National Gallery Technical Bulletin

Volume 26, 2005

National Gallery Company
London

Distributed by
Yale University Press

Series editor **Ashok Roy**

First published in Great Britain in 2005 by
National Gallery Company Limited
St Vincent House, 30 Orange Street
London WC2H 7HH

www.nationalgallery.co.uk

British Library Cataloguing in Publication Data
A catalogue record for this journal is available from the British Library

ISBN 1 85709 341 0
ISSN 0140 7430
525046

Publisher **Kate Bell**
Project manager **Jan Green**
Editor **Diana Davies**
Designer **Tim Harvey**
Picture research **Xenia Corcoran and Kim Klehmet**
Production **Jane Hyne and Penny Le Tissier**

Printed in Italy by Conti Tipocolor

FRONT COVER
Rubens, *The Judgement of Paris* (NG 194), detail of plate 1, page 4.

TITLE PAGE
Joachim Beuckelaer, *The Four Elements: Air* (NG 6587), detail of serving girl.

Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries

CATHERINE HIGGITT AND RAYMOND WHITE

Recent examination of the binding medium of a number of Italian school works ranging in date from the late fourteenth to the early sixteenth century have revealed an interesting, and a rather more sophisticated, approach to the use of egg tempera and oil-based binding media than had previously been assumed. This period corresponds to one of transition in Italy, as artists shifted away from the use of predominantly egg tempera to the use of oil. It is becoming clear that oil was being used earlier and more extensively than had been thought and that egg continued to be used, in various ways, in parallel or in combination with oil throughout this period.[1] As the results presented here and in other recent studies demonstrate, the ways in which the various binding media were used was complex (see Table 1, p. 98).[2]

In the earliest works included in Table 1, two mid-fourteenth-century panels by the Sienese artist the Master of the Palazzo Venezia Madonna, depicting *Saint Corona* and *Saint Vittorio of Siena* (Copenhagen, Statens Museum fur Kunst), the use of oil is reserved for glazes over metal leaf. The panels are painted with egg tempera in a traditional way, but linseed oil is used in the green glaze over Saint Vittorio's gilded sword scabbard and similar glazes over the *sgraffito* work on Saint Corona's robe. This egg/oil technique was still in use late into the fifteenth century as the *Saint Francis* panel (NG 598), recently reattributed to Botticelli and dated to the 1480s, shows.[3] The painting has a gilded background and is painted in egg tempera, the use of oil being reserved for the glazes – traces of which remain in the incised lines on the angels' gilded wings (plate 1). In general, the practice in Florence and its sphere of influence appears to have been more traditional,[4] and the majority of the Florentine paintings presented here from the Botticelli workshop are executed in egg tempera.[5]

Some very late occurrences of paintings entirely in egg tempera may be linked to requirements of a specific commission. While Perugino was predominantly using oil by the late fifteenth century, the *Combat between Love and Chastity* (Paris, Musée du Louvre, 1505) was painted in egg according to the wishes of the patron, Isabella d'Este. The work was commissioned to decorate Isabella's Studiolo in the ducal palace of Mantua and the stipulation that the medium should be tempera was to ensure a match with the existing work by Mantegna in the room. The *Combat between Love and Chastity* has a quite matt appearance, like another early sixteenth-century work associated with the Perugino workshop, *The Virgin and Child between Saint Jerome and Saint Augustine* (Bordeaux, Musée des Beaux-Arts, 1505–10?), which is also in egg tempera.[6]

Giannicola di Paolo (active 1484; died 1544) is associated with Perugino's workshop, and his panel of *The Annunciation* (NG 1104) clearly reflects his master's influence. The work is likely to have formed the upper part of an altarpiece, although it was cut down at some point. It had previously been thought, perhaps because of the relatively late date (*c.*1500) and his master's typical working practice at this period, and also because of the rough impasto-

plate 1 Detail from Sandro Botticelli, *Saint Francis of Assisi with Angels* (NG 598), *c.*1475–80. Macro photograph taken during cleaning, showing residues of coloured glazes over the angel's wing (trapped in the incised lines). Traces of blue nineteenth-century retouching are also visible. Poplar, 49.5 × 31.8 cm.

like quality of the background paint (where a texture similar to brushstrokes is seen), that it was painted in oil. However, when samples were examined, it became clear that the main body of the work was in egg tempera.[7] Like the other tempera works associated with the Perugino workshop, *The Annunciation* has quite a matt appearance and it is possible that, with its rather pastel colours and lack of rich, glossy or glazed passages, it was perhaps intended to mimic the effect of fresco. Alternatively, within the Perugino workshop, there may have been artists, such as Giannicola, who perhaps learnt their technique elsewhere; thus Giannicola's use of an egg-tempera medium may simply have reflected his training.

In works securely attributed to Botticelli, the use of binding media is rather more complex and sophisticated.[8] In a number of his works, the binding medium is predominantly egg tempera but in others he employs an oil medium more widely.[9] Oil is used in conjunction with egg tempera or in the deeper, glaze-like colours, even where there is no metal leaf present. Egg tempera and oil are used in combination in his *The Virgin adoring the Sleeping Christ Child* (*Wemyss Madonna),* (Edinburgh, National Galleries of Scotland), dating from the first half of the 1480s.[10] The *Wemyss Madonna*, like *The Birth of Venus* and *Pallas and the Centaur* (both Florence, Galleria degli Uffizi, and dated to *c.*1482–5), is painted on a canvas support prepared with a gesso ground. The lighter or more opaque passages are executed in egg tempera, as, essentially, are the two works from Florence.[11] However, in the *Wemyss Madonna*, the red lake glaze and the deep blue folds of the Virgin's tunic and mantle are painted in heat-bodied walnut oil, exploiting the higher refractive index of oil to give these areas a rich, transparent and saturated appearance. Work carried out in the 1950s suggests that the *Adoration of the Kings* (NG 592), a work on panel by Botticelli and Filippino Lippi, was painted in a similar manner, with egg tempera in light colours and underlayers, and oil in darker colours and in final glazes.[12]

In the work of the Sienese artist known as the Master of the Story of Griselda, an even more sophisticated and individual approach to the use of different binding media is seen. The three panels NG 912, 913 and 914, dating from around 1493–1500, illustrate the last story of Boccaccio's *Decameron* (10:10) and were probably cassone panels or intended as *spalliere* (backboards) of benches or chests in a room furnished for a newly-

