National Gallery Technical Bulletin

VOLUME 33

National Gallery Company
London

Distributed by
Yale University Press

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

Series editor: Ashok Roy

First published in Great Britain in 2012 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 is available from the British Library.

ISBN: 978 1 85709 549 4
ISSN: 0140 7430
1034206

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

Photographic credits

All photographs reproduced in this Bulletin are © The National Gallery, London unless credited otherwise below.

CHICAGO
The Art Institute of Chicago, Illinois © 2012. Photo Scala, Florence: fig. 9, p. 77.

FLORENCE
Galleria dell'Accademia, Florence © Galleria dell'Accademia, Florence, Italy/The Bridgeman Art Library: fig. 45, p. 45; © 2012. Photo Scala, Florence – courtesy of the Ministero Beni e Att. Culturali: fig. 43, p. 44.

LONDON
The British Library, London © The British Library Board: fig. 15, p. 91.

MUNICH
Alte Pinakothek, Bayerische Staatsgemäldesammlungen, Munich © 2012. Photo Scala, Florence/BPK, Bildagentur für Kunst, Kultur und Geschichte, Berlin: fig. 47, p. 46 (centre pinnacle); fig. 48, p. 46 (centre pinnacle).

NEW YORK
© The Frick Collection: fig. 11, p. 79; © Courtesy of Richard L. Feigen, New York: fig. 47, p. 46 (lateral pinnacles); fig. 48, p. 46 (lateral pinnacles).

PARIS
© Archives de la Seine, Paris: fig. 31, p. 99; © Archives Vuillard, Paris: fig. 8, p. 88; fig. 9, p. 88; fig. 12, p. 89; fig. 14, p. 91; fig. 29, p. 98; fig. 35, p. 101; fig. 36, p. 101; Musée d'Orsay, Paris © RMN-GP (Musée d'Orsay)/Hervé Lewandowski: fig. 3, p. 85.

PRATO
© Fondazione Cassa di Risparmio di Prato: fig. 46, p. 45.

PRIVATE COLLECTION
© Photo courtesy of the owner: fig. 4, p. 87; fig. 5, p. 87; fig. 6, p. 87; fig. 7, p. 87; Photo © Archives Vuillard, Paris: fig. 13, p. 90.

FRONT COVER
Edouard Vuillard, *La Terrasse at Vasouy, The Lunch* (NG 6373), 1901, reworked 1935 (detail).

TITLE PAGE
TOP LEFT: Adolphe Monticelli, *Subject Composition* (NG 5010), reverse, probably 1870–86 (detail).
TOP RIGHT: Pierre-Auguste Renoir, *The Umbrellas* (NG 3268), *c*.1881–6 (detail).
BOTTOM LEFT: Niccolò di Pietro Gerini, *Saint Peter: Left Tier Main Panel* from *Baptism Altarpiece* (NG 579.2), 1387 (detail).
BOTTOM RIGHT: Edouard Vuillard, *La Terrasse at Vasouy, The Lunch* (NG 6373), 1901, reworked 1935 (detail).

Colourless Powdered Glass as an Additive in Fifteenth- and Sixteenth-Century European Paintings

MARIKA SPRING

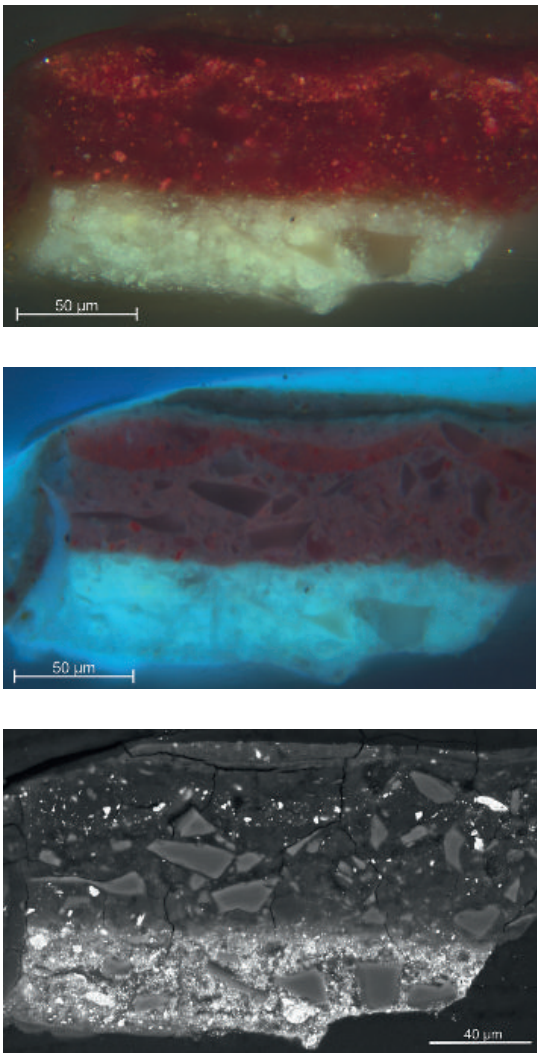
Introduction

References in historic documentary sources to the use of colourless powdered glass as a paint additive have long been noted and discussed. Mary Philadelphia Merrifield included a substantial consideration of this subject in the introduction to her 1849 book *Original Treatises, dating from the XIIth to XVIIIth centuries on the Arts of Painting*.[1] Other significant contributions include that by Van de Graaf, in 1962, which focused on the difficulties in interpretation of the terms that might refer to glass in the documentary sources,[2] and Kirby Talley's comments on its possible function in his 1981 review of the English technical literature before 1700.[3] Until relatively recently, rather few scattered published examples where it had been observed in paint samples existed, generally in individual paintings and polychrome sculpture,[4] although it had been reported to have been used in many early works by Gainsborough.[5]

It is only in the last few years that it has come to be appreciated that colourless powdered glass was used extensively by artists all over Europe during the fifteenth and sixteenth centuries.[6] The first paintings of this period in the National Gallery in which it was possible to establish with certainty, through analysis, that it was glass that was present in the samples rather than some other silicaceous material were those by Raphael. In *The Ansidei Madonna* (NG 1171) the particles are particularly large, making it easy to see their characteristic angular shape, especially when the cross-sections of paint samples are viewed under ultraviolet light and by backscattered electron imaging in the scanning electron microscope (SEM) (FIGS 1, 2 and 3). The particle size also made it possible to extract an individual particle from a paint sample from *The Mond Crucifixion* (NG 3943) to view, in transmitted light under the microscope, the characteristic conchoidal fracture and stress lines of glass (FIG. 4). Energy-dispersive X-ray analysis (EDX) of individual particles in the SEM showed a series of elements that are typical of glass (FIG. 5). Silicon and oxygen are the major elements present, together with significant amounts of sodium, potassium and calcium and more minor quantities of magnesium, aluminium, phosphorus, titanium, manganese and iron.

These findings on paintings by Raphael were first presented in 2003 at a symposium on the materials and technique of paintings by Pietro Perugino, organised by the EU-funded project LabsTech. Perugino also regularly added colourless powdered glass to his paint, as can be seen not only from the National Gallery contributions to the symposium postprints, but also those from Martin and Rioux and from Seccaroni.[7] In 2004, a workshop on Raphael's working practices, organised by the follow-on EU project Eu-ARTECH, expanded considerably the number of known occurrences of powdered glass in paintings by Raphael and other artists working in the same period.[8] The circumstances of these conferences, held as part of cooperative European projects, led to unusually close interaction between authors, both before and after each conference, and an awareness among them of the possibility that powdered glass might be present. A large proportion of the published occurrences are therefore in works by these artists, a circumstance that needs to be borne in mind when considering the patterns of use of this material that they suggest. Quantitative elemental analysis of the glass particles, presented for the first time at the Raphael conference, allows them to be securely distinguished from the other silicaceous materials often encountered in paint, and also showed that in Italian works the composition is of the soda-ash type typical of Italy, made using marine plant ash as the flux. Most of the glass that had been found in northern European paintings at this time was instead made with wood or fern ash, following the same general geographical trends that were known from analyses of archaeological vessel glass. More examples in German paintings published by Lutzenberger et al. have since shown that soda ash glass, probably imported, can also be found in works from these areas.[9]

This article will bring together and review the work of these earlier publications, and also significantly extend the number of examples of the use of colourless



FIGS 1, 2 AND 3 Raphael, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari ('The Ansidei Madonna')* (NG 1171), 1505. Cross-section of Saint John's red drapery. Transparent angular glass particles are visible in the off-white priming, on top of which are several translucent paint layers containing red lake and vermilion in varying proportions. Large jagged and angular glass particles are revealed in the paint as well as the priming in ultraviolet light (middle) and the backscattered electron SEM image (bottom).

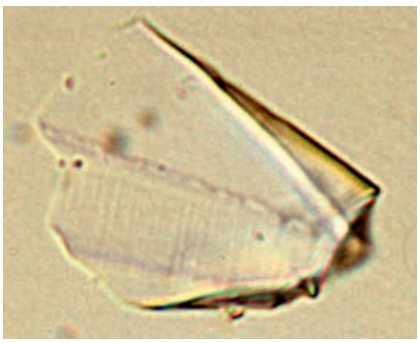


FIG. 4 Raphael, *The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion)* (NG 3943), *c*.1502–3. Particle of glass extracted from a sample from Saint John's red cloak, in transmitted light.

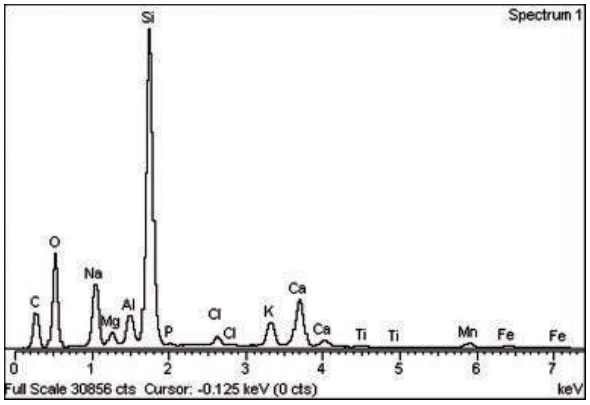


FIG. 5 NG 1171, EDX spectrum of one of the glass particles in a sample.

powdered glass in National Gallery paintings of the fifteenth and sixteenth centuries to more than 70. This allows a more expansive discussion of the patterns of use, and begins to provide a statistically significant basis for consideration of the relationship of the type of glass with the geographical area in which the work was made.

Historical documentary sources

Merrifield's summary of references to pulverised glass as a paint additive in the introduction to her 1849 book, based on the sources she transcribes as well as others, still forms a useful basis for discussion of this subject. She comments that the addition of pulverised glass to orpiment was an 'ancient custom', mentioned in a Bolognese manuscript, where it is suggested that it was added 'in order to grind it quickly'.[10] As Lutzenberger has pointed out, Cennini describes the same practice.[11] Both these sources, dating from the first half of the fifteenth century, concern painting in a tempera medium. The combination of orpiment and ground glass continues to appear, however, in later treatises in the context of painting in oil. Lomazzo advises such a mixture in his treatise on painting of 1584, without an indication of the purpose, but Richard Haydocke's 1598 translation adds the note 'as a dryer' in the margin at this point in the text.[12] In the seventeenth century Sir Theodore de Mayerne included in his manuscript a comment ascribed to Van Dyck which stated that to make orpiment in oil dry it was necessary to add a little 'verre broyé'.[13] Pacheco (1649) also noted that orpiment in oil needs a drier, and

that some people used glass ground with water.[14] As late as 1835 George Field mentions that 'levigated glass' was used with orpiment as a drier, although it is clear from the context that he is referring to historical rather than contemporary practice.[15]

Powdered glass is also mentioned as a drier for other colours, ground directly with the pigments and oil, or as an ingredient in the preparation of boiled oils. Among those references where the pulverised glass is simply mixed with the paint, both discussed by Merrifield, are Pacheco's recommendation that it be used as a drier for carmine,[16] and a seventeenth-century Paduan manuscript, which suggests that it be used 'To make lake, indico, and lamp black, dry quickly', with the instructions 'Grind them with oil, then take glass ground to a very fine powder, and incorporate with the colours by grinding them together again', adding the further information that 'in the space of 24 hours, they will dry'.[17] This manuscript is among several sources that stress the need for the glass to be of small particle size, another example being that written by the English painter Marshall Smith, in 1693, which stated '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 White, Ultramarine, &c. and is much us'd in Italy.'[18] In addition to the comment relating to orpiment mentioned above, the De Mayerne manuscript includes several other references where powdered glass is added to the paint as a drier; 'un peu verre pillé impalpablement' for red lake,[19] and for colours that do not dry well 'verre chrystallin pulverisé'.[20] A note beside an entry which discusses driers for mixing with colours, taken from *Le Petit Peintre*, specifies 'Verre de Venise', as does another entry.[21] The 1635 Brussels manuscript written by the painter Pierre le Brun uses the term *cristal broyé*, stating simply that 'mixed with the colours [it] is good to make them dry'.[22]

