Raphael's Materials: Some New Discoveries and their Context within Early Sixteenth-Century Painting

Marika Spring
Scientific Department of The National Gallery, London

The paper by Joyce Plesters in the publication that resulted from the Princeton Raphael symposium of 1983 established the basic palette of most of the paintings by Raphael in the National Gallery.[1] The preparation for the exhibition *Raphael: from Urbino to Rome* (National Gallery, October 2004 – January 2005) was an opportunity for technical examination of those paintings not included in Plesters' paper, and for re-examination of the materials in the other works with the more sophisticated analytical techniques that have since become available. The results of this work were published in detail in Volume 25 of the National Gallery Technical Bulletin (2004),[2] so this paper will not give a full description of the materials of each painting. Instead, it will concentrate on the two new materials that were discovered – bismuth metal powder and colourless powdered glass – and place them in context by drawing comparisons with other sixteenth-century paintings in the National Gallery.

Bismuth metal powder

Bismuth metal powder was used as a dark grey pigment in the architecture of Raphael's *Ansidei Madonna* (National Gallery, London, NG 1171), which is dated 1505 (Fig. 1). Distinctive small pinkish-grey particles with a metallic lustre (mixed with lead white) are visible in a cross section from the architecture (Fig. 2). These were found by EDX analysis in the scanning electron microscope to contain bismuth and identified as metallic bismuth by x-ray diffraction.[3] Once ground to a powder to be used as a pigment, bismuth does not have a metallic lustre, so Raphael did not use it to give the paint a metallic appearance. It is not the only black pigment used in the painting – coal black with a deep velvety brownish hue was used in small amounts mixed with other pigments in the shadows of some of the draperies. This suggests that Raphael deliberately chose the bismuth pigment for the architecture, probably because it is a dark grey rather than a true black.

Bismuth was probably also used in the paint of the grey horse in Raphael's *Procession to Calvary* (National Gallery, London, NG 2919); no samples were taken from this area, so this has not been confirmed by analysis, but a pigment with a very similar appearance to that in the architecture in *The Ansidei Madonna* was seen when examining the surface with a stereomicroscope. Further evidence that the pigment is bismuth is provided by the infrared reflectogram, where the shadows on the horse appear very dark grey, even though under normal light they are a relatively light grey colour; this is characteristic of bismuth, which has a strong infrared absorption. The pigment was almost certainly also used in the grey underchemise of the Madonna in the *Madonna of the Pinks* (National Gallery, London, NG 6596), discussed in the paper by A. Roy in this volume, although again it was not possible to sample the paint to confirm this by analysis.

A bismuth-containing grey pigment was reported for the first time in a number of paintings by Fra Bartolommeo.[4] One other occurrence of bismuth as a pigment has been identified in a painting in the National Gallery, in Francesco Granacci's *Portrait of a Man in Armour*, which was painted in Florence and is thought to date from about 1510.[5] Here it was used for the grey mid-tones and highlights of the man's armour (with the deeper black coal being used for the deepest shadows) and was also mixed with other pigments in the brown wall behind the figure. A further occurrence in an Italian work is reported in the paper in this volume by I. Borgia et al., in the predella for Perugino's Altarpiece in Santa Maria Nuova at Fano (1497). In the panels of the predella it was used for the pale grey shadows of white draperies (but not in the architecture).

The main use of bismuth in the period in which Raphael was working was in alloys for type metal, but in Southern Germany bismuth was being used to imitate metal leaf on decorated wooden boxes, a technique known as *wismutmalerei*.[6] It has also been reported in a German bible of the fifteenth century, where it was used to imitate silver ink.[7] Recently Nancy Turner and Karen Trentelman at the Getty Conservation Institute have identified bismuth in the miniatures in the illuminated manuscript *The Hours of Louis 12th* from around 1500, by Jean Bourdichon, who was working in Tours. It was found in dark brown and grey paint in the landscape, tree trunks, and shadows of architectural elements.[8] This is closer to the way in which bismuth powder was being used by Raphael, since it is being used as a grey pigment rather than to imitate silver.

It was also used in other branches of the arts, for example in the lustre ceramics being produced during Raphael's time in the Umbrian towns of Gubbio and Deruta.[9] Interestingly there is some evidence that the use of bismuth in lusterware is characteristic of that produced in Gubbio; it has not been

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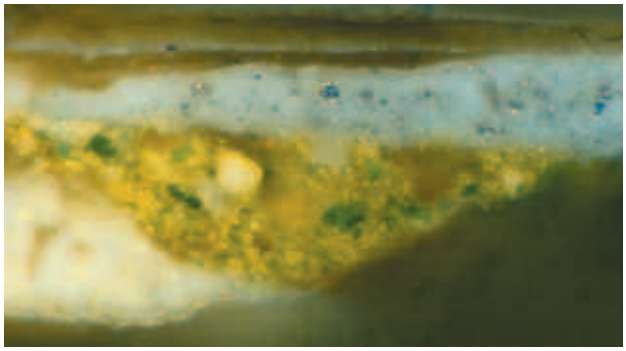