PLATE 2 Macro photograph of woman's face from Master of the Story of Griselda, *The Story of Patient Griselda, Part III* (NG 914), probably *c.*1493–1500, showing the tempera-bound *verdaccio* layer beneath the pink flesh paint in oil. Panel, 61.6 × 154.3 cm.

wed couple. The paintings have recently been conserved and the opportunity was taken to study the artist's technique in detail.[13] The panels are predominantly painted in walnut oil, although the very glossy green paint seen in a number of passages contains linseed oil.[14] However, the artist uses a green earth-containing underpaint (*verdaccio*) in the areas depicting flesh, an approach usually associated with a tempera technique (PLATE 2). The green underpaint is indeed bound in egg tempera while the upper pink flesh paint is oil-based. Egg tempera was also found in a few other specific areas of the works. It is used to bind the very coarse malachite/azurite pigment mixture of the blue-green paint on the underside of the arches of the colonnade in NG 914 (and elsewhere on the three panels where this malachite/azurite mix is used in the landscape). The very delicate greyish marbling in the background architecture in NG 913 also has an egg-tempera medium. The artist also seems to have used egg tempera to paint the very fine raised lines that pick out the brocade design on the tablecloth (the beige background of which is in oil) in NG 914, although it is not clear if the egg was used alone, or in combination with oil.[15] Finally, egg tempera appears to have been used for the red lake pigments.[16] Normally, the transparency and saturation that can be achieved with an oil medium are exploited when using red lake pigments, so this result is rather unusual.[17]

The ready adaptation to the use of different media and the very specific ways in which media were exploited for particular effects may be linked to the way in which artists were trained and worked. Many of these artists were trained in a variety of

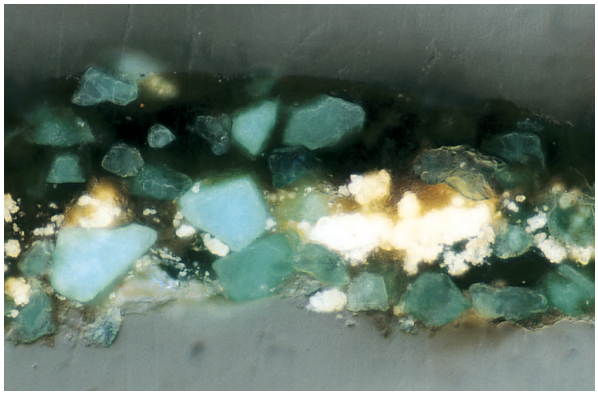
techniques and would have been quite aware of the different effects that could be achieved.[18] Although artists may have tended to adopt traditional methods learnt during their training, an interest in producing particular visual or decorative effects probably also influenced their choice of materials. Vincenzo Foppa for example, who otherwise favoured the use of an oil medium, exploited the working properties of egg tempera in the *sgraffito* work on Balthazar's tunic in the *Adoration of the Kings* (NG 729, *c.*1500).[19]

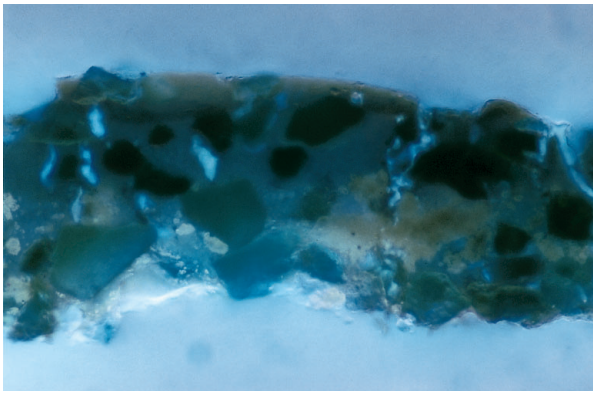
Analysis has shown that during this period, egg and oil were used together by artists in a number of ways. The simplest, and perhaps closest to the older tradition, is the use of egg and oil for different colours or pigments, as seen in the *Wemyss Madonna*. Typically, egg tempera is found in the lighter coloured passages or in underpaints, while oil was used in other areas, usually the richer, darker colours, or in final glazes. In some works, there is evidence that a little oil has been mixed with egg tempera (enriched egg tempera or *tempera grassa*) in certain colours, rather than being used in separate colours or layers.[20] Botticelli may have employed this technique also. While the majority of the samples from his two panels depicting scenes from the life of Saint Zenobius (NG 3918 and 3919, *c.*1500) contain egg tempera, samples from the richer, more glaze-like areas suggest the presence of egg and a little oil (perhaps *tempera grassa*).[21] His *Trinity* panel (London, Courtauld Institute of Art Gallery, 1490–5) is also mainly in egg, but with a little oil in the red robe and green cloak.[22] Analysis of two other works on panel, the *Primavera* and the *Coronation of the Virgin* (both Florence, Uffizi), suggest that egg and *tempera grassa* were used here also, with the oil particularly associated with the greens.[23]

The use of *tempera grassa* has long been postulated (particularly in Italy) by restorers and writers on technique, although no contemporary descriptions are known.[24] As many analysts examining paint samples will know, it is very easy to obtain results that suggest the presence of egg and oil together, but understanding what this signifies is not so straightforward. In practice *tempera grassa* is one of the most difficult media to identify and the term is often used without any analytical basis. Before assuming that an artist has employed *tempera grassa*, it must be established that the media are truly employed as a mixture or emulsion and are not present as two separate layers.[25] Further, it must be confirmed that the small amounts of oil detected do not simply represent contamination from another layer.

Egg-tempera films are often quite leanly bound, with coarse pigment particles, so that the paint surface may be quite uneven or porous. Oil, from surface layers, coatings or oil-containing varnishes, can therefore remain trapped in the paint texture or penetrate a surprisingly long way into a film, making it very difficult to avoid contamination. These paintings often have a long history of past restoration interventions, and therefore the possibility of contamination with materials added during such treatments, including retouching media, is high. Further, old oil glazes may be present at the surface in more or less intact layers, over egg-tempera underpaint.[26] A number of reasons why an artist might employ *tempera grassa* have been proposed, but perhaps the most likely reason was to raise the refractive index of the medium to increase saturation, transparency and the glaze-like quality in dark colours such as reds, browns, blues and greens, in exactly the same way that later artists used heat pre-polymerised oils and oil-resin mixtures.[27] Unfortunately, it is precisely with such colours that obtaining a clean sample is often most difficult. The rich, glossy passages are the very areas that have tended to be approached with caution by restorers and so frequently retain multiple surface layers. The paints are often quite dark (or have darkened through reaction of the pigment with the medium), again making it difficult to separate varnishes from the paint below.[28]