Merrifield does not discuss earlier recipes of this type, but one is included in the Marciana manuscript from the second half of the sixteenth century; a mordant for gilding in which one of the ingredients is 'vetro macinato prima con acqua et poi asciutto' (glass first ground in water and then dried), together with lead white, ochre, lead-tin yellow and boiled oil.[23] A South Netherlandish recipe book of the sixteenth century in the Plantin Moretus Museum, Antwerp, gives the following list under the heading 'On mixtures for all manners of working in oil'; 'Spaens groen met massicot. Root met menie. Blau met glase. Swart met coperrot als spaens groen. Sinober met glas'. Although it does not state that 'glas' is included as a drier, it is perhaps implied by the context, since all the other mixtures include a material that could perform this function.[24]

The use of the word 'glas' in this last documentary source raises the question of the difficulties in interpretation of the term, as discussed in detail by Van de Graaf.[25] He takes as an example two varnish recipes in the eleventh-century writings of Theophilus, arguing that the term 'glassa' is used as a qualifier together with 'fornis' to signify a hard resin, further suggesting that there is a connection with the Latin word 'glaesum', meaning amber. He goes on to demonstrate that in a fifteenth-century Strasburg manuscript 'fornis glassa' becomes 'virnis glas'. In two varnish recipes in the *Liber illuministarum* from around 1500, which Van de Graaf considers to derive from Theophilus, the term is used again, as well as the term 'venedigisch glas' which is taken to mean another type of resin. Van de Graaf further points out that references to resins as a siccative do exist, including Armenini's description of the preparation of a varnish made from mastic resin and oil, which he advises can be added to fine blues, lakes and other colours so that they dry more quickly.[26]

Van de Graaf considered that the seventeenth-century recipes where powdered glass is an ingredient, including those where it is mentioned as a drier, result from mistranslation of these terms, further propagated over the centuries through reliance of subsequent treatises on earlier sources. This seems very probable in some of the recipes for boiled oils or varnishes, especially those cited by Van de Graaf that include as much as two parts 'glas' to three parts oil.[27] The analytical evidence from paintings, however, shows that artists did in fact regularly add glass to their paint, so it seems reasonable to suppose that at least some of the references in the documentary sources do genuinely refer to powdered glass. A recipe for 'Olio cotto' in Baldinucci's *Vocabulario del Disegno* (1681), for tempering colours that are slow drying, instructs that the linseed or nut oil should be boiled with glass that had been finely ground in water,[28] and indeed this method of grinding is also mentioned in several of the references quoted above. It seems unlikely that a resin would be prepared for addition to oil in this way, and it seems reasonable to conclude here that the intended ingredient could really have been glass and not a resin. Palomino (1724) includes a recipe for a linseed oil drier where an ounce of litharge, an ounce of ground

glass and a head of garlic were boiled together with half a pound of oil. This was followed by a similar recipe for 'A drier for blues and whites' made from walnut oil to which was added 'some ground glass and a little bit of litharge and white lead ground with the same oil, and another bit of red lead, in the proportion of about one ounce of each ingredient for half a pound of walnut oil', boiled together over a water bath. Here the glass forms a relatively minor component of the boiled oil recipe, and again can probably be interpreted as true glass.

Palomino continues immediately with 'other driers that may be used on the palette' which are 'excellent for all colours', including one 'made of glass, very well ground with linseed oil or walnut oil, and tempered like any other colour, and reground very well. It can be kept like other colours, in little pouches…and some may be taken out and placed on the palette when needed.' It seems doubtful that Van de Graaf's premise of a mistranscription of 'glas' applies to this recipe, and the others discussed above, where the glass is added on the grinding slab rather than heated with oil, since it would be unlikely that powdered resin would be added to the paint or oil in this manner.[29]

Occurrences in paintings

Table 1 lists the fifteenth- and sixteenth-century paintings in the National Gallery in which the presence of powdered glass has been confirmed through the analysis of paint samples, as well as a few works from outside the collection.[30] As already noted above, the use of powdered glass has been reported in later paintings, but this paper focuses specifically on earlier works, with the purpose of tracing it backwards to as early a date as possible. The table does include one painting from the very first years of the seventeenth century, by Annibale Carracci, since his career began in the late years of the sixteenth century.

The paintings are divided according to the location in which they were made and then listed in chronological order. Marshal Smith's comment that glass 'was much used in Italy' has proved to be quite accurate.[31] So far, it has been found in samples from 40 National Gallery paintings of this period from all over Italy. Raphael seems to have used it particularly extensively and it has been found in all except one of his works in the collection that have been sampled. Going back to the previous generation of artists working in Italy, it is present in the red lake-containing oil glazes in *The Virgin and Child* (NG 751) by Raphael's father Giovanni Santi, from about 1488, and in a painting by Justus of Ghent and workshop of *Music* (NG 756), probably painted in Urbino. This work, which is in oil, dates from the 1470s and is the earliest of the paintings from Italy in which it has so far been found.

All the glass particles analysed contain manganese in varying amounts, up to as much as 2% in some cases, which has proved to be a useful marker that can be detected using portable X-ray fluorescence (XRF) analysis, a non-destructive technique. It is known that in Italy from at least as early as the end of the thirteenth century manganese-containing minerals were deliberately included in glass recipes to counteract the greenish colour that can result from iron impurities in the sand or pebbles, so that a colourless product was produced. Manganese can also originate from the ashes used as a flux.[32] Four of the works in the table were analysed by a visiting research group from ENEA (Rome) using XRF, which was able to detect small, but significant levels of manganese in areas painted with red lake where it had been established from samples that glass was present.[33] Manganese was also detected during this XRF campaign in a further eight Florentine paintings in the National Gallery dating from about 1515 to about 1570 (none of which were sampled), allowing occurrences in other works by Pontormo and Bacchiacca from the series of scenes from the Story of Joseph, painted for the Borgherini Bedchamber (NG 6451, NG 6453, NG 1131 and NG 1218), to be added to those listed in the table (NG 1219, NG 6452). The analyses also confirmed that powdered glass had been used by other artists not represented in the table, including Andrea del Sarto, Marcello Venusti and Giovanni Antonio Sogliani.[34]

The use of XRF analysis by the Italian research group from ENEA (the Italian National Agency for New Technologies, Energy and Sustainable Economic Development) has allowed results from a large number of Italian paintings to be collected.[35] In addition, the publications following the workshops on Perugino and Raphael mentioned in the introduction above produced many further examples in works by these artists and their contemporaries. As well as the three works by Perugino included in Table 1, it was reported in four paintings by him in French museums,[36] as well as 23 works by him or his assistants studied by XRF by Claudio Seccaroni.[37] Seccaroni analysed a total of 44 paintings on panel and canvas, spanning almost the whole of Perugino's

career from 1473 to his death in 1523. Manganese, and therefore glass, was found in areas painted with red lake in almost all of his works made after 1490 but not in the earlier paintings.

Glass has been found in seven paintings by Raphael in the National Gallery, used much more abundantly than by Perugino in paint of a variety of colours; it has also been reported in a further eight works in other collections.[38] Seccaroni has, with XRF, found manganese in the red lake glazes of another 41 Italian works of this period, including fourteen panels painted for the Borgherini Bedchamber between 1515 and 1519 (by Andrea del Sarto, Pontormo, Bacchiacca and Granacci), as well as six other paintings by Pontormo, four works by Fra Bartolommeo and paintings by Parmigianino and Bronzino.[39] Other studies have shown that Lorenzo Lotto also followed this practice.[40] Michelangelo used glass in the National Gallery's *Entombment* (NG 790), listed in the table, and in addition XRF analysis has suggested that it is present in his *Doni Tondo* (Uffizi Gallery, Florence).[41]

This review of published occurrences of powdered glass in Italian paintings of this period demonstrates just how commonly it was used as a paint additive, and makes it evident that this was not a material employed only occasionally by artists but a habitual aspect of their technique. Seccaroni has speculated, from the broad perspective given by XRF analysis of a large number of Italian works, that it was most widely used between around 1490 and 1530, particularly by artists working in Florence, or who had worked there at some point during their career. The list in Table 1 does seem to support this, although this apparent pattern of use might reflect the degree of attention that has been devoted to the technical examination of paintings by the important artists working there at that time. More recent technical examination of the majority of the National Gallery's sixteenth-century Italian paintings from Ferrara and Bologna, in support of a forthcoming scholarly catalogue, produced a significant number of occurrences from these areas of Italy, particularly in works by Lorenzo Costa and Francesco Francia.[42] It is interesting, however, that although Garofalo also worked in Ferrara and Bologna, no glass was found in an extensive study of all his paintings in the National Gallery.

There are also a few examples in Table 1 of artists working further north in Verona, Brescia and Milan. Works from northern regions of Italy have not been so systematically studied, but even so there are some indications that it was not so extensively used there. A recent survey of ten Leonardeschi paintings produced in Milan included only one work in which colourless glass was identified, the *Angel in Green with a Vielle* (NG 1661) attributed to Francesco Napoletano (*?*), which was part of the altarpiece for which Leonardo's *Virgin of the Rocks* (NG 1093) was the central panel. Marco Marziale used colourless powdered glass with red lake in the Virgin's red drapery in his altarpiece dated 1507 (NG 804), made for a church in Cremona and painted either there or in Marziale's home town of Venice. This is the only work in the table that might possibly be Venetian. A number of paintings by Bellini and Cima have been analysed by XRF by Seccaroni without finding any evidence of the use of glass as an additive in red lake glazes,[43] although care needs to be taken in interpretation of these results since, as can be seen in Table 1, the glass in the paintings from outside Tuscany and Umbria generally seems to have a lower manganese content. A study of samples, however, did not reveal any glass in any of the early paintings by Titian in the National Gallery from before about 1520, although one occurrence in the later *Venus and Adonis* (J. Paul Getty Museum, California) has been reported.[44] Lutzenberger et al. have found glass in three paintings by Tintoretto, but mixed with the famously difficult-to-grind orpiment, where its purpose could have been quite different.[45]

There are twelve German school paintings and fifteen Netherlandish School paintings in the table, including Rogier van der Weyden's *Magdalen Reading* (NG 654), and two paintings by Jan van Eyck: *The Arnolfini Portrait* (NG 186) and *The Annunciation* in the National Gallery of Art, Washington. These three works all date from the 1430s and are the earliest paintings in which colourless powdered glass has been found, although it has also been reported in a German painting of around the same date, by Lukas Moser.[46] Within each painting, it seems to have been used in a rather more limited way than in the Italian works, and rather fewer occurrences in northern European works have been confirmed than in Italian paintings. This may, however, be a reflection of the number of works that have been studied with the possible presence of glass in mind: two further examples in Netherlandish paintings and twelve in German paintings have been published by Lutzenberger et al.[47] This includes *Saint Anne with Mary and Child* (Bayerische Staatsgemäldesammlungen, Munich) by the Cologne painter the Master of the Saint Bartholomew altarpiece, and indeed it was found in all three National

Gallery works by this artist that were included in this study. Colourless glass particles have also been observed in many different areas of paint in Hans Holbein the Elder's 'Graue Passion' of around 1495 (Frankfurt).[48]

French paintings of this period are not well represented in the National Gallery, so the table includes only two works, one by the Master of Saint Giles and one by the Master of Moulins (Jean Hey). Powdered glass has also been reported in red lake glazes on three fifteenth- and sixteenth-century French works elsewhere: *A Portrait of a Man* by Jean Perréal (1493, Musée du Louvre, Paris), *The Immaculate Conception Triptych* by Jean Bellegambe (*c.*1521) and a *Pietà* by Rosso Fiorentino (*c.*1530, Musée de la Chartreuse, Douai).[49] Similarly there are very few Spanish works of this period in the National Gallery, but the *Virgin and Child* (NG 1229) by Luis de Morales, which probably dates from around 1570, serves to show that artists there also used colourless powdered glass as an additive.