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Fig. 1 – Raphael, The Ansidei Madonna *(NG 1171). Detail showing the pale grey architecture painted with bismuth.*

Fig. 2 – Raphael, The Ansidei Madonna*(NG 1171). Cross section from the architecture. The uppermost grey layer contains pinkish-grey particles with a metallic lustre which are bismuth, mixed with lead white and some angular colourless particles of glass.*

found in Spanish lustre pottery of the same period.[10]

Bismuth doesn't seem to have been a material that was difficult to obtain, but nevertheless it was rare to use it as a pigment. All the occurrences known so far date from the very end of the fifteenth century and the first two decades of the sixteenth century. In the same period, a few other artists seem also to have been experimenting with grey pigments, using other materials with similar properties to bismuth powder, perhaps to expand their palette with the aim of achieving more subtle colours. For example on the *Certosa di Pavia* altarpiece by Perugino a grey tin-rich bronze metal powder was used for Saint Michael's armour and the pale grey underpaint of the Angel Raphael's blue dress.[11] Other artists used stibnite (antimony sulphide) and galena (lead sulphide), which although not metallic, are materials that have a metallic lustre in bulk form. In fact the similar properties and appearance of all these materials meant that at this period the distinction between them was not clear and they were often confused with each other or with the corresponding metal.[12]

Stibnite has already been reported in paintings by Correggio, Fra Bartolomeo, Francesco Bonsignori, Lorenzo Costa and in the *Deposition* begun by Filippino Lippi but completed by Perugino (Accademia Gallery, Florence). In an altarpiece of *The Virgin and Child with Saints* by Gianfrancesco Maineri and Lorenzo Costa (National Gallery, London, NG 1119), from about 1499, galena, (lead sulphide) was used for the armour of the saint.[13] In Marco Marziale's *Circumcision* (National Gallery, London, NG 803, Fig. 3), signed and dated 1500, both stibnite and galena were used, mixed together in the grey decorative border of the red cloak of the boy kneeling in the foreground of the painting (Figs. 4 and 5).[14] These pigments have such similar properties that it seems unlikely that these artists knew which they were using, and they can therefore be treated as a group. The occurrences found so far do seem to indicate that in easel painting at least their use in Italian easel paintings is restricted to the late fifteenth and early sixteenth century.

Colourless powdered glass as a drier

The other new discovery during this recent campaign of technical examination was that a colourless glass, ground into a powder, had been mixed into the paint in all of the works by Raphael that were examined (Table 1).[15] It was most abundant in the red lake glazes, but had also been mixed into other colours of paint and into the pale yellow priming layer.[16]

Figure 6 shows a cross section from the red drapery of the figure of Saint John the Baptist in the *Ansidei Madonna* (NG 1171, see Fig. 11 in the contribution by Billinge in this volume), which is one of the areas in which glass was found. At the bottom of the cross section is the off-white priming, above which are several paint layers containing red lake mixed with a small amount of vermilion. Under ultraviolet light (Fig. 7), the separate layers of paint become visible, as well as many distinctive angular jagged particles which are glass. It is also present in the off-white priming (mixed with lead white and a small amount of lead-tin yellow), and here it is clear that it is colourless. A priming of identical composition was found on all the early paintings by Raphael in the National Gallery that it was possible to sample.

Powdered glass was also used extensively in Raphael's *Mond Crucifixion* (National Gallery, London, NG 3943, see Fig. 7 in the contribution by Billinge in this volume), including in Saint John the Evangelist's red cloak. In dispersions of the red paint from the Saint's cloak the particle characteristics of the glass particles can be seen more clearly. The particles show the characteristic conchoidal fracture, stress lines and jagged edges typical of broken glass (Fig. 8). These characteristics distinguish it from silicaceous minerals, which can otherwise appear quite similar under the microscope.

The red cloak in Raphael's *Saint Catherine of Alexandria* (National Gallery, London, NG 168, Fig. 3 in the contribu-

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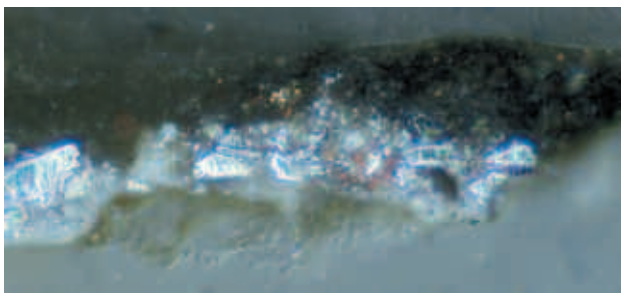

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Fig. 3 – Marco Marziale, The Circumcision *(NG 803).*

Fig. 4 – Marco Marziale, The Circumcision *(NG 803). Detail showing the boy in a red cloak with a grey decorated border.*