Two of the samples in Table 1 illustrate how easily surface residues can interfere with analysis. A sample from the egg tempera and malachite-containing blue-green arches in NG 914 (described above) was found also to contain a small amount of drying oil. These results might suggest the use of *tempera grassa*. However, FTIR microscopy revealed traces of Prussian blue in the sample and it appears that residues of an oil-based retouching were present, trapped by the very coarse pigment particles of the original paint. Samples from the green lining of the Virgin's mantle, also painted with malachite, from Botticelli's *Wemyss Madonna*, reveal that two paint layers are present. Examination of the medium indicated that the darker upper layer, and the lower, lighter coloured green layer both contained traces of pine resin and linseed oil in addition to egg tempera. It was not obvious how components more commonly associated with a varnish layer could have penetrated down into the sample, and even the underlayer, until the sample





PLATES 3 and 4 Sandro Botticelli, *The Virgin adoring the Sleeping Christ Child* (*Wemyss Madonna*), *c.*1480–5. Edinburgh, National Gallery of Scotland. Cross-section from the green lining of the Virgin's mantle, showing penetration of varnish into the layer structure. Photographed in normal light (*left*) and in UV light (*right*), original magnification 400×, actual magnification 350×.

was examined in cross-section (PLATES 3 and 4). This revealed cracks through the paint layers that extended right down into the underlayer, which contained fluorescent material that is likely to be residues of varnish.

PLATE 5 Marco Marziale, *The Virgin and Child with Saints* (NG 804), 1507. Panel, 221 × 142.2 cm.

Although a little oil was found in conjunction with egg tempera in many of the samples described in Table 1, in the majority of cases the oil is thought to be a contamination. However, the *Battle of San Romano* by Uccello (NG 583, probably *c.*1438–40) is an example of a painting where *tempera grassa* does appear to have been used.[29] Uccello has mainly used an egg-tempera technique, but seems to have exploited the slightly different characteristics of walnut oil-enriched tempera (*tempera grassa*) in certain areas, including the more saturated dark foliage greens in the main part of the panel.[30] There is a dark translucent glaze-like modelling over the silver leaf of the armour. Analysis reveals that the glaze contains a resin or softwood pitch,[31] mixed with walnut oil. Similar pitch glazes have been found in a number of other works,[32] including the two large altarpieces executed by Marziale (see Table 1 and PLATE 5). In the works by Marziale (NG 803 and 804), the pitch is used in the shadows in the vaulting over the figures, again combined with walnut oil. Samples from elsewhere on the two altarpieces also contain walnut oil, tempered with pine resin in the rich transparent reds and greens.[33] Although slightly later in date than the works by Marziale, very similar materials are used in the two panels depicting *Tanaquil* and *Marcia* by the Sienese artist Domenico Beccafumi (NG 6368 and 6369). Walnut oil is used, with a little conifer resin added to the more transparent green paints. In the transparent brown shadows, Beccafumi has also used a softwood or resin pitch.

As well as using various combinations of binding media, Botticelli also produced works entirely painted in oil. Walnut oil was used for both the '*Mystic Nativity*' (NG 1034, 1500), a work

on canvas, and the *Bardi Altarpiece* (Berlin, Gemäldegalerie, 1484–5), a panel painting. In these works the green pigment used is verdigris.[34] In all the works in egg tempera, where the green pigment has been examined, malachite has been found.[35] Thus, while there seems to be no clear link between Botticelli's use of binding media and the nature or size of the support,[36] or the date of the work, there are links between the choice of medium and the colour of the paint, or the pigment used (as is also found with many of his contemporaries).

Although walnut oil was the more common oil medium, linseed oil has also been found in a number of fifteenth-century paintings in Italy, and is often encountered combined with darker or poorer drying pigments.[37] For certain artists such as Cima and Costa, the use of linseed oil seems to have been favoured over that of walnut.[38] During the course of the sixteenth century, the use of linseed oil becomes the dominant practice and interestingly, while the *Tanaquil* and *Marcia* panels are executed in walnut oil, in the other work by Beccafumi that was examined, *The Story of Papirius* (NG 1430), some linseed oil was also found. *The Story of Papirius* post-dates the *Tanaquil* and *Marcia* panels by some 25 to 30 years. Use of oil media by a number of other Italian artists of the period has been covered in recent publications.[39]

An interesting exception to the usages described above is Andrea Mantegna, who perhaps more than anyone else fully exploited the possibilities offered by distemper techniques (PLATES 6 and 7). Distemper (binders such as glue, egg or possibly gum, which are water-soluble when used initially) seems to have been Mantegna's preferred non-mural medium and few, if any, instances of his use of an oil medium have been confirmed.[40] Mantegna's choice of medium, and its link to the support and finish applied to the work, has been much discussed and it has been suggested that his works can be divided into three groups.[41] In the first group are works in egg tempera on panel with a glossy surface, including *The Agony in the Garden* (NG 1417) and *The Vestal Virgin Tuccia with a Sieve* (NG 1125.1).[42] The gessoed and varnished panel of the *Tuccia* allowed the artist to imitate marble and gilded bronze.

The other two groups of works by Mantegna are based on textile supports but differ in their binding medium and in the preparation of the support. Some of the works are on canvas with a conventional thick isolating gesso ground, giving the artist a relatively smooth white surface on which to paint. When working on such gessoed canvases, Mantegna generally employed egg tempera, as in *The Virgin and Child with the Magdalen and Saint John the Baptist* (NG 274).[43] Canvases prepared with a gesso ground presumably developed from use of panel supports and are commonly encountered, used with egg or oil, throughout this period in Italy (the works by Botticelli on canvas described here are of this type for example). Other works by Mantegna have little more than a thin size layer, are often on linen, and have a glue medium.[44] These glue-bound works have a very matt finish (and were presumably never intended to be varnished) and must be related to the Northern *tüchlein* technique.[45] Mantegna used a rather more substantial glue-size layer and rather more opaque paint in *The Introduction of the Cult of Cybele at Rome* (NG 902), *Samson and Delilah* (NG 1145) and the *Holy Family with Saint John*

PLATE 6 Andrea Mantegna, *The Virgin and Child with the Magdalen and Saint John the Baptist* (NG 274), probably 1490–1505, detail. Egg tempera on canvas, 139.1 × 116.8 cm.