Leaving aside the possibility of finding colourless glass in tempera paintings together with orpiment, having been used as an aid for grinding the pigment, according to Cennini's suggestion, the practice of using it as a paint additive in other colours does seem to be associated with an oil medium. The works listed in Table 1 are all oil paintings, and for a large number of them this has been confirmed by analysis.[50] This can be further supported by considering the paintings by Costa, where powdered glass was found in several works that are in oil, but not in the two glue size paintings that are part of a series depicting the *Story of Moses* (NG 3103 and NG 3104).[51] Similarly, Seccaroni's XRF survey of a large number of works by Perugino or his workshop found that manganese (and therefore glass) was present in all the works painted after 1490, except those which had a matt surface and paint texture that suggested an egg tempera medium.[52]

Artists did not add colourless powdered glass to their paint in a universal manner, to all of the paint in a single work, at every stage and to every colour. It is of interest to consider where and how it was used, since, as well as perhaps indicating how a particular painter chose to use this material, it might provide clues as to the motivations of the artist in adding it. For each work listed in Table 1, the location on the painting in which colourless powdered glass was seen and the pigments with which it was mixed are described. The view that this gives of where and how glass was used in each painting is not complete, but is dependent on which areas had been sampled during earlier examinations, as none of the samples were taken specifically for this study. However, for the artists such as Raphael and Perugino, whose work has been the subject of deeper, more complete technical investigation, it is possible to gain a more representative idea of their practice.

The earliest references in historical documentary sources do not give information about the purpose of the glass. Those from the seventeenth century onwards, however, recommend glass for pigments with poor drying qualities – those specifically mentioned are red lakes, indigo, blacks and orpiment – as well as in mordants for gilding, where again good siccative properties are required. Merrifield stated that Venetian glass was rich in lead, and might therefore be able to perform this function. She also mentions that Italian glass could contain manganese. Both these metal ions were already known to accelerate the drying of oil.[53] The analyses show that the glass added to paint at the period considered in this paper was not generally lead glass, but does contain manganese at varying levels, exceeding 2% in a significant number of the paintings (Table 1). Lutzenberger et al. have pointed out, however, that it is not certain that its mobility in glass is sufficient to allow it to act on the oil over a short timescale. They have proposed that the glass might instead have an optical function, possibly increasing the depth of colour, and acting as a transparent filler, since it has a similar refractive index to the oil. [54] Martin and Rioux have suggested that using it as an extender would allow thick layers to be applied without too deep a saturation of colour.[55] This supposition was confirmed by reconstructions by Pinheiro de Melo et al. of red lake mixed with glass in oil; they also noted that it produced a paint with a creamy consistency, more body and good working properties.[56]

The particle size of the glass must also be an important factor in considering both whether it could act as a siccative and its effect on the working and optical properties of the paint. An approximate range, estimated from the backscattered electron image in the SEM, is included in Table 1. It seems to be typically more finely ground in the Netherlandish and German paintings than in Italian paintings, often averaging only 2–5 microns across and usually needing EDX mapping in the SEM to locate the particles. The glass in the priming and the paint of the red cloak in *Christ Crowned with Thorns* (NG 1083) by Dirk Bouts, seen in the silicon EDX map (FIGS 7 and 8), is typical, with most of the particles

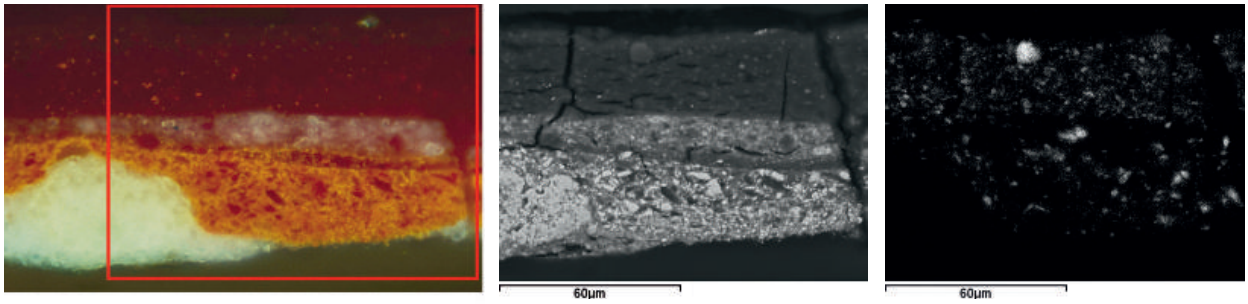
being in this range, even if one or two larger particles are also present. The very high surface area that this creates needs to be borne in mind when considering whether manganese within the particle might be able to react with the oil, as does the practice mentioned in several sources of grinding the glass in water, sometimes drying it and then grinding it again, since this might create a more active surface. Among the Northern European paintings it is only in Martin van Heemskerck's *Virgin and Saint John the Evangelist* (NG 6508.1) that the majority of the particles are larger, averaging 30 microns in size (FIGS 9 and 10). The red paint in this work includes a very large proportion of glass, but often, particularly in the earlier Netherlandish works by van Eyck, Campin and van der Weyden, rather less is used and only a few particles can be seen in a cross-section. In the Italian paintings a particle size as large as 30 microns seems instead to be quite common, with even more coarsely ground glass of around 40–50 microns in several works.

It is clear from the table, and from earlier published studies, that glass was most commonly added to translucent red lake-containing paint. In most of the Netherlandish and German paintings it is the only area in which it was used. It is not only present in the final uppermost layers that are rich in red lake, however, but is also quite frequently mixed with opaque pigments in the underpaints. In *Two Tax Gatherers* (NG 944) from the workshop of Marinus van Reymerswaele, in fact, the silicon EDX map shows that it is not present at all in the final thin glaze, which has a blotted texture from application with a cloth, but that it is in the thicker initial overall red lake layer as well as in the underpaint (FIGS 11, 12, 13 and 14). This is perhaps evidence that the artist did not choose to add glass to give particular optical properties to the surface paint in this case, but added it to the layers below in the belief that it would allow them to become touch dry as quickly as possible so that the final touches could be applied. Artists had a choice of driers, but powdered glass would be particularly suitable for red lakes as it would not compromise the colour or transparency.

There are also a few northern European examples where it is present in oil mordants for gilding: in Jan van Eyck's *Annunciation*, in two paintings from the workshop of the Cologne painter known as the Master of the Life of the Virgin, one work by the Master of Cappenberg and one by the Master of the Saint Bartholomew Altarpiece.[57] All these mordants are heavily pigmented and the glass is only a minor component, mixed with other siccative pigments such as lead white and lead-tin yellow, as well as yellow earth, exactly the same combination mentioned in the recipe in the Marciana Manuscript.

Colourless powdered glass was used far more generally in the Italian paintings. Again it is most commonly found together with red lake, but is also used very widely as a component of primings. The only Italian painting in the National Gallery in which it has so far been found in a mordant is Raphael's *Ansidei Madonna* (NG 1171) where, unlike in the northern European paintings, it is used alone, without any pigments. A similar mordant containing glass has been reported on Raphael's *Angel with a Scroll* (Musée du Louvre, Paris) and for the gilding on the book held by Saint James in Perugino's *Saint Ercolano and Saint James the Less* (Musée des Beaux Arts, Lyon).[58] For both the primings and the mordants it seems unlikely that glass had an optical function, since it is hidden beneath the paint or gold leaf. Instead it is likely to have modified the handling and perhaps the drying properties, and may have given greater body to the paint, which could have been desirable, in particular for a mordant.

In Raphael's *Ansidei Madonna* (NG 1171), where glass is present in paint that is not rich in red lake, it is in the grey architecture and the orange-brown paint



FIGS 6, 7 AND 8 Dirk Bouts, *Christ Crowned with Thorns* (NG 1083), *c.*1470. Cross-section of Christ's red cloak, showing several thick layers of paint based on red lake, on a more opaque orange-red underpaint of vermilion and red lake (left). The small glass particles in all the paint layers are visible in the backscattered electron SEM image (middle) and the silicon EDX map (right).

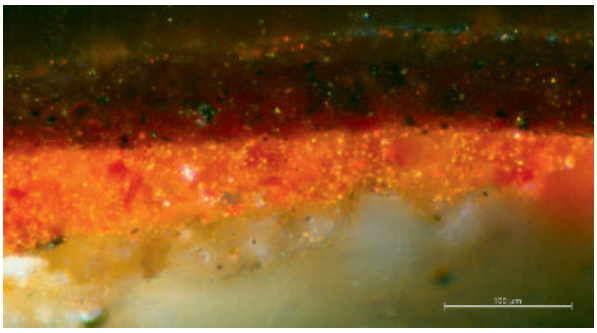


FIG. 9 Martin van Heemskerck, *The Virgin and Saint John the Evangelist* (NG 6508.1), *c.*1540. Cross-section of Saint John's red drapery, normal light.

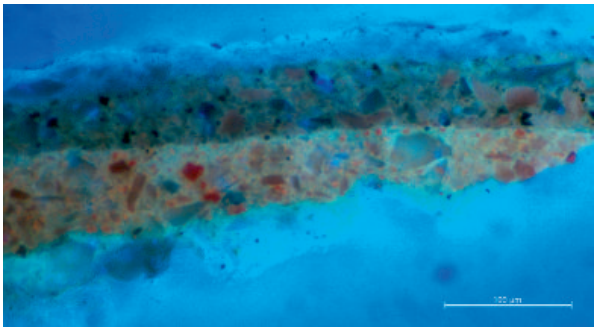
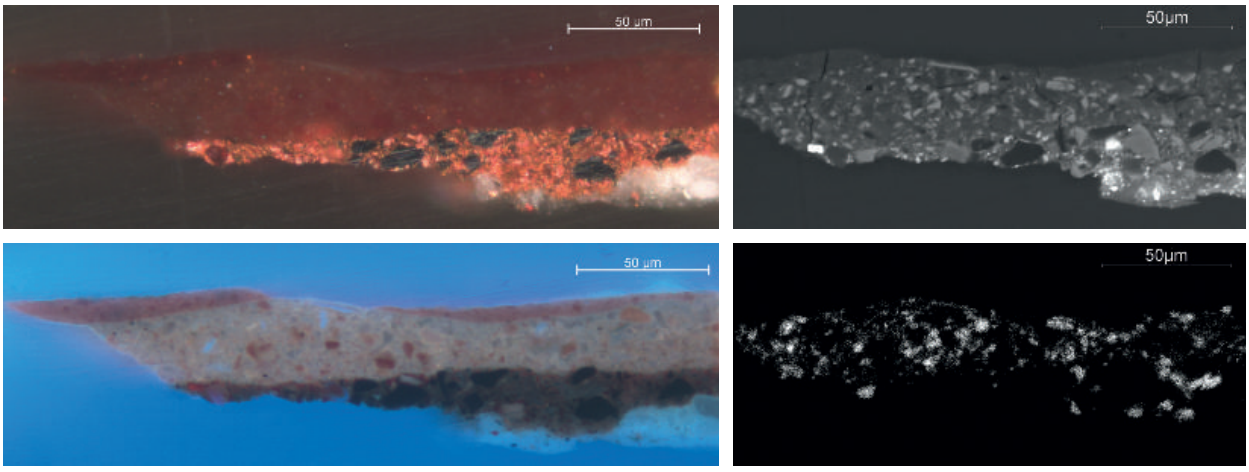


