazzotta in London 2002 (cited in note 2), pp. 124–7. Further confirmation of the transfer method is provided by the survival of the pricked cartoon (New York, Pierpont Morgan Library) for the *Agony in the Garden* from the same predella (New York, The Metropolitan Museum). See again Meyer zur Capellen, pp. 176–8.
- 20 J.-D. Passavant (*Kunstreise durch England und Belgien*, Frankfurt am Main 1833, pp. 104–5) was the first to relate the cartoon to the painting when he recorded the two together for the first time in the collection of Lady Sykes; see also Plesters in Shearman and Hall 1990 (cited in note 2), p. 18.
- 21 Confirmation of the presence of dots from pouncing was first published in J. Dunkerton, S. Foister, D. Gordon and N. Penny, *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, London 1991, pp. 169–70.
- 22 A tracing of the figure of Saint Catherine was placed over the Louvre cartoon and the outlines were shown to coincide, except in the outline and features of the head which must have been adjusted at this late stage, possibly by reference to another drawing (see London 2004, cited in note 1). A map of the holes in the Louvre cartoon was then used to locate the dots from pouncing in the infrared reflectogram mosaic of the London painting. This work was carried out by R. Billinge, C. Plazzotta, J. Dunkerton and T. Henry, with the kind assistance of Catherine Goguel of the Département des Arts Graphiques at the Louvre.
- 23 The Perugian *pie* (foot) for woodwork and other purposes ('*da legname e fabbriche*') was apparently equivalent to about 36.4 cm. This was subdivided into 12 inches (*once*) of about 3 cm: see A. Martini, *Manuale di metrologia ossia misure, pesi e monete in uso attualmente e anticamente presso tutti i popoli* (Turin 1883), reprinted Rome 1976, p. 518. It should, however, be noted that another source gives a value of 36.6 cm to the foot measure used for agricultural and surveying purposes, while the general foot measure is given as about 33.4 cm, equivalent to half a *braccio lungo* (66.8 cm), so one *uncia* less. See *Tavole di ragguaglio sia le misure e pesi dello stato pontificio*, Rome 1857, pp. 651, 655–6. We are grateful to Jo Kirby for supplying this information.
- 24 Owing to the size of the panel it was not possible to carry out X-radiography.
- 25 For the results of analysis of the binding medium of the *Mond Crucifixion*, see J.S. Mills and R. White, 'The Gas Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis', in *Conservation and Restoration of Pictorial Art*, eds N. Brommelle and P. Smith, IIC Congress, Lisbon 1972, London 1976, Table 9.1, p. 74.
- 26 For example, the pair of panels by the workshop of Filippino Lippi, of about 1500: *Moses brings forth Water out of the Rock* (NG 4904) and *The Worship of the Egyptian Bull God, Apis* (NG 4905). See J.S. Mills and R. White, 'Organic Analysis in the Arts: Some Further Paint Medium Analyses', *National Gallery Technical Bulletin*, 2, 1978, pp. 74–5.
- 27 See Mills and White 1976 (cited in note 25). Results of analysis of the

- binding medium for the *Procession to Calvary* are published in R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 16, 1995, pp. 86–95. Plesters in Shearman and Hall 1990 (cited in note 2). See also note 56.
- 28 *La Pinacoteca Vaticana. Catalogo Guida*, eds C. Pietrangeli, A.M. De Strobil, F. Mancinelli, Rome 1993, p. 44.
 - 29 J. Dunkerton, 'Osservazione sulla tecnica della Madonna londinese di Giovanni Santi', in *Giovanni Santi, Convegno internazionale di studi, Urbino 1995*, ed. R. Varese, Milan 1999, pp. 57–60.
 - 30 Garibaldi 1999 (cited in note 13).
 - 31 D. Bomford, J. Brough and A. Roy, 'Three Panels from Perugino's Certosa di Pavia Altarpiece', *National Gallery Technical Bulletin*, 4, 1980, p. 30.
 - 32 J. Dunkerton and A. Roy, 'The Materials of a group of late Fifteenth-century Florentine Panel Paintings', *National Gallery Technical Bulletin*, 17, 1996, pp. 21–31.