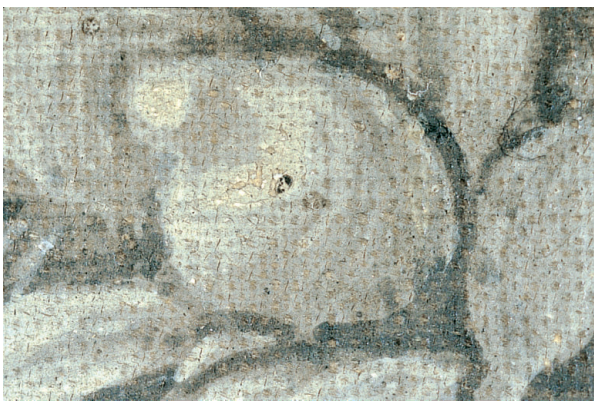


PLATE 7 Andrea Mantegna, *Samson and Delilah* (NG 1145), *c.*1500. Glue distemper on linen, 47 × 36.8 cm. Macro photograph.

(NG 5641) than the Northern *tüchlein* artists, but all are bound with glue.[46]

The range of pigments found in the paintings described in Table 1 is typical of the period: vermilion, lead white, carbon black, earth pigments, azurite, lead-tin yellow, verdigris, lake pigments, malachite and ultramarine.[47] FTIR microscopic examination of the samples that contained ultramarine revealed that a small sharp band at *c.*2340 cm^{-1} was always observed (in addition to other bands expected for complex sodium aluminosilicates). A study undertaken by the Getty Conservation Institute of ultramarine pigments in fifteenth- and sixteenth-century Italian paintings also found that this band was observed, but that it was not seen in samples of synthetic ultramarine.[48] The study demonstrated that this band is also seen in lapis lazuli (the mineral source of ultramarine) and natural ultramarine samples obtained from the ancient quarries in Badakhshan (now in Afghanistan) but was absent in samples from Chile or Siberia. The Badakhshan mines were the source of practically all of the lapis lazuli used in Europe; the other major deposits in the Chilean Andes and near Lake Baikal in Siberia do not seem to have been used before the nineteenth century.[49] The *c.*2340 cm^{-1} band has been linked to the presence of high proportions of the mineral haüynite,[50] in lapis from the Badakhshan mines, and it is suggested that it is a marker for natural ultramarine from this source. In all of the samples presented here, the band at *c.*2340 cm^{-1} was observed; in the few cases where the band was absent, the samples corresponded to overpaint.[51] These findings suggest that the Badakhshan mines were indeed the major source of ultramarine and that the alternative Old World source, Lake Baikal, does not seem to have been used during this period in Italy.

Acknowledgements

We are grateful to our colleagues in the Scientific, Conservation and Curatorial Departments, and especially to Marika Spring, Jill Dunkerton, Rachel Billinge and Luke Syson. We would also like to thank Gisela Helmkampf of the Gemäldegalerie der Staatlichen Museen zu Berlin, for samples from the *Bardi Altarpiece* by Botticelli, Michael Gallagher of the National Galleries of Scotland, Edinburgh, for samples from *The Virgin adoring the Sleeping Christ Child* (*Wemyss Madonna)*, also by Botticelli, and Troels Filtenborg of the Statens Museum for Kunst, Copenhagen, for samples from the *Saint Corona* and *Saint Vittorio of Siena* panels by the Master of the Palazzo Venezia Madonna. We are also grateful to Jennie Pilc who laid the foundations for much of the IR work reported.

Appendix: Formation of metal oxalates

In addition to the potential contamination problems referred to in the main text when trying to confirm the use of *tempera grassa*, a number of other analytical challenges have been encountered, giving potentially contradictory or misleading binding medium identification. Such problems again emphasise the importance of understanding what else is in the sample and of using more than one analytical technique. Some of the potential problems that can arise when analysing samples containing smalt or glass siccatives are discussed elsewhere.[52]

In a large number of the samples included in Table 1, two bands are observed in the IR spectrum which indicate the presence of calcium oxalate.[53] A strong, broad band is seen at *c.*1640 cm^{-1}, but the more characteristic band is the smaller, sharper band at *c.*1320 cm^{-1}. Although the source of this material is not clear, from the range of samples examined here it seems that it is most prevalent in samples containing pigments such as red lake, smalt and ultramarine, or in coating layers over such pigments, and is frequently associated with greyish-brown, highly insoluble surface 'crusts' (which often also contained calcium carbonate and sulphate).[54] In areas of degraded green paint containing copper-based pigments, a related species is sometimes detected in the discoloured surface regions. This material, characterised by a broad band at *c.*1660 cm^{-1} and a small, sharp doublet at *c.*1365 and 1320 cm^{-1}, seems to be copper oxalate (FIG. 1).[55]

Metal oxalates are not often reported in the context of easel paintings,[56] although oxalate crusts or patinas seem to be ubiquitous in other types of art work and can be quite obscuring.[57] Calcium oxalates are commonly encountered in glass artefacts and wall paintings;[58] copper oxalates have been reported in wall paintings and are frequently found associated with bronze artefacts.[59] A number of sources for the oxalates have been postulated in the literature. In the works discussed here, oxalates are likely to be deterioration product formed during breakdown of organic binders, coatings or other components (especially proteinaceous materials), possibly mediated by micro-organisms.[60] In some cases the oxalate cation source is the pigment (especially with copper), but most of the calcium is likely