Fig. 5 – Marco Marziale, The Circumcision *(NG 803). Cross section from the grey border of the kneeling boy's red cloak showing particles of galena and stibnite with a metallic lustre.*

tion by Billinge in this volume) also contains powdered glass. As in the examples mentioned above the particles are not immediately obvious in the cross section when viewed under the microscope with normal light. They are however easily visible in the back-scattered image in the scanning electron microscope. The light grey angular particle in the middle of the image in figure 9 is a particularly large particle of glass, approximately 30 microns in size, within a matrix of red lake pigment. The glass particles were analysed by EDX and the composition was found to be very consistent. The EDX spectrum in figure 10 shows the elements present in the particles, which are typical of the range that would be expected to be present in glass; silicon is of course the major component; also present are sodium, magnesium, aluminium, potassium, calcium, titanium, manganese and iron.

Glass is made from a silica source such as sand or pebbles, and a flux, which at this period would have been some kind of plant ash. A variety of plant ashes were used, which are of different compositions, reflected in the bulk composition of the glass.

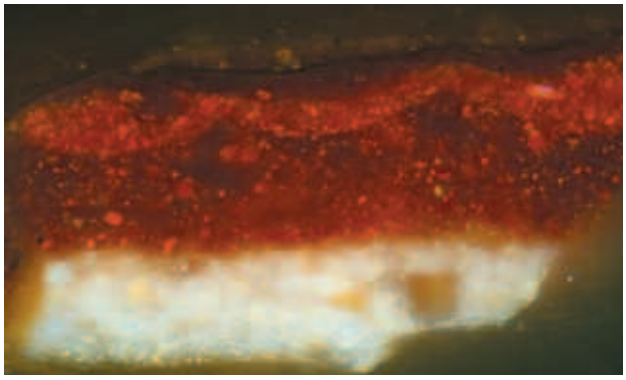
From the results of quantitative analysis of the glass in Raphael's *Saint Catherine* the type of glass can be determined (see Table 2). The glass is rich in sodium, nearly 12%, so it is therefore a soda-lime glass, made with ashes from marine plants as a flux. The other elements also come from the plant ash. The levels at which these are present indicate ordinary colourless glass rather than the higher quality *cristallo* glass, which used purified plant ash.[17] The glass also contains some manganese, which could have come

Table 1: Occurrences of manganese-containing powdered glass confirmed by analysis in paintings by Raphael in the National Gallery, London.

Painting title, cat. no. and date	**Areas in which powdered glass was confirmed by EDX analysis**
The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion), NG 3943, c.1502–3.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow. - Saint John's red drapery, mixed with red lake. - Brownish-gold sun ray, mixed with orpiment and a little lead-tin yellow. - Brown shadow of the drapery of the angel in yellow, mixed with black, vermilion, red earth and red lake.
The Procession to Calvary, NG 2919, c.1504–5.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow. - Pale pink underpaint of Saint John's red drapery, mixed with lead white and faded red lake. - Greenish paint of the foreground, mixed with lead white, lead-tin yellow, yellow earth and azurite. - Orange-yellow tunic of the man on the brown horse, mixed with lead-tin yellow and yellow earth. - Saint Catherine's red cloak, mixed with red lake. - Yellow-brown paint of the wheel, mixed with lead white, red earth, umber and a little azurite and vermilion. - Brownish-green paint of the background landscape, mixed with lead-tin yellow, azurite, yellow earth and a little black.
The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansidei Madonna), NG 1171, 1505.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow. - Dark purple underside of the canopy over the throne, mixed with red lake, with a little vermilion and black. - Saint John's red drapery, mixed with red lake. - Pale grey architecture, mixed with lead white and bismuth metal powder. - Mordant for the gilded decoration on the throne (used alone). - Yellow of the 'wood' on the throne, mixed with lead-tin yellow and a little orange-red earth.
Saint John the Baptist Preaching, NG 6480, 1505.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow. - Grey hose of the figure fourth from the left, mixed with lead white and coal black. - Red of cloak of figure second from the left, mixed with red lake and vermilion. - Brownish-green foreground, mixed with lead white, lead-tin yellow and a little azurite and verdigris.
The Madonna of the Pinks, NG 6596, c.1506–7.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow.
Saint Catherine of Alexandria, NG 168, c.1507.	- Pale yellow priming, mixed with lead white and a little lead-tin yellow. - Saint Catherine's red cloak, mixed with red lake. - Yellow-brown paint of the wheel, mixed with lead white, red earth, umber and a little azurite and vermilion. - Brownish-green paint of the background landscape, mixed with lead-tin yellow, azurite, yellow earth and a little black.

Table 2 - Quantitative analysis of powdered glass particles, normalised and expressed as weight % oxide.

