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. 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).

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. 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, and the majority of the Florentine paintings presented here from the Botticelli workshop are executed in egg tempera.

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.

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-
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. 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. In a number of his works, the binding medium is predominantly egg tempera but in others he employs an oil medium more widely. 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. *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. 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.

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* (10:30) and were probably cassone panels or intended as *spalliere* (backboards) of benches or chests in a room furnished for a newly-wed couple. The paintings have recently been conserved and the opportunity was taken to study the artist’s technique in detail. The panels are predominantly painted in walnut oil, although the very glossy green paint seen in a number of passages contains linseed oil. 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. Finally, egg tempera appears to have been used for the red lake pigments. 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.
techniques and would have been quite aware of the different effects that could be achieved. 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...
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.

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.\textsuperscript{34} In all the works in egg tempera, where the green pigment has been examined, malachite has been found.\textsuperscript{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,\textsuperscript{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.\textsuperscript{37} For certain artists such as Cima and Costa, the use of linseed oil seems to have been favoured over that of walnut.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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).\textsuperscript{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).\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{47} FTIR microscopic examination of the samples that contained ultramarine revealed that a small sharp band at $c.2340 \text{ cm}^{-1}$ 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.\textsuperscript{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.\textsuperscript{49} The $c.2340 \text{ cm}^{-1}$ band has been linked to the presence of high proportions of the mineral haüynite,\textsuperscript{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 $c.2340 \text{ cm}^{-1}$ was observed; in the few cases where the band was absent, the samples corresponded to overpaint.\textsuperscript{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.

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**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 small or glass siccatives are discussed elsewhere.\textsuperscript{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.\textsuperscript{53} A strong, broad band is seen at $c.1640 \text{ cm}^{-1}$, but the more characteristic band is the smaller, sharper band at $c.1320 \text{ cm}^{-1}$. 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).\textsuperscript{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 $c.1660 \text{ cm}^{-1}$ and a small, sharp doublet at $c.1365$ and $1320 \text{ cm}^{-1}$, seems to be copper oxalate (FIG. 1).\textsuperscript{55}

Metal oxalates are not often reported in the context of easel paintings,\textsuperscript{56} although oxalate crusts or patinas seem to be ubiquitous in other types of art work and can be quite obscuring.\textsuperscript{57} Calcium oxalates are commonly encountered in glass artefacts and wall paintings;\textsuperscript{58} copper oxalates have been reported in wall paintings and are frequently found associated with bronze artefacts.\textsuperscript{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.\textsuperscript{60} In some cases the oxalate cation source is the pigment (especially with copper), but most of the calcium is likely...
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. \(^6\) 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. \(^6\) 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 approximately 1650\(\text{cm}^{-1}\) and 1550\(\text{cm}^{-1}\) in IR spectra, assigned to the asymmetric carboxylate stretches of the oxalates and soaps respectively. \(^6\)

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. \(^6\)

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. \(^6\) 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 for references


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 Botticelli and the workshop and the opportunity was taken to analyse the technique of these, and autograph, works. While the workshop and autograph paintings all conformed to contemporaneous 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.


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 for a varnish-like effect. In works by Perugino where glass has not been found in red lake glazes (in which 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. Secarà, P. Mosoli, I. Borgia, R.G. Brusetti and A. Sgamellotti, ‘Four anomalous pigments in Perugino’s palatte: 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 varnish.

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).


15 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. 29–54. 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.

16 See note 9.


20 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).

21 From Dunkerton 1996 (cited in note 10); see also Dunkerton and Roy 1996 (cited in note 1); Roy 2004 (cited in note 2).

22 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.

23 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. R.S. Garland, Yale University Art Gallery, New Haven and London 2003, pp. 120–31.

24 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.

25 In paint containing copper-based pigments it can be very difficult to
catherine higgitt and raymond white
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. Rivero, J.-J. Girerd and J.-C. Chottard, 'Chemical reactions between copper pigments and oleoresinous media', Studies in Conservation, 47, 2002, pp. 12–21.
30 In Uccello's Saint George and the Dragon (c.1470, NG 6294), walnut oil is used over a ground by 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 nine-
teenth-century Italian restorers' practice might be an alternative explanation for the detection of tempera graea.
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 Alleyway of Lives, NG 1564; Uffizi: used in conjunction with a sulphur-rich organic black coal in the background of Vivarini's Portrait of a Man, NG 2672, see M. Spring, R. Groust 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.
33 Where samples from workshop and autograph works by Botticelli have been examined, malachite has always been found used in egg tempora, and verdigris in oil. This was discussed by M. Spring and C. Higgitt in a letter given at J. Dunkerton and A. Roy, 'The Technical 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 6.
34 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).
35 Only one of the Botticelli workshop paintings examined was painted in oil (NG 2497) and here the green pigment seems to be verdigris also.
36 Where samples from workshop and autograph works by Botticelli have been examined, malachite has always been found used in egg tempora, and verdigris in oil. This was discussed by M. Spring and C. Higgitt in a letter given at J. Dunkerton and A. Roy, 'The Technical 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 6.
37 With other artists there is a clearer link between scale and medium. Where this choice is made, egg tempora 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).
38 Lead-based paints were used in conjunction with the malachite used in the background of Vivarini's Portrait of a Man, NG 2672, see M. Spring, R. Groust 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.
40 The Adoration of the Magi, c.1495–1505, The J. Paul Getty Museum, Malibu, is similar, see references in note 46.
41 Bomford et al. 1989 and Dunkerton and Roy 1996 (both cited in note 1).
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 1995 (cited in note 6), Halpine 1995 (cited in note 41), Dunkerton 1999 (cited in note 40).
47 Haüynite (or haüyne) is a sulphate-containing mineral of the sodalite series, closely related to natrite, the other mineral responsible for the blue colour of ultramarine.
48 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 Badakshan mines.
50 There is some evidence that the presence of glass may depress the azelaic to palmitic acid ratio for oil films analysed by GC–MS.
52 The surface 'crusts' are essentially inorganic in composition, can contain trapped dirt and so may be quite discoloured, disguising and highly scattering. They are extremely difficult to remove because of the very low solubility of oxalates. The solubility product constants (Ksp) at 25°C are 4.4×10–10 and 3.2×10–20 for CaC2O4 and CaC2O4·H2O respectively.
54 For examples of the detection of calcium oxalate in easel painting see N. Salvado, T. Pradell, E. Pants, M.Z. Papia, 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',


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).


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


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. 75–93. Vibrational modes associated with the deterioration of various pigments are also seen in this region, as are water bending modes (coordinated water).