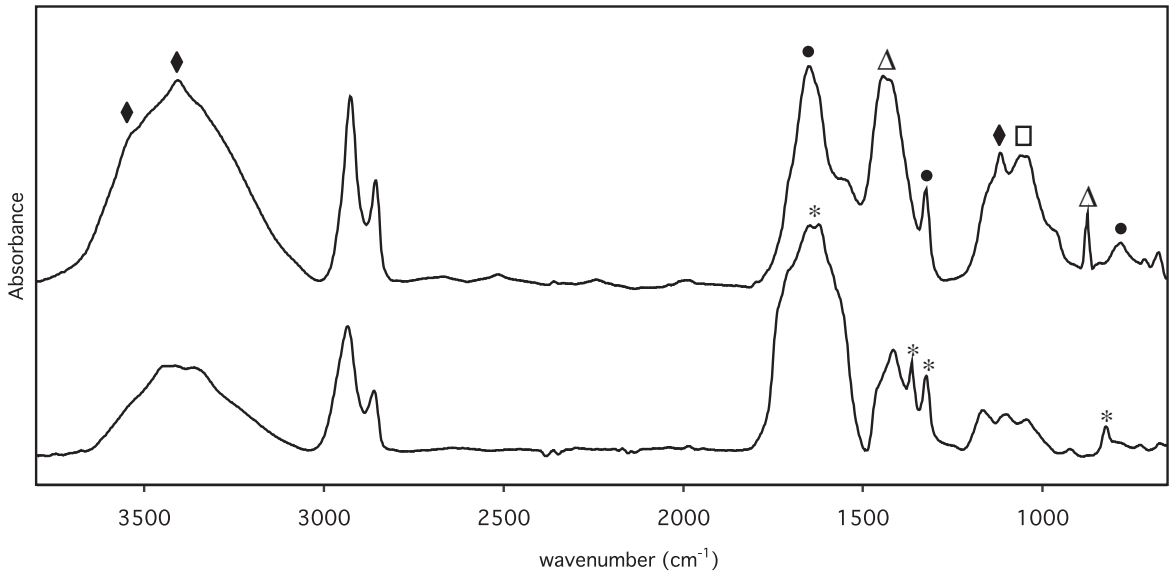


FIG. 1 IR spectrum (3800–650 cm^{-1}): (i) copper oxalate (✻) in a sample of browned glaze over Saint Corona's robe, from the Master of the Palazzo Venezia Madonna, *Saint Corona* (Copenhagen, Statens Museum fur Kunst), *c.*1350 (*lower trace*); (ii) calcium oxalate (●) in a sample of the surface crust over the architecture in Giannicola di Paolo, *The Annunciation* (NG 1104), late 15th century (*upper trace*). The crust also contains calcium carbonate (Δ), sulphate (♦) and phosphate (□).

to come from the environment. As mentioned above, oxalate formation seems to be particularly pronounced with certain pigments but it is not clear if this implies that such pigments enhance oxalate formation directly, or if the paints where these pigments are used are associated with certain types of binder, are especially medium rich, or are commonly given surface coatings.[61] In certain cases, the oxalate source could also include conservation treatments, although this is less likely with easel paintings.

Vibrational spectroscopic techniques (Raman and IR) are very well suited to the detection of metal oxalates (in the absence of band overlap), but X-ray diffraction and chromatographic techniques have also been used.[62] It is important to be able to detect oxalates when they are present to avoid misidentification of the organic components in samples if IR spectroscopy is the only analytical technique used. If both metal oxalates and soaps (formed when certain pigments react with an oil binding medium) are present in a sample, then bands are seen at *c.*1650 and *c.*1550 cm^{-1} in IR spectra, assigned to the asymmetric carboxylate stretches of the oxalates and soaps respectively.[63] The amide I and II bands of proteins give rise to two IR bands in the same regions of the spectrum, potentially leading to confusion over the nature of the binding medium.[64]

Evidence for what appears to be an attempt by an earlier restorer to re-saturate an oxalate-containing 'crust' was found in Cima's *Virgin and Child* (NG 2506). A rather resistant grey-brown layer composed mainly of calcium oxalate was present directly on top of the Virgin's red robe. Lying over the calcium oxalate layer was another layer containing heat-bodied linseed oil and fir balsam resin from the *Abies* species – probably Strasbourg turpentine (*olio d'abezzo*) from *Abies alba* or Canada Balsam from *Abies balsamea*.[65] Fresh fir balsam is fairly viscous and colourless and gives a film of high refractive index, moderate gloss, which is tougher than those for soft resins such as pine resin (*Pinus* species). In this painting, the presence of the oxalate 'crust' on the surface of the rich red lake paint must have resulted in a rather scattering and unsaturated surface, and the fir balsam may have been applied during a past restoration in an attempt to reduce its visual impact.

Notes and references

1 For general discussion of the painting techniques of the period, see D. Bomford, J. Dunkerton, D. Gordon and A. Roy, *Art in the Making: Italian Painting Before 1400*, London 1989, pp. 1–51; J. Dunkerton and A. Roy, 'The Materials of a Group of Late Fifteenth-century Florentine Panel Paintings', *National Gallery Technical Bulletin*, 17, 1996, pp. 20–31.

2 J. Dunkerton, N. Penny and M. Spring, 'The Technique of Garofalo's Paintings at the National Gallery', *National Gallery Technical Bulletin*, 23, 2002, pp. 20–41; A. Roy, M. Spring and C. Plazzotta, 'Raphael's Early Work in the National Gallery: Paintings before Rome', *National Gallery Technical Bulletin*, 25, 2004, pp. 4–35; A. Roy, 'Perugino's *Certosa di Pavia Altarpiece*: new technical perspectives', 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. 13–20.

3 S. Korman, 'A St Francis by Botticelli in the National Gallery', *Apollo*, 2003, pp. 42–9 (with an appendix by J. Dunkerton, 'A note on the restoration of the *St Francis*').

4 While the continued use of an egg-tempera technique in Florence and its sphere of influence followed traditional practice, it was presumably also a deliberate choice to obtain a particular visual effect. It may be linked to the emphasis that Florentine artists placed on the depiction of three-dimensional space, rather than on the decorative finish of a work, see Bomford et al. 1989 (cited in note 1).

5 S. Korman recently studied the National Gallery paintings ascribed to the Botticelli workshop and the opportunity was taken to analyse the technique of these, and autograph, works. While the workshop and autograph paintings all conformed to contemporary practice, it was not possible to identify different hands on this basis. S. Korman presented her work in a lecture given at 'Botticelli: Investigating a Painter's Practice', a Symposium held at the Courtauld Institute of Art, University of London, 7–8 March 2003. The results of the study are presented here; for completeness, some results published previously are included.

6 E. Martin and J.P. Rioux, 'Comments on the technique and the materials used by Perugino, through the study of a few paintings in French collections', 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. 43–56; S. Delbourgo, J.P. Rioux and E. Martin, 'L'analyse des peintures du Studiolo d'Isabelle d'Este au Laboratoire de Recherche des Musées de France. II – Étude analytique de la matière picturale', Laboratoire de Recherche des Musées de France, *Annales*, 1975, pp. 21–8.

7 Recent examinations of many works in oil by Perugino, Raphael and other fifteenth- and sixteenth-century artists have revealed the addition of colourless, manganese-containing crushed glass to red lake glazes, possibly as a siccative. In works by Perugino where glass has not been found in red lake glazes (and where the medium has been examined) aqueous media have been found. See Roy, Spring and Plazzotta 2004 (cited in note 2); M. Spring, 'Perugino's painting materials: analysis and context within sixteenth-century easel painting', pp. 21–8, and C. Seccaroni, P. Moioli, I. Borgia, B.G. Brunetti and A. Sgamellotti, 'Four anomalous pigments in Perugino's palette: statistics, context and hypotheses', pp. 29–41, both in *Quaderni di Kermes*, 2004 (cited in note 6). No glass was found in the red lake-containing paint here, lending further support to the argument that the role of the glass was as a siccative.