Artist, Painting title, cat. no. and date	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**FeO**	**Glass type**
Raphael, *Saint Catherine of Alexandria* (NG 168), c. 1507.	11.42	2.64	3.36	66.49	0.51		3.64	8.29	0.10	2.33	0.70	Soda-lime
Dirk Bouts, *Christ crowned with Thorns* (NG 1083), c. 1470.	1.88	3.59	4.37	58.13	4.14	1.24	3.70	19.69	0.28	0.94	0.31	High lime
Master of the Saint Bartholomew Altarpiece, *Saints Peter and Dorothy* NG 707), 1505–10.	1.64	3.00	1.83	58.91	3.12	0.81	4.93	23.42	0.33	0.73	0.64	High lime
Workshop of Durer, *Virgin and Child* (NG 5592), 1500–10.	2.32	3.36	5.64	55.16	3.49	1.80	4.87	20.95	0.25	1.03	0.49	High lime
Maarten van Heemskerck, *The Virgin and Saint John the Evangelist* (NG 6508.1), c.1540.	1.91	4.93	1.68	55.80	3.39	0.53	11.58	17.74	0.31	0.85	0.80	Mixed alkali
Jan van Eyck, *The Arnolfini Portrait* (NG 186), 1434.	1.41	2.85	2.61	53.11	4.26	1.83	11.62	17.97	0.18	1.10	1.14	Mixed alkali
Rogier van der Weyden, *The Magdalen Reading* (NG 654), before 1438.	0.29	2.28	2.27	49.85	4.10	6.97	16.35	14.85	0.45	1.38	0.24	Mixed alkali



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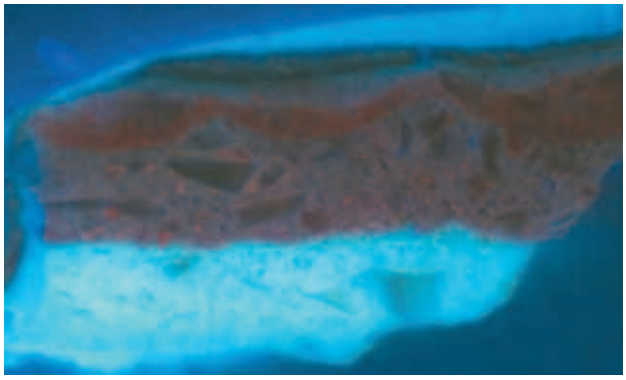

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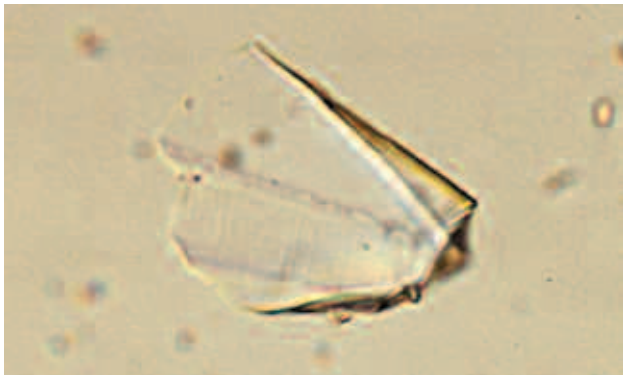

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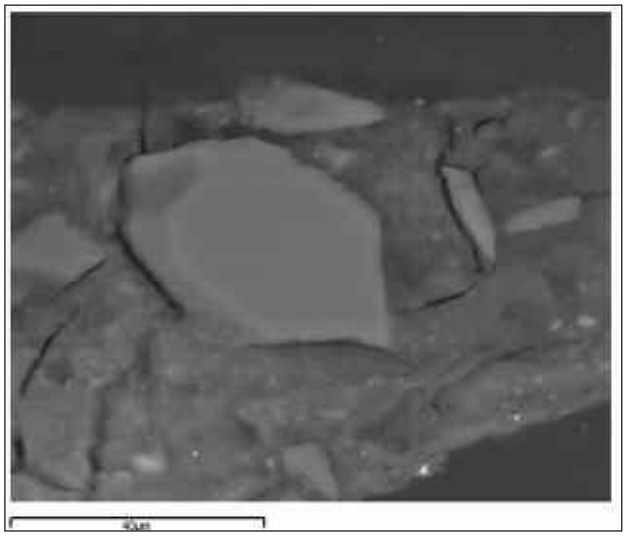
Fig. 6 – Raphael, The Ansidei Madonna *(NG 1171). Cross section from the red drapery of Saint John the Baptist.*

Fig. 7 – Cross-section in Fig. 6 under ultraviolet light.

Fig. 8 – Raphael, The Mond Crucifixion *(NG 3943). Dispersion of paint from Saint John's red drapery showing a particle of glass.*

from the plant ash, or could have been added deliberately in the form of manganese oxide; in either case it would act as a decolouriser by counteracting the naturally green tinge given by the low levels of iron usually present in the sand or pebbles which are the silica source.