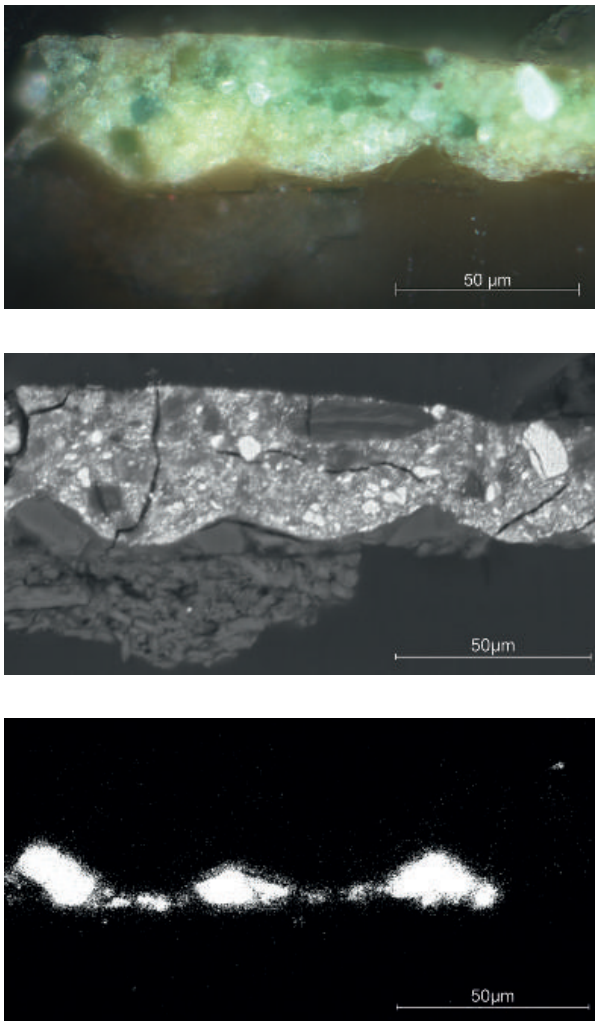
FIG. 10 NG 6508.1, cross-section of Saint John's red drapery in ultraviolet light, showing large jagged colourless glass particles in both the opaque red underpaint and the translucent dark red upper layer based on red lake.

depicting wood on the throne. In *Saint John the Baptist Preaching* (NG 6480), one of the predella panels that belongs with this altarpiece, it is again used in grey and orange paint, as well as the greenish-brown foreground. The same pattern of use for colours other than red – grey, orange, brown and brownish-green paint (this last colour always in the landscape) – recurs in all the other paintings in the table by Raphael, suggesting that a deliberate choice was made as to where to include the powdered glass. Martin and Rioux also found glass in the paint of the grey architecture of the *Angel with a Scroll*. The other artists in the table for whom more or less all the paintings in the collection have been comprehensively studied are Costa and Francia, where interestingly a similar trend appears, with the paint in which glass is present (but not associated with red lake) being either grey or brown, or, in the case of Costa's *Concert* (NG 2486), black.

In 27 of the Italian paintings glass was used in the priming (applied over gesso in every case). The priming on Domenico Beccafumi's *Story of Papirius* (NG 1430) has a translucent yellow-brown appearance and in previous studies it had been thought to be unpigmented (FIGS 15, 16 and 17). It is only in the backscattered SEM image that it can be appreciated that it contains glass, unmixed with pigments so that only the colour of the oil is evident. In other primings the glass has been mixed with only a small amount of lead white, so that again it is quite translucent and had previously been thought simply to be medium-rich. These include Costa's *Concert* (NG 2486), as well as the altarpiece he finished after



FIGS 11, 12, 13 AND 14 Workshop of Marinus van Reymerswaele, *Two Tax Gatherers* (NG 944), *c.*1540. Cross-section of the red cloak of the man at the right of the painting (top left). In ultraviolet light (bottom left) a thick layer of red lake with a thin final red glaze over it is visible above the opaque orange red underpaint. The backscattered electron SEM image (top right) and the silicon EDX map (bottom right) show that glass particles are not present in the final glaze but are abundant in the lower layers.



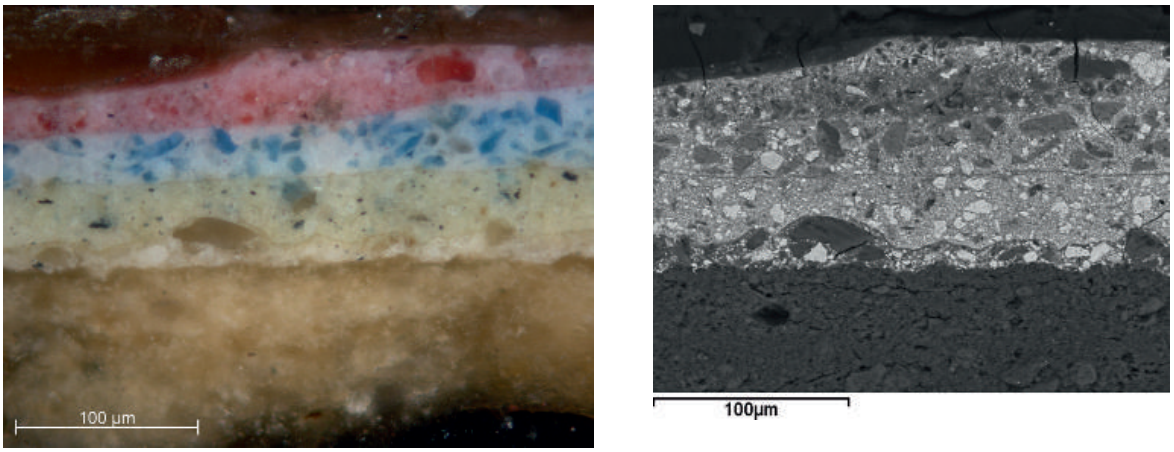
FIGS 15, 16 AND 17 Domenico Beccafumi, *The Story of Papirius* (NG 1430), mid 1520s. Cross-section showing the translucent priming containing only colourless powdered glass beneath the green paint of the standing female figure at the right of the painting (top). The backscattered electron SEM image (middle) and the silicon EDX map (bottom) reveal a few very large angular glass particles.

Mainieri had painted part of it (NG 1119), Foppa's *Adoration of the Kings* (NG 729), *The Incredulity of Saint Thomas* (NG 1051) by Giovanni Battista da Faenza, Antonio da Vendri's *The Giusti Family of Verona* (NG 749) and Gerolamo dai Libri's *Virgin and Child with Saint Anne* (NG 748).

Far more frequently, however, a distinctive mixture of lead white, colourless glass and a little lead-tin yellow was used for the primings in the Italian paintings in the table.[59] It is found on all of Raphael's paintings in the National Gallery except *Portrait of Pope Julius II* (NG 27). Seven more of his paintings in other collections can be added to this list, the earliest being the *Saint Nicholas of Tolentino* altarpiece (Louvre, Paris) from around 1500 at the very beginning of his career, and the latest in date being *La Fornarina* (Palazzo Barberini, Rome) from around 1518–19,[60] showing that remarkably he regularly used this type of priming for nearly two decades, almost the whole of his working life. All of the paintings by Perugino examined in this study also had this type of priming, as did four paintings by this artist in French collections.[61] It was also used in the preparation of both the panel by Bacchiacca and that by Pontormo painted for the Borgherini bedchamber, and it seems likely that the others in the series were prepared in the same way. In total nineteen of the paintings in the table, from Florence, Umbria, Ferrara, Bologna and Rome, have this type of priming, the earliest being Perugino's *Certosa di Pavia* altarpiece (NG 288.1–3) from around 1496–1500 and the latest being Beccafumi's *Tanaquil* and *Marcia* (NG 6368 and NG 6369) from around 1519. An even later example has been reported in Lorenzo Lotto's *Madonna delle Grazie* (State Hermitage Museum, Saint Petersburg) dating from 1542.[62]

Riitano and Seccaroni carried out experiments to investigate the behaviour of this type of paint mixture, and to try to understand the role of the glass, making reconstructions of primings consisting of lead white and lead-tin yellow in oil, with or without glass. To simulate what was found in the paintings as accurately as possible, a similar proportion of lead-tin yellow and Tuscan sixteenth-century manganese-containing glass was used. This was applied onto a board prepared with gesso onto which black lines in different media had been drawn to simulate underdrawing. There seemed to be little difference in transparency, but they found that the priming containing glass did dry more quickly, and noted that freshly crushed glass was more effective in this respect. They also noted that the surface of the priming that contained glass had a slightly gritty texture.[63] The uneven surface of the priming on Gerolamo dai Libri's *Virgin and Child with Saint Anne* (NG 748) evident in the backscattered SEM image of a sample (FIGS 18 and 19), clearly caused by the coarsely ground glass in this case, suggests that it too would not have been smooth but would have had a perceptible surface texture, although there is no particular evidence that the same was true for other paintings, or that this was an important property conferred by the glass and the motivation for its use.

Lutzenberger et al. and Pinheiro de Melo et al. both describe reconstructions of oil paint composed of red lake together with glass,[64] the former using soda-lime glass and lead glass, the latter using only lead glass. In



FIGS 18 AND 19 Gerolamo dai Libri, *The Virgin and Child with Saint Anne* (NG 748), 1510–18. Cross-section of the red sleeve of the angel at the left, showing the off-white priming on top of the gesso ground, including some large translucent particles of glass (left). The backscattered electron SEM image (right) shows the boundary between the priming and paint and the protruding glass particles giving the priming an uneven surface.

both trials it was found that where glass was included the working properties were improved and the paint had more body, while still maintaining an acceptable depth of colour. Neither noted any decrease in the drying time, but Pinheiro de Melo commented that they did not consider that their experiments, carried out on a small scale, allowed a firm conclusion to be reached on this particular question, and it can further be added that the modern glass that was used does not closely mimic that found in paintings in terms of composition.

The composition of the glass

Glass was made from a silica source such as sand or pebbles, and a flux, which at this period would have been some kind of alkali-rich wood or plant ash. Generally, in the Mediterranean area the ash of sodium-rich coastal halophytic plants was used, while in northern Europe the flux could have been various types of wood ash or fern ash in which the alkali content was predominantly potassium. The type of plant ash, and the way it was prepared, influenced the composition of the glass, as did the purity of the silica source. Quantitative SEM–EDX analysis (Table 1) of the major element composition provides information on the type of glass used in each painting, and on the possible raw materials used to make it, the interpretation of which is aided by the extensive published literature on the composition of medieval and post-medieval vessel and window glass from around Europe. Analysis was carried out on samples prepared as polished cross-sections. Spot measurements were made on several particles in each sample, from which it was possible to assess the consistency of the composition, and to determine whether more than one type of glass was present, or whether there were variations due to differing degrees of leaching of alkali as a result of ageing. Where all the particles were reasonably homogeneous, the values quoted in the table are an average of the results. In the samples where some of the glass was leached, the composition of the least altered particle is listed, as this will be closest to its original state. For some paintings, the results from different particles could be sorted into distinct compositional groups, each of which is included in the table.

The experimental details are given in the Appendix, including an assessment of the accuracy of the SEM–EDX analysis using Corning Museum of Glass standards. In addition, there are other limitations that affect the quantitative measurements that are not due to the analytical technique used but stem from the character of the samples, which need to be considered when interpreting the results. The interaction volume of the beam is sometimes larger than the particles, if they are small, so that elements from the pigments around the glass contribute to the spectrum, most commonly lead from lead white and aluminium from red lake. Red lake pigments can additionally contain other elements which are inconvenient in that they are also found in glass, particularly potassium and phosphorus, the latter present at higher levels in lakes prepared from insect dyestuffs. It is also not possible to know the thickness

of the glass particles, so that elements from behind as well as around them might interfere. For this reason, the largest particles in a sample were chosen for analysis. A consequence of normalisation of the data is that for those paintings where there is evidently leaching of alkali even in the best-preserved particles in the sample, the calculated values for the metal ions will be higher than the true value. Another possible pitfall when searching for glass is that paint often contains silicaceous material in various forms, and it is important to distinguish between this and glass; this is an issue particularly where earth pigments are present, or ultramarine, which always includes numerous different complex colourless associated silicates, or red lake, where small particles of a silicaceous nature can be present that originate from the dyestuff source.[65]

Glass in Italian paintings

The raw materials for clear, high-quality Venetian glass were carefully chosen and controlled. From the middle of the fourteenth century onwards in Venice, sand was replaced by quartz pebbles from the Ticino and Adige rivers, a much more pure silica source that contained less of the metal ions such as iron that could colour the glass. The soda ash used in Italy for glassmaking was imported, either from the eastern Mediterranean (Levantine ash, from Syria or Egypt) or from the western Mediterranean, especially from Alicante in Spain (Barilla). Certain species of plant from particular areas were used, since those in which the alkali was mainly present in the form of the more soluble carbonates and hydroxides were more suitable than those which contained chlorides and sulphates. In Venice the more expensive and higher quality Levantine ash was used. It is known both from glass analyses and from historic documents that in Italy manganese oxide was added when making colourless glass to oxidise the iron to counteract the green or yellow colour that it imparted. The use of consistent and familiar raw materials allowed glass of a reliable quality and predictable working properties to be made.