8 Some of this work has been described previously; C. Higgitt in a lecture given at a Symposium held at the Courtauld Institute of Art, 2003 (cited in note 5). See also Roy 2004 (cited in note 2).

9 Two works predominantly in egg tempera include the Saint Zenobius panels (NG 3918 and 3919). See R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 16, 1995, pp. 85–95; Dunkerton and Roy 1996 (cited in note 1).

10 T. Clifford, 'Botticelli's *Wemyss Madonna*', *Apollo*, 2000, pp. 3–10; P. Jeromack, 'The "Forgotten" Botticelli', *National Art Collections Fund Quarterly*, Spring 2000, pp. 38–44.

11 M. Matteini and A. Moles, 'Indagini sui materiali e le stesure pittoriche del dipinto', in 'La Nascita di Venere e l'Annunciazione del Botticelli restaurate', *Gli Uffizi, Studi e Ricerche* 4, Florence 1987, pp. 75–82.

12 H. Ruhemann, 'Technical Analysis of an Early Painting by Botticelli', *Studies in Conservation*, 2, 1955, pp. 17–40.

13 Details of the conservation treatment, the technique and identity of the Master of the Story of Griselda will be the subject of forthcoming publications by J. Dunkerton and L. Syson. NG 914 was the most damaged of the series and offered the greatest scope for analysis.

14 The use of verdigris in linseed oil may follow contemporary practice. Treatises describe the preparation of such green glazes. A 'pre-prepared' green glaze may also have been available. Elsewhere in the work, verdigris, as part of a pigment mixture, is found bound in walnut oil.

15 The egg component in the paint may have assisted in the production of these delicate raised lines. The use of egg tempera for the malachite/azurite green (presumably chosen for the colour/texture as others greens are used elsewhere) followed traditional practice, and may also have been for visual effect. A similar argument probably applies to the use of an egg binder for the areas depicting marble. This visually sophisticated approach and interest in the decorative finish seem to be more typical of Sienese than of Florentine artists, at least in the thirteenth and fourteenth centuries, see Bomford et al. 1989 (cited in note 1).

16 Paint pigmented with red lake was bound in egg tempera, but the medium of the transparent red lake-containing glaze over gold was not analysed. It is possible that these passages had an oil medium.

17 No glass was found in the red lake in NG 912–14, although some glass was found in oil passages elsewhere. The red lake was bound with egg tempera, a binder that does not require a drier, adding further support to the argument that the role of the glass was as a drier, see note 7.

18 Artists produced works using a variety of techniques (tempera, oil, mixed media, *buon fresco* etc.) or at least such commissions were being undertaken within single workshops, see Roy 2004 and Roy, Spring and Plazzotta 2004 (both cited in note 2).

19 J. Dunkerton and C. Plazzotta, 'Vincenzo Foppa's *Adoration of the Kings*', *National Gallery Technical Bulletin*, 22, 2001, pp. 18–28. See Bomford et al. 1989, pp. 130–6 (cited in note 1), for a description of the *sgraffito* technique.

20 The origin and use of *tempera grassa* in fifteenth-century Italian painting is discussed in J. Dunkerton 'Modifications to traditional egg tempera techniques in fifteenth-century Italy', in *Early Italian Paintings: Techniques and Analysis*, Symposium, Maastricht 1996, ed. T. Bakkenist, R. Hoppenbrouwers and H. Dubois, Limburg Conservation Institute, Maastricht 1996, pp. 29–34. Although many of the works in Table 1 contain both egg and oil, most of the artists appear to have used the media separately in different layers or colours rather than mixed. Passages executed in tempera grassa have been found in other paintings, but no works entirely painted with *tempera grassa* are known.

21 See note 9.

22 R. North, 'The Holy Trinity with Saints John the Baptist, Mary Magdalen, Tobias and Raphael by Botticelli and assistants: A technical examination for attribution', *The Conservator*, 21, 1997, pp. 3–11.

23 M. Matteini and A. Moles, 'Tecnica di esecuzione e stato di conservazione', pp. 226–33, in catalogue entry '39. Alessandro Botticelli, La Primavera', pp. 207–50 in *Metodo e Scienza: operatività e ricerca nel restauro*, ed. U. Baldini, Florence 1982; *L'Incoronazione della Vergine del Botticelli: restauro e ricerche*, ed. M. Ciatti, Florence 1990.

24 From Dunkerton 1996 (cited in note 20). See also Dunkerton and Roy 1996 (cited in note 1); Roy 2004 (cited in note 2).

25 In a typical chromatographic analysis, the whole sample is derivatised and submitted for analysis. All components are examined together and information about where these components are within the layer structure is lost. It is therefore very important to interpret the analytical data in the light of information from spatially resolved techniques such as the examination of cross-sections (whether by visible or infrared microscopy, or using microchemical tests).

26 In a number of works, oil glazes are present over passages of egg tempera, especially in areas of blue, green and red, see Dunkerton and Roy 1996 (cited in note 1). In certain cases, glazes seem to have been lost during cleaning, see A. Roy and J. Dunkerton, 'Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London' in *Early Italian Paintings: Approaches to Conservation*, Proceedings of a Symposium at the Yale University Art Gallery, April 2002, ed. P.S. Garland, Yale University Art Gallery, New Haven and London 2003, pp. 120–31.

27 R. White and J. Kirby, 'Rembrandt and his Circle: Seventeenth-Century Dutch Paint Media Re-examined', *National Gallery Technical Bulletin*, 15, 1994, pp. 64–78. Similar problems occur when trying to determine if a small amount of resin has been added to an oil medium or if it represents varnish contamination.

28 In paint containing copper-based pigments it can be very difficult to

distinguish a discoloured glaze/paint (that was originally green) from a brown glaze/paint or a discoloured varnish layer. Further, migration of copper from paints or glazes into surface coatings can occur: M. Gunn, G. Chottard, E. Rivière, J.-J. Girerd and J.-C. Chottard, 'Chemical reactions between copper pigments and oleoresinous media', *Studies in Conservation*, 47, 2002, pp. 12–23.