The results listed in the table are an average taken from spot measurements from several particles in one sample, or



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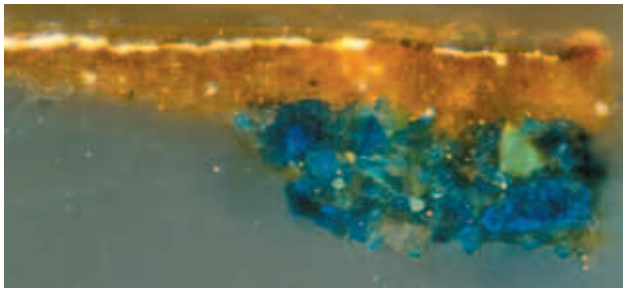

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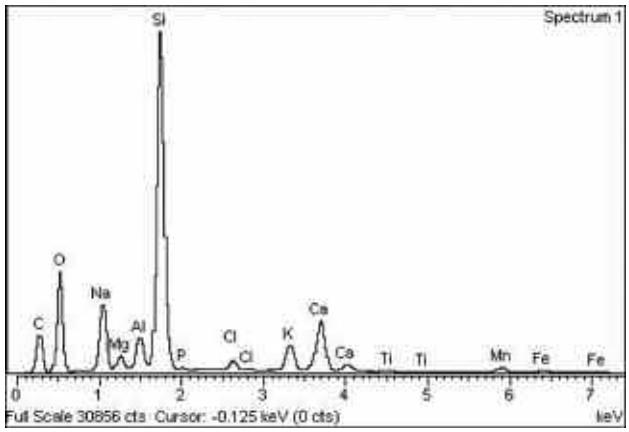

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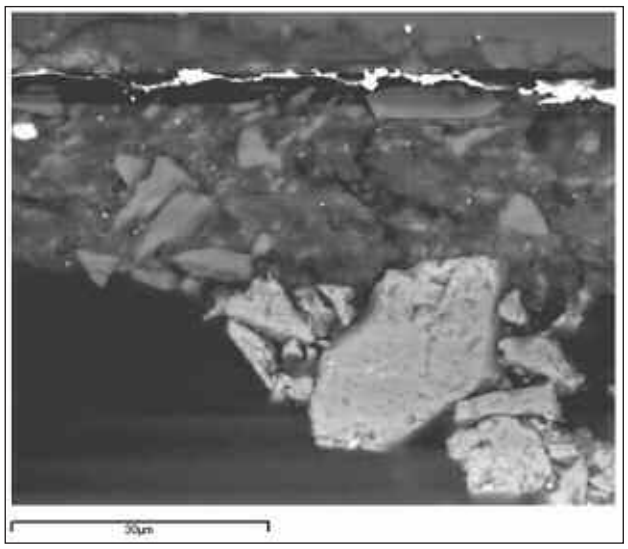

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Fig. 9 – Raphael, Saint Catherine of Alexandria *(NG 168). Back-scattered image in the SEM of a cross-section from Saint Catherine's red cloak.*

Fig. 10 – Raphael, Saint Catherine of Alexandria *(NG 168). EDX spectrum of the large glass particle in the centre of Fig. 9.*

Fig. 11 – Raphael, The Ansidei Madonna *(NG 1171). Cross section of the mordant gilding on the throne showing the translucent yellow mordant layer immediately beneath the gold leaf.*

Fig. 12 – Raphael, The Ansidei Madonna *(NG 1171). Back-scattered image in the SEM of part of the cross-section in Fig. 11.*

in different samples from various areas of a painting. Limitations on the accuracy of the quantitative results were the small size of the particles and the fact that they were mixed with pigments. Analysis of Corning glass standards indicated that generally the sodium values were too low and the accuracy of elements present in small amounts was not particularly high. Despite this, the quantitative results are accurate enough to indicate the type of glass, although they do not bear more detailed further interpretation. Loss of alkali ions (particularly sodium) due to migration of the alkali ions during analysis, or due to deterioration of the glass, also needs to be considered.[18]

The manganese content of the glass is key in understanding its function in the paint. Powdered glass is mentioned as a siccative for oil paint in several seventeenth-century treatises,[19] as well as in Haydocke's 1593 translation of Lomazzo,[20] and the fact that the glass contains manganese means it is capable of acting as a dryer. It would have been a very suitable siccative for paint containing red lake since is transparent and colourless. The context in which it is found in Raphael's paintings also suggests that it was used as a dryer.

Figure 11 shows a cross section from the mordant gilding on the throne in Raphael's *Ansidei Madonna*. The mordant layer immediately beneath the gold leaf consists entirely of powdered glass, with the translucent yellow colour of the layer coming from the discoloured oil binder. These are visible in the back-scattered image of the cross section (Fig. 12). Here the glass could not have had an optical function because the mordant is hidden beneath the gold leaf, and is not an extender since it has been used on its own, so must have been used as a siccative for the oil. Powdered glass was found mixed with cheap pigments such as earths in Raphael's paintings, which also argues against it being an extender (see Table 1).