From the middle of the fifteenth century Venetian documents mention three types of colourless glass: *vetro commune* (common glass, slightly tinted), *vitrum blanchum* (colourless glass) and the very high quality *cristallo* (crystal glass), which was made from purified ashes. This process removed insoluble iron compounds from the ash, as well as calcium and magnesium. Venetian *cristallo* glass can therefore be recognised by its typical CaO content of around 5% coupled with a low MgO content of around 1.8%, and a low iron content (0.2–0.3%), with a correspondingly lower manganese content, since less needed to be added to counteract the tinting effect of the iron. *Vitrum blanchum* and common glass instead contain around 10% CaO and 3.5% MgO, with common glass containing considerably more iron than the other two types (0.7–1.0 Fe_2O_3) as well as more manganese.[66] Although the documentary sources that refer to powdered glass as a paint additive do sometimes specify that the 'whitest glass' should be used, or in one case 'verre crystallin', which might be *cristallo*,[67] it seems possible that painters might also have used the slightly tinted *vetro commune*, since once ground to a powder it would be very pale in colour and probably little different in appearance from the other, higher quality glasses.

A study by Cagno et al. of vessel glass fragments dating from the ninth to the sixteenth centuries from archaeological sites of glass production in Tuscany identified several different compositional groups that corresponded to the use of two different types of ash (Levantine and Spanish) and two different silica sources (river pebbles and local sand). There were clear differences in the K_2O content of the glasses. One group contained about 3% K_2O, which is typical of Levantine ash, while another group with about 6% K_2O could be identified, probably made with Spanish (Barilla) ash in which the potassium content is higher. Generally, in both of these groups the CaO content was around 10%, but among the glasses made with Levantine ash there were some that contained only around 5% CaO, suggesting the use of purified ash. The two silica sources could be distinguished by the Al_2O_3 content of the glass. Some of the glasses contained 1.6–2.3% Al_2O_3 and are likely to have been made with river pebbles. Other glasses had a particularly high Al_2O_3 content of more than 3.5%, not found in Venetian glass, which was proposed to be Tuscan sand from a local source such as that at La Casina.[68]

In Table 1 it can be seen that the colourless glass in all but one of the Italian paintings is sodic, as would be expected, containing in general more than 10% Na_2O, except where some leaching of the alkali has taken place. The K_2O content is almost never as high as would be expected for Barilla ash but instead ranges between 2 and 4%, indicating that all of the glass was made with Levantine ash.[69] The most significant compositional

distinction that can be made, however, is based on the Al_2O_3 content. Taking only the results from large particles where it can be seen that there is little contribution of Al from the red lake around them, or from paint that does not contain this pigment, it can be seen that in some samples it is very high, at around 4–5%, while in others it hovers at levels around only 1–2% (the reliable high-Al results are marked 'h' in the table). These two groups are comparable to those identified in the study of Tuscan archaeological glass as being made from either Al-rich Tuscan sand or from purer river pebbles similar to those used for Venetian glass. Interestingly, all of the Al-rich glass is found in paintings from Tuscany, or in paintings by Raphael and Perugino, who were working in both Florence and Perugia or other locations in Umbria. There is one painting, however, which does not fit this possible pattern: *Noli me Tangere* (NG 639), which is catalogued as by an Imitator of Andrea Mantegna since the composition is in the style of his work of the 1460s. A large date range of 1460–1550 has been ascribed to it, but it is thought to be a north Italian work, probably of the late fifteenth or early sixteenth century. Rather little is known about when and where this work might have been produced, so this finding does not necessarily negate the idea of a possible compositional trend, but it does signal that further work is needed, particularly in gathering further occurrences in paintings from the northern part of Italy. In addition, other than for Venice, studies of archaeological glass to use as comparative data are also rather sparse for this area of Italy; one study of glass production in Liguria during the fourteenth and fifteenth centuries seems to indicate that the glass produced there was also rich in aluminium.[70]

In the Italian paintings the glass particles within one sample or separate samples within one painting were generally very consistent in composition. The only exceptions were Raphael's *Ansidei Madonna* (NG 1171), his *Saint John the Baptist Preaching* (NG 6480), which is a predella panel from the same altarpiece, and Perugino's *Virgin and Child with Saints Jerome and Francis* (NG 1075). In the samples from these paintings two well-separated compositional groups could be identified, one of which was high in aluminium and likely to be the sand from a Tuscan source proposed by Cagno, the other of which is low in aluminium and was therefore most probably made with river pebbles. In all the examples of glass made from Tuscan sand the manganese content was higher than in the glass made from river pebbles, ranging from 1.5 to 2.5%, indicating that more manganese dioxide was added during production to compensate for the higher iron content of the less pure silica source. This difference in Mn content is also evident in the two types of glass in these paintings.

In the sample from the painting by Perugino, the Al-rich glass also has a lower CaO content of around 5.3%, together with a lower Mg content of 2.0%, which is an indication that the ash has undergone some kind of purification process similar to that used during the making of Venetian *cristallo*. The study of Tuscan vessel glass also identified some examples where purified ash was used together with Tuscan sand and, as here, it was found that they were too high in iron content to be considered true Venetian *cristallo*, so were designated by Cagno et al. as 'Tuscan cristallo'.[71] Cagno considered that a CaO content of less than 7% indicated that the glass was made with a purified ash; the only other paintings in the table in which it is so low are Raphael's *Garvagh Madonna* (NG 744), where again it is combined with an Al-rich source of silica such as Tuscan sand, Sebastiano's *Raising of Lazarus* (NG 1) and Bronzino's *Portrait of Piero de' Medici* (NG 1323).

The glass that is low in aluminium is probably made with similar raw materials to those used for Venetian glass, as the composition resembles that for Venetian common glass or *vitrum blanchum*. The higher quality *vitrum blanchum* is significantly lower in iron content than common glass, and in the table a few samples do seem to contain glass made with a silica source of higher purity. The glass containing the least iron is, in fact, that in the only Venetian painting in the table, by Marco Marziale (NG 804). Others which appear to be made with a very pure silica source include Raphael's *Mond Crucifixion* (NG 3943) and *Madonna of the Pinks* (NG 6596), Beccafumi's *Tanaquil* and *Marcia* (NG 6368 and NG 6369), Antonio da Vendri's *Giusti Family of Verona* (NG 749) and Dosso's *Adoration of the Kings* (NG 3924).

Beccafumi's *Marcia* has been transferred from its original panel, while its companion *Tanaquil* is still on its original support. This is evident in the considerable difference between them in the degree of leaching of alkali ions from the glass in the paint, with the highest sodium content measured in samples from *Marcia* being only 5.2%. The other paintings in the table that have been transferred have been similarly affected. In Sebastiano del Piombo's *Raising of Lazarus* (NG 1) the leaching is so extreme that in all the particles there is almost no sodium remaining. The composition of the glass in this painting,

which seems to be of the *cristallo* type, very low in the stabilising CaO, may have exacerbated this effect. Many of the particles of *cristallo* glass in Raphael's *Garvagh Madonna* (NG 744) are also very depleted in sodium, even though it is still on its original support, indicating that leaching is not necessarily only associated with the conservation history of a work but is also influenced by the stability of the glass.

The only other Italian painting in the table in which the glass has a very low sodium content is *The Adoration of the Kings* (NG 729) by Vincenzo Foppa. Here instead it is clear that it was made from different raw materials: the most abundant alkali is potassium, the phosphorus content of *c*. 4% is far higher than in the soda ash glasses and the silica content of around 50% is lower, all of which indicates that the glass was made with wood ash. According to Verità, this type of glass first appears in Italy around the thirteenth century in windows at the Abbey of San Fruttuoso of Camogli (Genova), and has also been found in several other stained glass windows in Italy dating from the thirteenth to the fifteenth centuries. It is thought that it was most probably imported from northern Europe, since it is only found in window glass and not in vessel glass in Italy at this time. Verità's review and reassessment of compositional data from a large number of samples from windows at several sites around Italy showed that the wood ash glass could be divided into a high lime–high potash group and a high lime–low potash group. The high lime–high potash group could be subdivided into two further groups: K1, which is high in MgO and P_2O_5, and K2, in which the content of these elements is lower.[72] The high lime–high potash glass in the painting by Foppa contains 4.1% P_2O_5 and 6.1% MgO, placing it solidly in the K1 group. This compositional group includes the important stained glass windows from the second half of the fifteenth century at the Certosa di Pavia, a short distance south-west of Milan, where Vincenzo Foppa is documented to have painted frescoes in the cloister (now lost), early in his career in the 1460s, and where he lived and worked at various times.[73]

Glass in paintings from Germany and the Netherlands

In five of the twelve German paintings in Table 1 the powdered glass was found to be of the soda ash type and similar in composition to that in Italian paintings, although this includes two paintings from the same triptych by the Master of the Aachen Altarpiece. Lutzenberger et al. reported a similar proportion of soda ash glass among the German paintings they studied, as well as one example in a work from the Netherlands by Colijn de Coter.[74] In the fifteenth century and early sixteenth century this is likely to have been imported from Italy, although a little later soda ash glass was being made in northern Europe, with the arrival of Italian glassmakers in centres such as Antwerp. One of the paintings in which soda ash glass was identified was *The Mass of Saint Hubert* (NG 253) attributed to the workshop of the Master of the Life of the Virgin, which is thought to be the right wing of the Werden altarpiece. On the left wing, *The Conversion of Saint Hubert* (NG 252), attributed to the master himself, the glass is of a wood ash–lime composition (high lime–low potash). They are not thought to have been painted by the same hand, although this cannot be implied from the difference in glass composition, as several types have sometimes been found in the same work, even within the same paint layer.

The glass in the other German paintings and in all of the Netherlandish paintings in the table has a low sodium content and is of a calco-potassic nature, prepared from ash from wood or terrestrial plants such as fern, which in north west Europe was used for glassmaking between 800 and 1800 AD. The predominant constituents, aside from silica, are potassium and calcium, with significant amounts of magnesium also being present. In the literature on analyses of vessel and window glass of this type, several compositional groups within this category have been identified, based on the proportions of K_2O and CaO, which show considerable variations due to differences in the raw materials or in the recipes used. Wedephol's studies have indicated that German glass from the earlier part of the 'wood and inland plant ash' period was richer in potassium, while after around 1300 it becomes progressively richer in calcium and the potassium levels become far lower. An increase in the CaO content could be achieved by the inclusion of lime in the raw ingredients, but could also result from a difference in the composition of the ash, since the CaO/K_2O ratio depends on the type of wood, on the growing conditions and also on the proportion of trunk to twigs and branches used to prepare it, as the bark is richer in calcium. Wedephol has suggested that with an increase in the production of glass after around 1300, wood ash prepared with a higher proportion of twigs and branches

came to be used, giving an ash richer in calcium. On the basis of analysis of a large number of samples of archaeological glass he identified several compositional groups, progressively richer in calcium and younger in age: glass with a CaO/K_2O ratio of around 1, similar to that in the trunks of beech trees, which he categorised as wood ash glass; glass which he categorised as 'wood ash–lime', which had a lower potassium content of around 7% and a CaO/K_2O ratio of around 3.4, which appears around 1300; and glass with a composition in which this ratio was even higher, sometimes as high as 9, which he considered could have been made with ash prepared from the twigs alone. This last type he called 'mixed alkali', as it often contained only around 3% K_2O together with comparable levels of Na_2O of around 2.5%, which he proposes was added as NaCl to compensate for the increase in melting temperature caused by the low potassium content.[75] Calcic glasses are also sometimes instead called high lime–low alkali or high lime–low potash. The more potassium-rich glasses can be designated potash glass.

The same spread of glass types is found in Netherlandish and French glass,[76] although there is some indication that the calcic glass becomes dominant a little later than in Germany. Studies of the composition of archaeological glass from northern France have found that while in the eastern part calcic glasses are common over the whole of the period of interest here, in more western areas both potassic and calcic compositions are found during the first part of the fifteenth century, and it is not until the second half of the fifteenth century that the latter becomes more predominant.[77] Analyses of the composition of the substrate glass of fifteenth-century stained glass windows in Flanders in the period *c*. 1400 to after 1550 in cities such as Bruges and Antwerp has found that potash glass with similar levels of K_2O and CaO, perhaps associated with a north French crown glass production centre, is very common in the earlier part of the fifteenth century, while later in the century high lime–low alkali glass appears much more frequently.[78]

Six of the examples of calco-potassic glass in German paintings in the table, dating from around 1500, have rather consistent compositions, with a high CaO content of 20–25%, a low K_2O content of 3.5–5% and a CaO/K_2O ratio between 5 and 6. This closely matches the calcic glass composition that predominates in Germany in this period, and indeed in some of these glasses the Na_2O content is around 2.5%, corresponding well with the 'mixed alkali' category specified by Wedephol. The literature on the composition of vessel and window glass is not always clear about the relationship between particular names for glass types and the composition, nor does it always specify the boundaries between the compositional groups, particularly regarding the CaO/K_2O at which it can be considered to be high lime–low potash. Here the composition of this calcic glass in the German paintings is used to designate a high lime–low potash category, as it gives a helpful distinction between the different compositions of wood ash–lime glass evident in the table.