29 A. Roy and D. Gordon, 'Uccello's *Battle of San Romano*', *National Gallery Technical Bulletin*, 22, 2001, pp. 4–17.

30 In Uccello's *Saint George and the Dragon* (*c.*1470, NG 6294), walnut oil is used throughout: J. Dunkerton and A. Roy, 'Uccello's *Saint George and the Dragon*: Technical Evidence Re-evaluated', *National Gallery Technical Bulletin*, 19, 1998, pp. 26–30. It should be noted that nineteenth-century Italian restorers' practice might be an alternative explanation for the detection of *tempera grassa*.

31 R. White, 'Brown and Black Organic Glazes, Pigments and Paints', *National Gallery Technical Bulletin*, 10, 1986, pp. 58–71.

32 Softwood pitch has been detected in the work of a number of other artists of this period, including Cima da Conegliano (*The Incredulity of Saint Thomas*, NG 816); Garofalo (*An Allegory of Love*, NG 1362; *Holy Family with Saints*, NG 170; *A Pagan Sacrifice*, NG 3928); Raphael (*Ansidei Madonna*, NG 1171); Titian (*The Holy Family*, NG 4). See J. Dunkerton and A. Roy, 'The Technique and Restoration of Cima's "The Incredulity of S. Thomas"', *National Gallery Technical Bulletin*, 10, 1986, pp. 4–27; White and Pilc 1995 (cited in note 9); see also references in note 2.

33 Although he was working slightly later, this combination of materials is very similar to that used by Garofalo, see Dunkerton, Penny and Spring 2002 (cited in note 2).

34 Only one of the Botticelli workshop paintings examined was painted in oil (NG 2497) and here the green pigment seems to be verdigris also.

35 Where samples from workshop and autograph works by Botticelli have been examined, malachite has always been found used in egg tempera, and verdigris in oil. This was discussed by M. Spring and C. Higgitt in lectures given at a Symposium held at the Courtauld Institute of Art, 2003 (cited in note 5). The Master of the Story of Griselda's practice is similar. In Uccello's *Battle of San Romano*, the green in the main panel is verdigris, but here it is mixed with lead white and lead-tin yellow and appears to be bound with *tempera grassa*.

36 With other artists there is a clearer link between scale and medium. Where this choice is made, egg tempera is used in small-scale works (including predella panels), with oil retained for use on the large scale. Such an approach was certainly typical of the Perugino workshop, see Roy 2004 and Roy, Spring and Plazzotta 2004 (both cited in note 2).

37 Linseed oil is used in conjunction with sulphur-rich organic black coal in the background of Vivarini's *Portrait of a Man*, NG 2672, 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, and is often used in red and green glaze-like paints.

38 J. Dunkerton, 'Titian's Painting Technique' in *Titian*, ed. D. Jaffé, London 2003, pp. 45–59; J. Dunkerton and M. Spring, 'The Technique and Materials of Titian's Early Paintings in The National Gallery, London', in *Restoration: Titian, Jacopo Pesaro being presented to Saint Peter by Pope Alexander VI*, Vol. 3, No. 1, Antwerp 2003, pp. 9–21.

39 See note 2.

40 A. Rothe, 'Andrea Mantegna's *Adoration of the Magi*', in *Historical Painting Techniques, Materials, and Studio Practice*, ed. A. Wallert, E. Hermens and M. Peek, Leiden (Preprints of a Symposium held at the University of Leiden, The Netherlands, 26–29 June 1995), The Getty Conservation Institute, 1995, pp. 111–16; J. Dunkerton, 'Mantegna's painting techniques' in *Mantegna and 15th Century Court Culture*, ed. F. Ames-Lewis and A. Bednarek, London 1993, pp. 26–38; A. Rothe, 'Mantegna's Paintings in Distemper' in *Andrea Mantegna*, exh. cat., ed. J. Martineau, The Royal Academy of Arts, London, and The Metropolitan Museum of Art, New York, 1992, pp. 80–8.

41 See Dunkerton 1993 and Rothe 1995 (both cited in note 40). See also H. Dubois and L. Klaassen, 'Fragile Devotion: Two Late Fifteenth-Century Italian *Tüchlein* Examined', pp. 67–75, and J. Cannon and C. Villers, 'Introduction', pp. vii–ix, both in *The Fabric of Images: European Paintings on Textile Supports in the Fourteenth and Fifteenth Centuries*, ed. C. Villers, London 2000.

42 *Judith and Holofernes*, National Gallery of Art, Washington, is similar: S. Halpine, 'An Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One-Hour Extraction Method', in *Conservation Research 1995, Studies in the History of Art 51, Monograph Series II*, Washington 1995, pp. 28–69 (esp. pp. 48–53).

43 Mantegna's works for Isabella d'Este's Studiolo, *Parnassus* (also known as *Mars and Venus*), *c.*1497, and *Pallas expelling the Vices from the Garden of Virtue*, *c.*1499–1502 (both Paris, Musée du Louvre) and *Christ Child Blessing*, *c.*1480/90 (Washington, National Gallery of Art) are similar. See Delbourgo, Rioux and Martin 1975 (cited in note 6); Halpine 1995 (cited in note 42); Dunkerton 1993 (cited in note 40).

44 See references in note 41 and Halpine 1995 (cited in note 42). In a section on works on cloth, Cennini appears to describe both approaches to working on cloth, see Cennino d'Andrea Cennini, *The Craftsman's Handbook, "Il Libro dell' Arte"* (1437), trans. D. V. Thompson, Jr., Dover, New York 1960, pp. 103–5. For other fourteenth- and fifteenth-century Italian works on textile supports see H. Dubois, H. Khanjian, M. Schilling and A. Wallert, 'A Late Fifteenth Century Italian Tüchlein', *Zeitschrift für Kunsttechnologie und Konservierung*, 2, 1997, pp. 228–37.

45 The *tüchlein* technique is described in R. Billinge, L. Campbell, J. Dunkerton, S. Foister, J. Kirby, J. Pilc, A. Roy, M. Spring and R. White, 'The methods and materials of Northern European painting 1400–1550', in *National Gallery Technical Bulletin*, 18, 1997, pp. 6–55, and D. Bomford, A. Roy and A. Smith, 'The Techniques of Dieric Bouts: Two Paintings Contrasted', *National Gallery Technical Bulletin*, 10, 1986, pp. 39–57.

46 The *Adoration of the Magi*, *c.*1495–1505, The J. Paul Getty Museum, Malibu, is similar, see references in note 40.

47 Bomford et al. 1989 and Dunkerton and Roy 1996 (both cited in note 1).

48 'Case Study 1: Ultramarine pigments' in M.R. Derrick, D. Stulik and J.M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles 1999, pp. 134–8 (Chap. 6).