Raphael did also add glass to paint consisting mainly of lead white, such as the priming layer on all the paintings, and the grey architecture on the *Ansidei Madonna* (see Fig. 2). Lead white paint dries without the need for addition of a siccative, so this might seem inconsistent with the argument presented above on the function of the glass. However, an English documentary source mentions using glass as a drier even with white; the painter Marshall Smith, in 1692, stated that 'For your Powder-Glass, take the whitest Glass, beat it very fine in a Morter, and grind it in water to an Impalpable powder; being thoroughly dry, it will dry all Colours without drying Oyle, and not in the least Tinge the purest Colours, as

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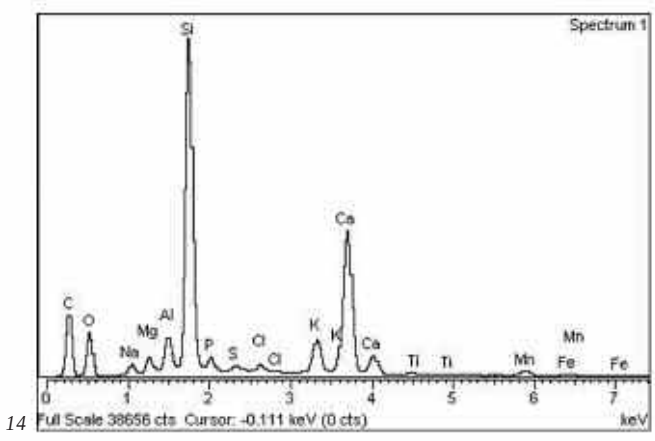

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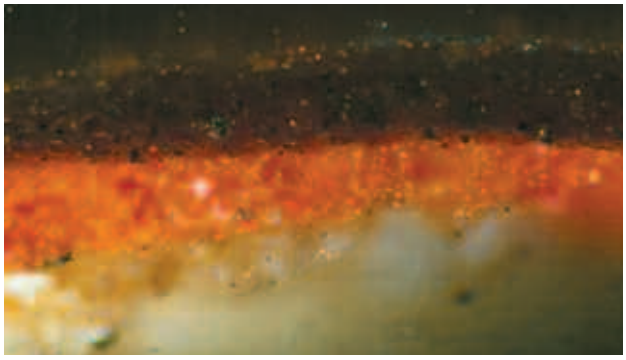
Fig. 13 – Dirk Bouts, Christ crowned with Thorns *(NG 1083).*

Fig. 14 –Dirk Bouts, Christ crowned with Thorns *(NG 1083). EDX spectrum of a glass particle in the red lake glaze.*

White, Ultramarine etc. and is much us'd in Italy'.[21] Although the source is from a later period, it might still suggest that there was some confusion about which pigments required a drier. Also of interest is the fact that Marshall Smith prescribes 'the whitest glass'. Since manganese is present in white or colourless glass, counteracting the green colour that glass naturally has because of the small iron content of the silica source used to manufacture it, it would have been more effective as a siccative than greenish glass.[22]

Marshal Smith's comment that glass 'was much used in



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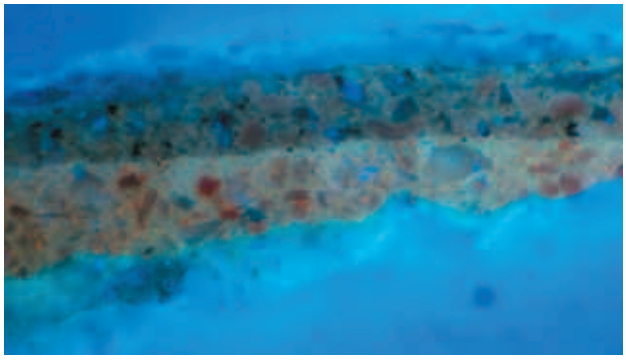

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Fig. 15 – Martin van Heemskerk, Virgin and Saint John the Evangelist *(NG 6508.1). Cross section from Saint John's red robe.*

Fig. 16 – Cross section in Fig. 16 under ultraviolet light.

Italy' has proved to be quite accurate. So far, the presence of glass in over 30 paintings of this period in the National Gallery from all over Italy has been confirmed, and this number is increasing all the time.[23] It has also been found extensively in works by Perugino, as reported at the Labstech workshop on Perugino's painting technique in Perugia in 2003, and many of the contributions to this volume give further examples in paintings by Raphael.[24]

With the aim of attempting to trace the use of colourless powdered glass to the previous generation of artists, samples from the archive of cross sections in the National Gallery Scientific Department were re-examined. A number of earlier examples were discovered, including in red lake-containing oil glazes on the Virgin's robe in *The Virgin and Child* dating from around 1488 by Raphael's father Giovanni Santi (National Gallery, London, NG 751), who was working in Urbino. Another example was found in a painting depicting an allegorical figure of *Music* (NG 756), attributed to Justus of Ghent and workshop, which was probably painted in Urbino. This painting is thought to date from the 1470s, so is the earliest Italian painting in which it has been found so far.