The glass in Neufchâtel's *Portrait of a Young Lady* (NG 184) from the second half of the sixteenth century is more difficult to categorise; the CaO content is high, but it is very rich in potassium, so it is not a high lime–low potash glass. It can still, however, probably be designated a wood ash–lime glass on the basis of the CaO/K_2O ratio. One of the two types of glass in a painting by Wolf Huber instead contains potassium and calcium at similar levels, with the potassium content being slightly greater, so can be considered a potash glass, probably wood ash glass, but perhaps with the potassium content supplemented by another type of ash or other potassium-rich ingredient such as tartar.

There are more examples of potassium-rich wood ash glasses among the Netherlandish paintings than among the German paintings, perhaps partly because more of the paintings date from earlier in the fifteenth century, while the earliest German work in the table is from around 1485–95. The 'type I' glass in van Eyck's *Arnolfini Portrait* (NG 186) and the glass in van der Weyden's *Magdalen Reading* (NG 654) contain more potassium than calcium, and also have fairly high MgO contents, which perhaps suggests the inclusion of some of the more potassium-rich fern ash in addition to wood ash.[79] The four paintings in which the glass is similar in composition to the high lime–low potash glass in the German paintings, with very low potassium levels of around 3.5–5% and CaO levels of 20–27%, all date from the second half of the fifteenth century. This is interesting, considering that the studies of vessel and window glass seem to suggest that more calcic glass compositions become predominant in the Netherlands and the western part of northern France during the course of the fifteenth century, rather later than in Germany, although at present there are so few results that caution should be exercised in placing great significance on this apparent trend.

Conclusion

The large number of paintings of the fifteenth and sixteenth centuries in which colourless powdered glass has been found as a paint additive demonstrates how widely it was used. In the northern European paintings studied here it was present in translucent red lake-containing paints and in mordants for gilding. In the Italian paintings in this study it was found not only in red lake glazes, and in several mordants, but also in paint of other colours, generally of grey, brown or orange hues. It was, in addition, a rather common component of the primings.

Aside from the references to powdered glass as an aid to the grinding of orpiment, the earliest documentary sources found so far in which it is mentioned are from the second half of the sixteenth century, but they do not indicate its purpose. It is not until the very last years of the sixteenth century in English documentary sources that it is suggested as a drier. In some sources there is some hint that it is being used specifically for colours that lack body. Experiments carried out to investigate its effect on the properties of oil paint have indeed confirmed that it does give a thicker paint with good handling properties. These reconstructions have not proved conclusive on the question of whether it has any influence on drying time, and further experiments that replicate the particle size and composition of the glass found in paintings, as well as following instructions in the sources, such as initial grinding in water, would be valuable. Even if the manganese in the glass is not sufficiently available to act on the oil, it may be that its alkalinity has an effect, since it is known that basic pigments can interact with acidic oxidation products which can otherwise soften a dried film.[80] Artists may have believed that it could act as a drier, even if in fact it was not capable of performing this function. It could also have been effective as a transparent filler or extender, appropriate for the relatively expensive red lake pigments. Translucency might be desirable in a priming layer since it would allow underdrawing beneath it to remain easily visible, but this cannot have been its purpose where it is used in mordant layers hidden beneath metal leaf. It is also unlikely to have been added as an extender where it has been found mixed with cheap earth pigments. The reasons for adding glass to the paint may have varied, but in Italian paintings, at least, the consistent manner and extent of its use seem to suggest that it was not dependent on the idiosyncrasies of individual artists but was instead an established general practice.

Artists appear to have used whatever colourless glass was available in the vicinity, whether it was locally made or imported, as the composition shows the same general geographical distribution established from studies of vessel and window glass. In the Italian paintings it is almost exclusively soda ash glass, with only one exception. In the German and Netherlandish paintings soda ash glass, wood ash and wood ash–lime glass are present, in common with what has been found in archaeological sites from these areas. In the results from Northern paintings presented here, the locally produced glass types are still predominant, although the number of analyses is rather more limited than those from Italian paintings, and more are needed before general conclusions can be reached. The quantitative analysis of the glass in Italian paintings has also made it evident that there are some differences in composition that can be related to the raw materials, particularly in the use of either sand or river pebbles as the silica source, and that this does seem to have some relationship to the location in which the painting was made. Again, while this does identify some possible directions for future investigation, no firm trends can be established until a more geographically diverse group of occurrences in paintings has been analysed, especially those in Northern Italian works, combined with a deeper comparison with the literature on glass-making practices and raw materials used in this period in this area.

The earliest paintings in which glass has been found are Netherlandish and German works from around 1430. It does seem to be associated with an oil medium and it is therefore not surprising that the earliest occurrence in a painting produced in Italy is from the 1470s, a time when Italian artists were beginning to use oil more widely but were still predominantly working in egg tempera. In Northern Europe it has a far longer history as a paint binder, and far earlier works in the Netherlands, Germany, England and Norway have been confirmed through analysis to have an oil medium. Further work to investigate the origins of this practice should therefore be concentrated on paintings from these areas.[81] Nevertheless, it is already interesting that artists added a material to their paint that did not function as a pigment but would have modified the working and handling properties, and perhaps also the drying properties, and that it can be traced back as far as the early Netherlandish artists such as van Eyck and

van der Weyden, who were famous for their ability to manipulate oil paint to achieve the remarkable detail and impressive effects that can be seen in their paintings.

Experimental appendix

Analysis of paint samples was performed using a Carl Zeiss EVO® MA10 variable pressure SEM, fitted with an Oxford Instruments X-Max 80 mm^2 EDX detector, using INCA 350 software (standardless ZAF quantification). The parameters used were 25 kV accelerating voltage, beam current 200 pA, chosen to produce an appropriate count rate, and 60s livetime. The optimum working distance for the EDX detector is 8.5 mm. The majority of the samples were carbon-coated and analysed under high vacuum conditions. Some samples were analysed uncoated under variable pressure conditions, to allow them to be examined subsequently using other techniques. Air was used as the chamber gas, at 50 Pa, allowing a compromise between adequate charge compensation and minimisation of beam skirting effects.[82]

Corning Museum of Glass standards A, B and D were used to assess the accuracy of the results. In general the measured sodium values were a little lower than the reference values (for Corning A an average of 13.9% was measured instead of the certified value of 14.3%), but were quite stable and under the analytical conditions chosen, specifically the low beam current possible with the large area EDX detector, there did not seem to be significant diffusion of this element. For most of the elements the values were within ± 5–10% (relative) of the reference value, with the least accurate being for those elements such as Ti which were present in the smallest quantity.

Acknowledgements

Particular thanks are due to Jo Kirby and Claudio Seccaroni for providing references and valuable advice on the relevant historic documentary sources, and to Ian Freestone for his useful comments on the text of this article. Discussions about the literature on the analysis of archaeological vessel glass compositions with Koen Janssens and Andrew Meeks were most helpful. The author would also like to thank Rachel Grout, who contributed to the analyses of paintings by Raphael during a fellowship in the National Gallery Scientific Department 2001–2002 (and who was responsible for FIG. 4), as well as Kate Stonor, Ashok Roy and Helen Howard, who contributed some of the occurrences of glass in the table.

Full scholarly information for the sixteenth-century Netherlandish paintings discussed in this article, and for those from Ferrara and Bologna, will appear in forthcoming National Gallery Catalogues: *The Sixteenth-Century Netherlandish Paintings and French Paintings before 1600*, by Lorne Campbell; and *The Sixteenth-Century Italian Paintings: Bologna and Ferrara*, by Giorgia Mancini and Nicholas Penny.

This article is available for download at:
http://www.nationalgallery.org.uk/technical-bulletin/spring2012

Table 1: Fifteenth- and sixteenth-century paintings in which colourless powdered glass has been identified in paint samples, in chronological order, together with quantitative SEM–EDX analysis of the particles, normalised and expressed as weight % oxide (not including elements present at values lower than 0.1%).

Artist, painting title, date and location[f]	Areas where powdered glass was found and estimated particle size	Glass type	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5[e]	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO
ITALIAN PAINTINGS														
Justus of Ghent and workshop, *Music* (NG 756) probably 1470s, probably Urbino.	Red of carpet, with red lake.[b]	soda ash	11.4	3.9	4.9[g]	60.5	0.6	2.3[d]	0.7	3.2	10.3	0.2	1.2	0.8
Lorenzo Costa, *A Concert* (NG 2486), *c.*1488–90, Bologna.	Off-white priming, with a little lead white; black background, with coal black and a little verdigris; underpaint of marbled ledge, with lead white, a little red lake and brown; purple cloak of figure at the right, with red lake and a little lead white in the upper layer and with coal black, a little red lake, vermilion and lead-tin yellow in underpaint, 10–30 µm.[b]	soda ash	11.2	3.7	1.7	66.0	0.3	2.9[d]	0.9	2.2	9.6	0.1	0.8	0.6
Giovanni Santi, *The Virgin and Child* (NG 751), *c.*1488, probably Urbino.	Crimson drapery underneath the Christ Child, with red lake.[a]	soda ash	7.9	2.8	1.8	68.9	0.4	0.7	0.9	2.6	12.2	0.1	1.0	0.6
Master of the Story of Griselda, *The Story of Griselda, Part III: Reunion* (NG 914), *c.*1494, probably Siena.	Grey of horse, with lead white and black, 5–10 µm.[a]	soda ash	11.2	2.9	4.5[h]	61.5	0.5	0.3	0.9	3.8	11.6	0.0	1.8	1.0
Pietro Perugino, *Three Panels from an Altarpiece, Certosa* (NG 288.1–3), *c.*1496–1500.	Pale yellow priming, with lead white and lead-tin yellow; Raphael's red robe, with red lake, 5–10 µm.[a]	soda ash; upper row, red paint;	11.2	3.4	5.0[g]	62.6	0.7	0.6	0.6	3.6	9.1	0.2	2.4	0.7
		lower row, priming (slightly leached)	7.1	2.9	4.0[h]	62.2	1.2	6.3[d]	1.1	3.4	9.1	0.2	2.0	1.0
Lorenzo Costa and Gianfrancesco Maineri, *The Virgin and Child Enthroned between a Soldier Saint, and Saint John the Baptist (La Pala Strozzi)* (NG 1119), probably 1499, probably Ferrara.	Off-white priming, with a little lead white; Virgin's red dress, with red lake; grey sword, with lead white and galena (lead sulphide); grey of architecture, with lead white and bone black; Saint John's red cloak, with red lake and azurite, 10–30 µm.[b]	soda ash	11.6	3.8	1.5	66.7	0.4	1.2[d]	0.9	2.1	9.8	0.1	1.4	0.5
Francesco Napoletano (?), *An Angel in Green with a Vielle* (NG 1661), *c.*1490–9, Milan.	Red sleeve of angel, with red lake, 20–30 µm.[b]	soda ash	10.4	3.3	0.9	66.3	0.4	1.3[d]	0.8	5.9	9.3	0.2	1.0	0.4
Vincenzo Foppa, *The Adoration of the Kings* (NG 729), perhaps *c.*1500, Lombardy.	Translucent priming layer, with a little lead white, 20–30 µm.[a]	wood ash	0.6	6.1	2.3	51.0	4.1	5.5[d]	0.4	13.1	15.6	0.2	0.9	0.6
Workshop of Francesco Francia, *The Virgin and Child with Two Saints* (NG 638), probably *c.*1500, Bologna.	Brown window ledge, with red earth and lead white, 10–30 µm.[b]	soda ash	10.8	3.5	1.4	67.5	0.4	1.1	1.0	2.4	10.4	0.1	0.5	0.8
Michelangelo, *The Entombment* (NG 790), *c.*1500–1, Rome.	Pale yellow priming, with lead white and a little lead-tin yellow, 5–20 µm.[a]	soda ash	12.5	4.3	1.4	68.5	0.7	0.6	1.0	1.7	8.3	0	0.6	0.4
Raphael, *The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion)* (NG 3943), *c.*1502–3, Umbria.	Pale yellow priming, with lead white and a little lead-tin yellow; Saint John's red drapery, with red lake; golden sun ray, with orpiment and a little lead-tin yellow; brown shadow of the drapery of the angel in yellow, with black, vermilion, red earth and red lake, 10–30 µm.[a]	soda ash	10.4	3.4	1.0	69.9	0.2	0.3	0.9	2.2	10.7	0.0	0.5	0.4
Raphael, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansidei Madonna)* (NG 1171), 1505, Umbria or Florence.	Pale yellow priming, with lead white and a little lead-tin yellow; dark purple underside of the canopy over the throne, with red lake, a little vermilion and black; Saint John's red drapery, with red lake; pale grey architecture, with lead white and bismuth metal powder; mordant for the gilded decoration on the throne (used alone); yellow 'wood' on the throne, with lead-tin yellow and a little red earth, 10–20 µm.[a]	soda ash; upper row high Al (sand);	11.8	2.4	5.0[h]	63.6	0.5	1.0	1.2	3.5	8.1	0.2	1.6	1.0
		lower row, low Al (pebbles)	10.9	3.2	1.5	66.6	0.2	1.4[d]	0.0	2.4	10.4	0.1	1.0	0.5
Raphael, *Saint John the Baptist Preaching* (NG 6480), 1505, Umbria or Florence (predella of The Ansidei Altarpiece).	Pale yellow priming, with lead white and a little lead-tin yellow; grey hose of figure fourth from the left, with lead white and coal black; red of cloak of figure second from the left, with red lake and vermilion; brownish-green foreground, with lead white, lead-tin yellow and a little azurite and verdigris, 10–20 µm.[a]	soda ash; upper row, high Al (sand);	11.5	3.0	5.5[h]	65.6	0.6	0.5	1.2	3.1	7.3	0.2	1.1	0.6
		lower row, low Al (pebbles)	8.7	3.0	2.2	67.2	0.8	3.7[d]	0.9	2.6	9.6	0.2	1.0	0.5