 - 33 In addition to the hatched modelling very frequently seen in paintings and frescoes by Perugino, and used also by Raphael, Perugino often applied small brushstrokes and dots of brownish green in the landscapes of his compositions on panel and in fresco.
 - 34 D. Bomford, J. Dunkerton, D. Gordon and A. Roy, *Art in the Making: Italian Painting before 1400*, exh. cat., National Gallery, London 1989, p. 29 and catalogue entries; Dunkerton and Roy 1996 (cited in note 32).
 - 35 H. von Sonnenburg, 'The Examination of Raphael's Paintings in Munich' in Shearman and Hall 1990 (cited in note 2), pp. 65, 71–2 and figs 79–81.
 - 36 Von Sonnenburg in Shearman and Hall 1990 (cited in note 2), p. 72. See also H. von Sonnenburg, *Raphael in der Alten Pinakothek. Geschichte und Wiederherstellung des ersten Raphael-Gemäldes in Deutschland und der von König Ludwig I. erworbenen Madonnenbilder*, Ausstellung der Bayer. Staatsgemäldesamml. aus Anlaß des 500. Geburtstages, Munich 1983.
 - 37 M. Chiarini, M. Ciatti and S. Padovani, *Raffaello a Pitti 'La Madonna del baldacchino': storia e restauro*, Florence 1991.
 - 38 See M. Spring, R. Grout and R. White, 'Black Earths: A study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century', *National Gallery Technical Bulletin*, 24, 2003, pp. 96–114. Here bismuth and other dark grey pigments are discussed more fully. The occurrences of bismuth in paintings by Fra Bartolommeo are published in E. Buzzegoli, D. Kunzelman, C. Giovannini, G. Lanterna, F. Petrone, A. Ramat, O. Sartiani, P. Moiola and C. Seccaroni, 'The use of dark pigments in Fra' Bartolommeo's paintings', *Art et Chimie, la couleur*. Actes du Congrès, Paris 2000, pp. 203–8.
 - 39 The characterisation of manganese-containing soda-lime glass in paint and the range of occurrence of this material will be described in a paper currently in preparation by Marika Spring.
 - 40 Spring 2004 (cited in note 14).
 - 41 J. Kirby and R. White, 'The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use', *National Gallery Technical Bulletin*, 17, 1996, pp. 56–80.
 - 42 Analysis by Raymond White using GC–MS of a brown glaze sample over green undermodelling on Saint Nicholas of Bari's cope in the *Ansidi Madonna* revealed this to contain partially heat-bodied walnut oil with a diterpenoid resinous component. The presence of retene, with a high level of 7-oxo-dehydroabietic acid and lesser amounts of dehydroabietic acid, indicates the product of pyrolysis on conifer resin or softwood (a conifer-based resin or softwood pitch).
 - 43 Silver was confirmed by laser microspectrography (LMA).
 - 44 The presence of glass has been confirmed by EDX analysis on samples from the brownish-gold ray of the sun, the ochre-brown shadow of the left leg of the angel in yellow and Saint John's red drapery.
 - 45 In the back-scattered image in the scanning electron microscope of a sample of the gilded pattern on the green cloak of Saint John it could be seen that the gold was not a continuous layer of gold leaf but was in the form of flakes. It is therefore likely to be shell gold. It seems more substantial than is usual for shell gold, but is similar to the gilding on the border of Saint John's robe in the *Ansidi Madonna*, where it is more certain that it is shell gold.
 - 46 Plesters in Shearman and Hall 1990 (cited in note 2), p. 17.
 - 47 The ornament-containing sleeves are a rather dull brownish-yellow colour; the pigment may have deteriorated.
 - 48 Samples from the priming layer, the sky paint and the green foreground were found to contain oil by FTIR microscopy. The presence of agglomerations of lead soaps, together with other bands indicative of a drying oil, was confirmed by FTIR microscopy. Additional bands at around 1620–50 cm⁻¹ and 1520–50 cm⁻¹ are more problematic. These could correspond to amide bands from a proteinaceous material, but could also arise from powdered glass (known to be present in the paint from EDX analysis) and lead soaps. The fact that relatively large lead soap agglomerations are visible in cross-sections of paint from these areas (suggestive of the use of an oil medium) makes it more likely that these IR bands arise from the glass and soaps rather than from the presence of a proteinaceous binding medium. Similarly, the pigments in Christ's blue robe interfered with the interpretation of the FTIR spectrum, but on balance it was concluded that the binding medium was likely to be oil.