When the Early Netherlandish and German paintings in the National Gallery were being examined for the revised scholarly catalogues, silicaceous particles were found in red lake glazes on many of the paintings. Having found powdered glass in the paintings by Raphael, it was realised that these silicaceous particles were also powdered glass. One example was *Christ crowned with Thorns*, attributed to Dirk Bouts (National Gallery, London, NG 1083), where again it was found in the red lake glazes of Christ's cloak (Fig. 13). In the back scattered image of Christ's cloak the glass particles (which are lighter grey than the red lake matrix) can be seen to be much smaller than in the paintings by Raphael (only around 2 –3 microns), and this was true generally of the Netherlandish and German paintings.

Figure 14 shows the EDX spectrum of one of the particles of glass, showing the series of elements that would be expected for glass. The relative size of the peaks is different to the EDX spectra of glass from Italian paintings however, and the quantitative analysis shows that this glass is not of the same composition, but is instead a different type of glass (Table 2). The percentage of sodium is rather low, so it was not made with marine plant ash but from wood or fern ash. The calcium content is high, averaging around 20%. This is typical of high lime glass which, according to the literature on the analysis of vessel glass, was common from the middle of the fifteenth century to the end of the sixteenth century.[25] The same type of glass was found in *Saints Peter and Dorothy* by the Master of the Saint Bartholomew Altarpiece (National Gallery, London, NG 707), which was painted in Cologne at the beginning of the sixteenth century, and also in the *Virgin and Child* from the same period attributed to the workshop of Durer (National Gallery, London, NG 5592).

In the *Virgin and Saint John the Evangelist* by Martin van Heemskerk (National Gallery, London, NG 6508.1), glass was abundantly used in the red of Saint John's robe, as can be seen in the cross section under ultraviolet light (Figs. 15 and 16). The glass here was found to be of a slightly different composition to that in the Northern European paintings mentioned above. Both the EDX spectrum and the results of quantitative analysis show that it contains very little sodium so, in common with the other Northern European examples, it was not made with marine plant ash. However, the levels of calcium are lower and potassium a little higher; this type of glass, which is usually called mixed-alkali glass, has also been found in vessel glass of the period, and the literature suggests that a different type of wood or fern ash was used than for the high-lime glasses.[26]

So far, the presence of glass has been confirmed in 18 northern European paintings. The earliest of these are Jan van Eyck's *Arnolfini Portrait* of 1434 (National Gallery, London, NG 186), where a mixed- alkali glass was used in the red glazes on the bed, and *The Magdalen Reading* by Rogier van der Weyden from before 1438 (National Gallery, London, NG 654) where the same type of glass was used for the red drapery at the left edge.

Although Raphael's paintings were the first in which manganese-containing colourless powdered glass was confirmed, it has become clear that it was used extensively in every part of Europe at this period already before his time. The regional variation in the composition of the glass is also interesting. All the glass found in Italian paintings was soda-lime glass. In Netherlandish and German paintings however, no soda-lime glass has been found so far; instead it can be identified by quantitative analysis as either high-lime or

mixed-alkali glass. Soda-lime glasses could be made in northern Europe, but because the raw materials had to be imported it would have been more expensive. Painters seem instead to have used ordinary locally-made cheaper colourless glass. More analysis is needed before this trend can be firmly established, but the composition of the glass seems to have the potential to be an indicator of the geographical location in which the painting was made, in the same way as chalk and gesso grounds.

In the Northern European paintings the glass was generally found only in red lake glazes, where a drier that did not affect the translucency of the paint would be desirable. Raphael used it much more abundantly in his paintings, and it was clearly fundamental to his oil painting technique.