Raphael, *The Procession to Calvary* (NG 2919), *c.*1504–5, Umbria or Florence.	Pale yellow priming, with lead white and a little lead-tin yellow; pale pink underpaint of Saint John's red drapery, with lead white and faded red lake; greenish foreground, with lead white, lead-tin yellow, yellow earth and azurite; orange-yellow tunic of the man on the brown horse, with lead-tin yellow and yellow earth, 5–15 µm.[a]	soda ash	10.9	3.4	5.1[h]	64.4	0.6	0.8	0.9	3.0	8.7	0.2	1.4	0.7
Lorenzo Costa, *High Altarpiece, Oratory of S. Pietro in Vincoli* (NG 629), 1505, probably Bologna, transferred from panel.	Pale yellow priming, with lead white and a little lead-tin yellow; deep red of Saint Philip's cloak, with red lake and a little lead white and vermilion; brownish-grey architecture, with lead white, verdigris, lead-tin yellow and galena (lead sulphide), 5–20 µm.[b]	soda ash	12.5	3.8	1.7	66.8	0.3	0.7	0.9	2.2	10.0	0.1	0.5	0.4
Attributed to Pietro Perugino, *Christ Crowned with Thorns* (NG 691), *c.*1500–05.	Pale yellow priming, with lead white and a little lead-tin yellow, *c.* 10 µm.[a]	soda ash	11.8	3.0	4.5[h]	60.3	1.1	2.7[d]	0.9	4.7	7.8	0.2	2.1	0.9
Raphael, *The Madonna of the Pinks (La Madonna dei Garofani)* (NG 6596), *c.*1506–7, Florence.	Pale yellow priming, with lead white and a little lead-tin yellow, 5–10 µm.[a]	soda ash	11.5	3.2	0.7	70.7	0.4	1.0	0.9	2.2	8.8	0.0	0.2	0.4
Raphael, *Saint Catherine of Alexandria* (NG 168), *c.*1507, Florence.	Pale yellow priming, with lead white and a little lead-tin yellow; Saint Catherine's red cloak, with red lake; yellow-brown paint of wheel, with lead white, red earth, umber and a little azurite and vermilion; brownish-green of the background landscape, with lead-tin yellow, azurite, yellow earth and a little black, 10–40 µm.[a]	soda ash	11.5	2.8	4.1[h]	64.3	0.6	0.4	0.0	3.7	8.8	0.2	2.4	0.7
Marco Marziale, *The Virgin and Child with Saints* (NG 804), 1507, Venice or Cremona.	Red of Virgin's robe, with red lake and white in the underpaint, and red lake only in upper layers, 10–30 µm.[a]	soda ash, leached	9.7	3.2	1.0	71.5	0.3	0.3	0.9	2.1	10.1	0.0	0.5	0.3
Pietro Perugino, *The Virgin and Child with Saints Jerome and Francis* (NG 1075), probably *c.*1507–15.	Pale yellow priming, with lead white and a little lead-tin yellow; Saint Jerome's red robe, with red lake, 10–20 µm.[a]	soda ash; upper row, high Al (sand); lower row, low Al (pebbles)	12.4 11.4	2.0 3.6	5.4[h] 1.1	68.0 62.4	0.6 0.1	0.2 7.7[d]	1.1 1.1	3.2 2.2	5.3 8.0	0.1 0.1	1.2 0.4	0.6 1.1
Raphael, *The Madonna and Child with the Infant Baptist (The Garvagh Madonna)* (NG 744), *c.*1509–10.	Pale yellow priming, with lead white and a little lead-tin yellow; Virgin's red dress, with red lake, 5–20 µm.[b]	soda ash, many particles very leached	13.5	1.9	5.4[h]	63.7	0.5	1.0	1.0	3.8	6.0	0.1	2.2	1.0
Gerolamo dai Libri, *The Virgin and Child with Saint Anne* (NG 748), 1510–18, Verona.	Priming, with some lead white; underpaint of the *cangiante* drapery of the angel on the left, 10–30 µm.[a]	soda ash, leached	8.1	3.2	1.9	67.1	0.5	0.3	0.4	3.7	12.7	0.1	1.5	0.4
Francesco Francia, *The Virgin and Child with Saint Anne and other Saints* (NG 179), *c.*1510–12, Bologna, transferred from panel.	Dark purple shadow in Saint Anne's robe, with red lake, a little ultramarine and a little lead white, 10–30 µm.[b]	soda ash	9.3	2.7	2.0	67.0	0.5	0.9	0.6	6.3	9.1	0.1	1.0	0.6
Giovanni Battista da Faenza, *The Incredulity of Saint Thomas* (NG 1051), *c.*1510–12, Faenza.	Priming; mainly glass with a little lead white and lead-tin yellow, 5–30 µm.[b]	soda ash	10.5	3.7	1.2	65.9	0.3	2.6[d]	1.2	1.9	11.3	0.1	0.6	0.7
Giovanni Battista da Faenza, *The Virgin and Child in Glory* (NG 282), *c.*1512–16, Faenza.	Priming, mainly glass with a little lead white, 5–30 µm.[b]	soda ash	10.4	3.4	1.7	68.1	0.3	1.6[d]	0.9	2.0	10.5	0.2	0.5	0.5
Lodovico Mazzolino, *The Holy Family with Saint Francis* (NG 82), probably *c.*1514–15, Ferrara.	Pale yellow priming, with lead white and a little lead-tin yellow.[a]	soda ash	9.0	3.0	1.1	69.5	0.4	0.7	0.7	2.4	10.5	0.1	2.3	0.5
Jacopo Pontormo, *Pharaoh with his Butler and Baker* (NG 6452), probably 1515, Florence.	Pale yellow priming, with lead white and lead-tin yellow; brown paint of architecture (Mn detected by XRF), 5–15 µm.[a]	soda ash	12.2	2.8	3.6	64.2	0.6	0.5	0.7	3.9	8.0	0.2	2.4	0.9
Bacchiacca, *Joseph pardons his Brothers* (NG 1219), probably 1515, Florence.	Pale yellow priming (a little), with lead white and lead-tin yellow (Mn detected by XRF), *c.* 5 µm.[a]	soda ash	12.3	2.7	4.5[h]	62.4	0.4	2.3[d]	0.8	3.3	7.6	0.2	2.6	0.9
Francesco Francia, *Mourning over the Dead Christ* (NG 2671), probably *c.*1515–16, Bologna.	Pale yellow priming, with lead white and a little lead-tin yellow; purple-red cloak of woman at right edge, with red lake, *c.* 5 µm.[b]	soda ash	11.9	2.7	1.1	68.8	0.2	2.0[d]	1.1	2.3	8.9	0.1	0.5	0.4
Imitator of Andrea Mantegna, *Noli me Tangere* (NG 639), perhaps 1460–1550.	Pale yellow priming, with lead white and a little lead-tin yellow, 5–15 µm.[a]	soda ash	14.2	2.8	3.8	63.8	0.6	0.7	0.8	3.2	6.9	0.1	2.4	0.8
Sebastiano del Piombo, *The Raising of Lazarus* (NG 1), *c.*1517–19, Rome, transferred from original panel.	Christ's red cloak, with red lake, a little ultramarine and lead white; brownish-pink flesh of the leg of Lazarus, with lead white and earth pigments, 15–50 µm.[a,i]	Very leached, probably soda ash (low P). Upper row, red paint; lower row, flesh paint	0.1 0.1	2.1 1.5	6.2[g] 0.8	77.4 88.3	0.9 0.4	2.8[d] 0.8	1.1 1.1	1.3 0.5	6.3 5.4	0.2 0.0	1.0 0.4	0.7 0.8
Domenico Beccafumi, *Tanaquil* (NG 6368), *c.*1519, Siena, transferred from panel.	Pale yellow priming, with lead white and a little lead-tin yellow, 10–30 µm.[b]	soda ash (leached)	5.2	2.8	0.9	75.9	0.6	2.1[D]	1.2	2.9	7.5	0.0	0.4	0.4
Domenico Beccafumi, *Marcia* (NG 6369), *c.*1519, Siena.	Pale yellow priming, with lead white and a little lead-tin yellow, 10–30 µm, one particle 80 µm.[b]	soda ash	11.6	2.5	0.9	66.4	0.3	4.7[d]	1.0	3.5	8.2	0.1	0.3	0.5