49 J. Plesters, 'Ultramarine Blue, Natural and Artificial', *Artists' Pigments. A Handbook of Their History and Characteristics*, Vol. 2, ed. A. Roy, Washington and Oxford 1993, pp. 37–65.

50 Haüynite (or haüyne) is a sulphate-containing mineral of the sodalite series, closely related to lazurite, the other mineral responsible for the blue colour of ultramarine.

51 The blue-grey retouching (bound with a medium containing linseed oil, mastic and pine resins) in the sky of Cima's *The Virgin and Child*, NG 2506, contains ultramarine which does not show the band, suggesting that it is either synthetic or comes from a source other than the Badakhshan mines.

52 Smalt is discussed in M. Spring, C. Higgitt and D. Saunders, 'Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt', in this *Bulletin*, pp. 56–70, and glass siccatives in Roy, Spring and Plazzotta 2004 (cited in note 2). There is some evidence that the presence of glass may depress the azelaic to palmitic acid ratio for oil films analysed by GC–MS.

53 Two forms of calcium oxalate are commonly found; a monohydrate (whewellite, IR: 1622–25 ν_a(COO), 1319–20 ν_s(COO) and 775–779 δ(OCO) cm^{-1}) and a dihydrate phase (weddellite, IR: 1641–43 ν_a(COO), 1329–30 ν_s(COO) and 781–783 δ(OCO) cm^{-1}), see F. Cariati, L. Rampazzi, L. Toniolo and A. Pozzi, 'Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation', *Studies in Conservation,* 45, 2000, pp. 180–8; M.J. Schmelz, T. Miyazawa, S.-I. Mizushima, T.J. Lane and J.V. Quagliano, 'Infra-red absorption spectra of inorganic co-ordination complexes – IX Infra-red spectra of oxalate complexes', *Spectrochimica Acta*, 9, 1957, pp. 51–8; R.L. Frost, 'Raman spectroscopy of natural oxalates', *Analytica Chimica Acta*, 517, 2004, pp. 207–14.

54 The surface 'crusts' are essentially inorganic in composition, can contain trapped dirt and so may be quite discoloured, disfiguring and highly scattering. They are extremely difficult to remove because of the very low solubility of oxalates. The solubility product constants (K_{sp}) at 25°C are 4.43×10^{-10} and 2.32×10^{-9} for CuC_2O_4 and $CaC_2O_4.H_2O$ respectively.

55 Copper oxalate and the mineral form, moolooite, give IR bands at *c.*1660 ν_a(COO), 1365–70 ν_s(COO), 1320–25 (CO_2 wag) and 820–825 δ(OCO) cm^{-1}, see H.G.M. Edwards, D.W. Farwell, S.J. Rose and D.N. Smith, 'Vibrational spectra of copper (II) oxalate dihydrate, $CuC_2O_4.2H_2O$, and dipotassium bis-oxalato copper (II) tetrahydrate, $K_2Cu(C_2O_4)_2.4H_2O$', *Journal of Molecular Structure*, 249, 1991, pp. 233–43, and Frost 2004 (cited in note 53).

56 For examples of the detection of calcium oxalate in easel painting see N. Salvadó, T. Pradell, E. Pantos, M.Z. Papiz, J. Molera, M. Seco and M. Vendrell-Saz, 'Identification of copper-based green pigments in Jaume Huguet's Gothic altarpieces by Fourier transform infrared microspectroscopy and synchrotron radiation X-ray diffraction',

Journal of Synchrotron Radiation, 9, 2000, pp. 215–22; M. Matteini, A. Moles, G. Lanterna, C. Lalli, M.R. Nepoti, M. Rizzi and I. Tosini, 'Characteristics of the materials and techniques', in *Giotto. The Crucifix in Santa Maria Novella*, ed. M. Ciatti and M. Seidel, Florence 2002 (English edition), pp. 387–403; Matteini and Moles 1982 (cited in note 23).

57 F. Bandini, G. Botticelli, C. Danti, M. Matteini and A. Moles, 'The restoration of Domenico Ghirlandaio's frescoes in the Cappella Maggiore of S. Maria Novella in Florence: problems, practical work, results', *Contributions to the IIC Bologna Congress on Case Studies in the Conservation of Stone and Wall Paintings*, 21–26 September 1986, ed. N.S. Brommelle and P. Smith, London 1986, pp. 186–9.

58 See Spring, Higgitt and Saunders in this *Bulletin*, pp. 56–70, and references therein for discussion of glass deterioration. For wall painting examples, see Bandini et al. 1986 (cited in note 57); Cariati et al. 2000 (cited in note 53).

59 For wall painting examples see E.A. Moffatt, N.T. Adair and G.S. Young, 'The occurrence of oxalates on three Chinese wall paintings', *Application of science in examination of works of art: proceedings of the seminar*, 7–9 September, 1983, Museum of Fine Arts, Boston, 1985, pp. 234–8. For bronze artefacts see M. Matteini, A. Moles and C. Lalli, 'Infrared Spectroscopy: A Suitable Tool for the Characterization of Components in Bronze Patinas', *ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen, 10–14 September 1984: Preprints*, ed. D. de Froment, Paris 1984, pp. 84.22.8–84.22.24.

60 Bandini et al. 1986 (cited in note 57); Cariati et al. 2000 (cited in note 53).

61 Oxalate crusts are often seen over paints containing red lake, smalt, ultramarine, copper greens, or which contain glass siccatives, see note 52.

62 Detection of oxalates by: synchrotron XRD (easel paintings) Salvadó et al. 2000 (cited in note 56); Raman microscopy (wall paintings) A. Perardi, L. Appolonia and P. Mirta, 'Non-destructive in situ determination of pigments in 15th century wall paintings by Raman microscopy', *Analytica Chimica Acta*, 480, 2003, pp. 317–25; GC–MS (easel paintings) Matteini et al. 2002 (cited in note 56).

63 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. Vibrational modes associated with the deterioration of various pigments are also seen in this region, as are water bending modes (coordinated water).

64 Amide I C–O stretch (1654), Amide II NH_2 deformation (1632 shoulder), Amide II (1542 cm^{-1}), R.J. Meilunas, J.G. Bentsen and A. Steinberg, 'Analysis of aged paint binders by FTIR spectroscopy', *Studies in Conservation*, 35, 1990, pp. 33–51.

65 J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn, London 1994, pp. 100–2; R. White and J. Kirby, 'A Survey of Nineteenth- and early Twentieth-Century Varnish Compositions found on a Selection of Paintings in the National Gallery Collection', *National Gallery Technical Bulletin*, 22, 2001, pp. 64–84.