Notes and references

1. Plesters J., '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 Shearman J. and Hall M.B., Princeton, New Jersey 1990, pp. 15–37 and figs. 1–29.
2. Roy, A., Spring M., and Plazzotta C., 'Raphael's Early Work in the National Gallery: Paintings before Rome', *National Gallery Technical Bulletin*, 25, 2004, pp. 4–35.
3. The identification of this pigment has already been discussed in Roy, A., Spring M., and Plazzotta C. cited in note 2, Spring M., Grout R., and White R., '"Black Earths": A Study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century,' *National Gallery Technical Bulletin*, 24, pp. 96–114, and Spring M., 'Perugino's painting materials: analysis and context within sixteenth-century easel painting', in Brunetti, B.G., Seccaroni, C. and Sgamellotti, A., eds., *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS Tech Workshop, Quaderni di Kermes*, Florence 2004, pp. 21–28.
4. Moioli P., Scafè R. and Seccaroni C., 'Appendice I, Analisi di fluorescenza x su sei dipinti di Fra' Bartolomeo', and Lanterna G. and Matteini M., 'Appendice II, Analisi SEM/EDS di un campione di film pittorico (sez. n. 5312 – s. 744.3 – Fra' Bartolomeo, pala Pitti)', *L'Eta' di Savonarola, Fra' Bartolomeo e la Scuola di San Marco*, ed. Padovani S., Scuderi M. and Damiani G., Venice 1996, pp. 314–18. See also Buzzegoli E., Kunzelman D., Giovannini C., Lanterna G., Petrone F., Ramat A., Sartiani O., Moioli P., and Seccaroni C., 'The use of dark pigments in Fra' Bartolomeo's paintings', *Art et Chimie, la couleur. Actes du Congrés*, Paris 2000, pp. 203–8. Bismuth was detected by XRF in the paintings discussed in these papers. The form in which Bi was present (metal or compound) was not established.
5. Spring M., Grout R., and White R. cited in note 3.
6. Mayr K, 'Wismutmalerei', *Restauratorenblätte*, 7, 1984, pp. 153–71.
7. Gold R., 'Reconstruction and Analysis of Bismuth Painting', *Painted Wood: History and Conservation, Proceedings of a symposium in Williamsburg, Virginia, November 1994*, eds Dorge V. and Howlett F.C., Los Angeles 1998, pp. 166–78.
8. Turner N., 'The Manuscript Painting Techniques of Jean Bourdichon', *A Masterpiece Reconstructed: The Hours of Louis XII*, eds Kren T. and Evans M., J. Paul Getty Museum, Los Angeles, 2005. The page on which the bismuth finding is discussed is p. 67.
9. Padeletti G. and Fermo P., 'Bismuth knowledge during the Renaissance strengthened by its use in Italian lustres production', *Applied Physics A. Materials Science and Processing*, 79, 2004, pp. 277–281.
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11. Spring M., Grout R., and White R. cited in note 3.
12. Spring M., Grout R., and White R. cited in note 3.
13. Ferretti M., Guidi G., Moioli P., Scafè R. and Seccaroni C., 'The presence of antimony in some grey colours of three paintings by Correggio', *Studies in Conservation*, 36, 1991, pp. 235–9. Seccaroni C., 'Some rarely documented pigments. Hypotesis [sic] and working observations on analyses made on Three Temperas by Correggio', *Kermes*, 34, January–April 1999, pp. 41–59. Spring M., Grout R., and White R. cited in note 3.
14. See the entry for Marco Marziale's Circumcision (NG 803) in Penny N., *National Gallery Catalogues. The Sixteenth Century Italian Paintings Volume 1. Paintings from Bergamo, Brescia and Cremona*, London 2004, p. 104.
15. Table 1 lists the areas in Raphael's paintings in the National Gallery where the presence of glass has been confirmed, and which pigments it is mixed with, but it may of course also be present in other areas that were not sampled. I am grateful to Rachel Grout for assisting in the analysis of these paintings during her fellowship in the Scientific Department of the National Gallery.
16. Occurrences of powdered glass in paintings by Raphael have been published in Roy, A., Spring M., and Plazzotta C., cited in note 2, and Spring M. in Brunetti, B.G., Seccaroni, C. and Sgamellotti, A., eds., cited in note 3.
17. Verità M., 'L'invenzione del cristallo muranese: una verifica analitica delle fonti storiche', *Rivista della stazione Sperimentale del Vetro*, 1985, pp.17–35.
18. The quantitative analysis of glass was carried out using an accelerating voltage of 25kV with the INCA 300 Oxford Instruments EDX system. Corning glass standards A–D were also analysed to check the accuracy of the analysis. The results are quoted exactly as given by the program, but can only be taken as a general indication of the type of glass since the variable contribution from other pigments in the paint (eg Al from the red lake pigment with which it is often mixed), and migration of alkali ions needs to be taken into account. This makes it inappropriate to make cor-

rections from the results of analysis of standards, since these extra uncertainties are inconsistent and to some extent random.

19. The treatises are discussed in Spring M. in Brunetti, B.G., Seccaroni, C. and Sgamellotti, A., eds., cited in note 3.
20. Haydocke R., *Tracte containing the Artes of curious Paintinge Cruinge and Buildinge written first in Italian by Jo. Paul Lomatius painter of Milan and englished by R.H. student in Physik*, 1598 (trans. of 1584 edn of Lomazzo), p. 101.
21. References to the use of powdered glass as a drier in historical documentary sources on painting are discussed and Marshall Smith is quoted in Kirby Talley M., *Portrait Painting in England: Studies in the Technical Literature before 1700*, Paul Mellon Centre for Studies in British Art, 1981, pp. 94-97.
22. Verità M., cited in note 17.
23. Detailed analysis and a full description of the occurrences of powdered glass in paintings in the National Gallery will be published elsewhere.
24. Brunetti, B.G., Seccaroni, C. and Sgamellotti, A., eds., *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS Tech Workshop, Quaderni di Kermes*, Florence 2004.
25. Janssens K., Deraedt I., Adams F., Veeckman J., 'Composition of 15-17th century archaeological glass vessels excavated in Antwerp, Belgium', *Microchimica Acta Supplementum*, 15 (1998) 253–267.
26. Barrera J., and Velde B., 'A Study of French medieval glass composition', *Archéologie Médiévale*, XIX, 1989, pp. 81–130.