 - 49 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.
 - 50 White and Pilc 1995 (cited in note 27). The results of analysis of four samples are reported. An egg tempera medium was noted in the dark blue paint of the distant landscape, the red drapery of Saint John and (together with walnut oil) in the green dress of the figure at the extreme left edge.
 - 51 The azelate/palmitate ratio reported in the earlier series of analyses of a sample from the pink robe by GC–MS was lower than would be expected for an oil medium, and so was interpreted as indicating the use of an egg tempera binding medium. However, recent work on the interaction of lead pigments with the oil medium has shown that the azelate level detected by GC–MS can sometimes be low even where the binding medium is drying oil. See Higgitt, Spring and Saunders 2003 (cited in note 49). Although the reason for this is not yet fully understood, there is some evidence to suggest that it is likely to affect paints containing 'alkaline' pigments such as red lead, lead-tin yellow and ultramarine. The powdered glass found in the cream underpaint of Saint John the Baptist's robe, and also in most of the other areas of the painting (except the dark greens), falls into this category of pigment.
 - 52 For a fuller discussion of this pigment and illustrations of the infrared images see Spring, Grout and White 2003 (cited in note 38).
 - 53 One of the constituents found in this sample by HPLC analysis has been reported in brazilwood samples by Witold Nowik. The constituent is brownish yellow in colour. See W. Nowik, 'The Possibility of Differentiation and Identification of Red and Blue "Soluble" Dyewoods. Determination of Species used in Dyeing and Chemistry of their Dyestuffs', *Dyes in History and Archaeology*, 16/17, 2001, pp. 129–44. The spectrum is illustrated on p. 136, although the constituent (often known as Nowik 'type C') has not been identified. A brazilwood lake prepared at the National Gallery in 1972 by Jo Kirby that had faded in the dark by 1974 was found, on HPLC analysis, to contain a large amount of the Nowik 'type C' component and little of anything else related to brazilin, the colouring matter of brazilwood.
 - 54 D. Saunders and J. Kirby, 'Light-induced Colour Changes in Red and Yellow Lake Pigments', *National Gallery Technical Bulletin*, 15, 1994, pp. 79–97.
 - 55 Spring, Grout and White 2003 (cited in note 38).
 - 56 The results of the earlier campaign of medium analysis are published in Plesters in Shearman and Hall 1990 (cited in note 2), p. 36. Here, the GC results from a sample of sky paint are interpreted as being indicative of an egg tempera medium, on the basis of the detected azelate to palmitate ratios. The recent analysis by FTIR of another sample of sky paint, however, showed that the medium was oil. The possible causes of azelate levels lower than would be expected for typical aged drying oils are discussed in note 51.
 - 57 Some chlorine was detected in the verdigris glaze by EDX analysis, suggesting that it contains a small amount of copper chloride. This is likely to be a secondary product resulting from the method of manufacture of the verdigris.
 - 58 In cross-section a thin brown layer is visible on the surface of the green glaze. This is not a separate glaze layer and may have formed as a result of reaction of the verdigris with an early varnish.
 - 59 *The Madonna of the Pinks* was cleaned and restored by Herbert Lank for the then owner of the picture, the Duke of Northumberland.
 - 60 Similar metalpoint underdrawing, using a stylus made from an alloy of lead and tin, has been identified, also by EDX analysis of a sample, on the *Garvagh Madonna* (NG 744), see Plazzotta in London 2002 (cited in note 2), p. 130.
 - 61 Bambach 1999 (cited in note 17). R. Hiller von Gaertringen, *Raffaels Lernerfahrungen in der Werkstatt Peruginos: Kartonverwendung und Motivübernahme im Wandel*, Munich 1999, pp. 247–51.
 - 62 Recent infrared examination by Rachel Billinge of the *Ansidi Madonna* (NG 1171) has demonstrated that areas known to contain metallic bismuth (the architectural arch) and presumed to contain this pigment (Saint Nicholas of Bari's grey inner garments) register as notably dark images in infrared light, in spite of the fairly light grey appearance of the paint layer. See also Spring, Grout and White 2003 (cited in note 38), pp. 104–5.