Domenico Beccafumi, *The Story of Papirius* (NG 1430), mid 1520s, Siena.	Translucent priming (glass only); red dress of woman at the centre of group below steps, mixed with red lake and azurite, 10–20 μm.[a]	soda ash	12.5	2.5	4.8[h]	62.4	0.7	1.2[d]	0.9	4.8	7.6	0.2	1.9	0.6
Ortolano, *Saints Sebastian, Roch and Demetrius* (NG 669), *c.*1520, Ferrara, transferred from original panel.	Red drapery, with red lake and some vermilion, *c.* 5 μm.[a]	soda ash, many particles very leached	11.6	3.6	4.5[g]	65.6	0.4	1.1	0.7	2.5	8	0.1	1.6	0.5
Antonio da Vendri, *The Giusti Family of Verona*(?) (NG 749), probably c.1520, Verona.	Translucent off-white priming layer; mainly glass, with a little lead white, 20–40 μm.[a]	soda ash	12.0	2.7	1.0	70.2	0.3	1.0	1.2	3.8	7.1	0.0	0.3	0.4
Dosso Dossi, *The Adoration of the Kings* (NG 3924), probably 1527–9, Ferrara.	Pink cloak of one of the kings, 5–10 μm.[a]	soda ash (leached)	5.6	1.9	1.5	75.6	0.3	0.9	1.2	4.4	7.6	0.0	0.5	0.4
Bronzino, *The Madonna and Child with Saint John the Baptist and Saint Elizabeth* (NG 5280), probably *c.*1540, Florence.	Virgin's red sleeve, with lead white and red lake (Mn detected by XRF), 5–7 μm.[b]	soda ash	11.5	2.7	4.8[g]	62.3	0.2	3.4[d]	0.0	5.0	7.2	0.1	1.2	0.6
Bronzino, *Portrait of Piero de' Medici ('The Gouty')* (NG 1323), probably *c.*1550–70.	Sitter's red tunic, with red lake and a little lead white (Mn detected by XRF), 2–3 μm.[a]	soda ash (leached)	6.4	2.7	10.5[g]	60.8	0.8	4.3[d]	0.7	4.6	6.6	0.1	1.7	0.7
Annibale Carracci, *The Dead Christ Mourned ('The Three Maries')* (NG 2923), *c.*1604.	Red of the Magdalen's drapery, with red lake, 5–15 μm.[a]	soda ash (leached)	9.0	2.8	4.4[g]	60.7	0.2	0.2	0.9	6.7	13.3	0.2	0.9	0.6
GERMAN PAINTINGS														
Master of the Life of the Virgin, *The Presentation in the Temple* (NG 706), probably 1460–75.	Mordant for the gilding on the Virgin's robe, with lead white, yellow earth and lead-tin yellow (*c.* 3–10 μm).[a]	soda ash (leached)	7.1	3.8	1.6	69.8	0.4	2.3[d]	1.3	1.8	10.2	0.1	0.7	1.1
Master of the Life of the Virgin, *The Conversion of Saint Hubert: Left Hand Shutter* (NG 252), *c.*1485–90.	Brownish-yellow mordant for gold harness on horse, with lead white, lead-tin yellow, some black and earth; red pattern on Saint Hubert's tunic, with red lake (*c.* 3–10 μm)[a]	wood ash–lime (high lime–low potash)	1.6	3.3	4.7	54.4	3.6	5.7[d]	0.3	3.6	21.1	0.3	0.4	0.7
Workshop of the Master of the Life of the Virgin, *The Mass of Saint Hubert*: *Right Hand Shutter* (NG 253), *c.*1485–90.	Red undersleeve of the figure behind Saint Hubert, with red lake, *c.* 10–20 μm.[a]	soda ash	11.7	4.0	2.6	66.6	0.3	0.5	1.0	2.1	10.3	0.1	0.2	0.5
Master of the Aachen Altarpiece, *The Crucifixion* (NG 1049), *c.*1490–5.	Shadow of the Magdalen's red cloak, with red lake, 7–20 μm.[a]	soda ash	10.0	4.3	2.7	67.0	0.4	2.2[d]	0.8	2.0	9.3	0.1	0.6	0.5
Master of the Aachen Altarpiece, *Pilate washing his Hands* (Walker Art Gallery, Liverpool, no. 1225), *c.*1490–5, wing panel belonging with NG 1049 above.	Red glaze on Christ's purple cloak, with red lake (applied over blue), *c.* 7–10 μm.[a]	soda ash	10.1	4.4	1.8	68.2	0.2	0.8	0.8	1.9	10.3	0.1	0.8	0.5
Workshop of Albrecht Dürer, *The Virgin and Child ('The Madonna with the Iris')* (NG 5592), *c.*1500–10.	Red dress and cloak of the Virgin, with red lake, 5–20 μm.[a]	wood ash–lime (high lime–low potash	2.4	3.0	5.8	55.5	3.3	2.0[d]	0.7	4.6	21.0	0.2	0.9	0.5
Master of the Saint Bartholomew Altarpiece, *The Deposition* (NG 6470), *c.*1500–05.	Shadow of Saint John's red cloak, with red lake, 2–10 μm.[a]	wood ash–lime (high lime–low potash)	0.5	2.2	4.3	51.1	3.6	5.3[d]	0.6	5.0	25.7	0.0	1.2	0.5
Master of the Saint Bartholomew Altarpiece, *Saints Peter and Dorothy* (NG 707), probably 1505–10.	Saint Dorothy's pink underdress, with red lake and lead white, 5–50 μm.[a]	wood ash–lime (high lime–low potash)	1.6	3.0	1.9	58.9	3.2	0.8	0.6	4.9	23.4	0.3	0.7	0.6
Workshop of the Master of the Saint Bartholomew Altarpiece, *The Virgin and Child in Glory with Saints* (NG 6497), *c.*1512.	Virgin's red dress, with red lake; yellow-brown mordant for gilding, with lead white, yellow earth and lead-tin yellow, 10–20 μm.[a]	wood ash–lime (high lime–low potash)	2.6	4.1	3.0	56.9	3.7	1.9[d]	1.0	3.5	21.5	0.4	0.9	0.5
Master of Cappenberg (Jan Baegert?), *Christ before Pilate* (NG 2154), *c.*1520.	Yellow mordant for gilding, with lead white, yellow earth and lead-tin yellow, *c.* 20 μm.[a]	wood ash–lime (high lime–low potash)	2.6	3.8	1.7	58.8	3.1	0.4	0.7	4.0	23.3	0.2	1.0	0.5
Wolf Huber, *Christ taking leave of his Mother* (NG 6550), *c.*1520.	Shadow of the red robe of the woman supporting Mary, with red lake, 5–50 μm.[a]	Type I (leached soda ash?)	8.2	2.7	1.7	67.7	0.5	0.5	0.9	3.5	11.9	0.1	1.5	1.0
		Type II (wood ash)	0.1	2.6	0.9	53.3	0.9	0.5	0.1	21.3	18.9	0.3	0.8	0.6
Nicolas de Neufchâtel, *Portrait of a Young Lady* (NG 184), probably 1561, Nuremberg.	Brownish-grey background, with lead white and black, 5–10 μm.[a]	wood ash–lime (high lime–low potash)	0.8	2.2	2.2	51.0	3.7	0.4	0.5	9.2	25.7	0.2	3.5	0.6
NETHERLANDISH PAINTINGS														
Jan van Eyck, *The Annunciation*, National Gallery of Art, Washington (inv.1937.1.39), *c.*1434–6.	Red paint, with red lake and coal black; yellow mordant for gold rays with lead white, yellow earth and a little lead-tin yellow; two types of glass, 5–20 μm.[b,c]	Type I (wood ash–lime)	1.0	4.0	2.4	57.1	3.0	1.1	0.1	7.5	22.0	0.2	1.1	0.5
		Type II (wood ash)	2.4	4.5	4.0	53.6	6.6	3.3[d]	0.6	7.2	16.2	0.2	0.6	0.9

Jan van Eyck, *The Arnolfini Portrait* (NG 186), 1434.	Red curtain, in underpaint (with vermilion, red lake, black and a little ultramarine) and surface paint (with red lake and a little lead white), *c.* 5 µm.[a]	Type I (wood ash with some fern ash?)	0.4	4.5	1.5	55.0	4.9	0.4	0.3	17.1	14.0	0.3	1.3	0.5
		Type II (wood ash)	3.2	6.3	2.9	49.7	6.0	1.8[d]	0.8	10.1	16.3	0.1	0.9	1.6
		Type III (wood ash–lime)	1.7	3.5	2.7	53.8	3.2	4.3[d]	0.4	6.3	22.2	0.1	0.9	0.8
Rogier van der Weyden, *The Magdalen Reading* (NG 654), before 1438.	Saint John's red cloak, in underpaint (with vermilion) and surface paint (with red lake and a little lead white), *c.* 5 µm.[a,c]	wood ash	0.7	4.5	2.3	54.5	5.2	4.4[d]	0.5	13.9	12.8	0.2	0.7	0.4
Follower of Robert Campin, *The Virgin and Child before a Firescreen* (NG 2609), *c.*1440.	Red cushion, with red lake, vermilion and a little lead white, *c.*10 µm.[b,c]	wood ash	1.3	4.1	4.7	53.0	4.6	4.2[d]	1.2	11.7	14.5	0.1	0.6	0.4
Attributed to the workshop of Rogier van der Weyden, *Pietà* (NG 6265), probably *c.*1465.	Saint Jerome's red cloak, with red lake and vermilion, *c.* 2–3 µm.[a,c]	wood ash	1.9	5.7	5.4	47.0	6.3	6.9[d]	0.7	9.7	15.1	0.0	0.5	0.7
Dirk Bouts, *The Virgin and Child* (NG 2595), *c.*1465.	Red pattern on cloth-of-gold hanging, with red lake and lead white, or with red lake only in darkest shadows, 5–20 µm.[b]	wood ash–lime	1.5	3.2	3.9	54.9	3.6	1.3[d]	0.9	6.6	21.6	0.2	1.7	0.6
Workshop of Dirk Bouts, *The Virgin and Child* (NG 708), *c.*1465.	Virgin's red cloak, shadow, with red lake, *c.* 5 µm.[a]	wood ash	2.0	5.7	3.2	54.6	4.6	3.9[d]	1.1	9.9	13.5	0.2	0.7	0.5
Dirk Bouts, *Christ Crowned with Thorns* (NG 1083) *c.*1470.	Christ's red cloak, in underpaint (with vermilion) and surface paint (with red lake and a little vermilion), 2–20 µm.[a]	wood ash–lime (high lime–low potash)	2.6	3.2	4.6	57.4	4.0	1.2[d]	0.7	3.9	20.7	0.3	1.0	0.4
Hieronymous Bosch, *Christ Mocked (The Crowning with Thorns)* (NG 4744), *c.*1490–1500.	Red headdress of figure at left, with vermilion and red lead in underpaint, with red lake in uppermost red glaze, 5–10 µm.[a]	wood ash–lime (high lime–low potash)	2.5	3.7	2.8	55.6	3.4	4.5[d]	0.9	4.1	21.2	0.2	0.6	0.4
After Robert Campin, *The Virgin and Child in an Apse with Two Angels* (NG 2608), *c.*1500?	Pale pink tile, with lead white and fluorite, *c.* 30 µm.[a]	wood ash–lime (high lime–low potash)	1.7	2.6	1.3	56.8	2.8	0.9	0.5	3.7	27.1	0.6	1.2	0.8
Workshop of Goossen van der Weyden, *The Flight into Egypt* (NG 1084), *c.*1515.	Shadow of Saint Joseph's red drapery; underpaint (with vermilion, black and white) and upper layers (with red lake and varying amounts of white and black), 5–10 µm.[a,c]	wood ash–lime (high lime–low potash)	1.8	3.4	6.2	51.4	4.8	5.6[d]	0.9	4.2	20.3	0.3	0.7	0.4
Workshop of Jean Bellegambe, *The Virgin and Child* (NG 265), *c.*1520.	Virgin's red cloak, with red lake, mostly 2–5 µm, one particle 70 µm.[b]	Type I (wood ash–lime, high lime–low potash)	2.0	3.1	3.1	59.3	2.6	0.4	0.5	5.4	22.1	0.2	0.6	0.7
		Type II (wood ash)	2.4	5.4	3.5	57.0	3.4	2.8	0.7	9.2	14.2	0.0	0.5	0.8
Workshop of Marinus van Reymerswaele, *Two Tax Gatherers* (NG 944), *c.*1540.	Shadow of red robe of man at right, with red lake (lower glaze layers only, and not final blotted glaze), *c.* 10–20 µm.[a]	wood ash–lime (high lime–low potash)	1.5	3.1	4.0	61.0	3.0	0.7	0.5	5.4	19.0	0.3	0.9	0.7
Martin van Heemskerck, *The Virgin and Saint John the Evangelist* (NG 6508.1), *c.*1540.	Saint John's red robe, in underpaint (with vermilion and red lake) and surface paint (with red lake and a little black), 20–30 µm.[a]	wood ash	1.9	4.9	1.7	56.0	3.4	0.4	0.6	11.6	17.7	0.3	0.8	0.8
Joachim Beuckelaer, *The Four Elements: Air* (NG 6587), 1570.	Red cloth in the basket in the foreground, shadow, with red lake, 10–20 µm.[a]	wood ash–lime	0.7	2.7	3.9	57.4	2.4	0.8	0.4	7.6	21.9	0.3	1.2	0.7
FRENCH PAINTINGS														
Master of Saint Giles, *The Mass of Saint Giles* (NG 4681), *c.*1500.	Red of altar cloth, in underpaint (with vermilion) and surface paint (with red lake and a little lead white), *c.* 10 µm.[a]	wood ash	1.0	4.7	2.1	56.9	4.5	3.6[d]	0.8	11.1	14.1	0.2	0.6	0.4
Master of Moulins (Jean Hey), *Charlemagne, and the meeting of Saints Joachim and Anne at the Golden Gate* (NG 4092), *c.*1500.	Purple of Joachim's cloak, in red glaze with red lake (over pale purple), 3–7 µm.[b]	wood ash	1.9	5.4	2.1	63.3	3.1	4.5[d]	0.9	6.3	11.1	0.1	0.8	0.5
SPANISH PAINTINGS														
Luis de Morales, *The Virgin and Child* (NG 1229), probably 1565–70.[a]	Red of Virgin's dress, with red lake and a little lead white, 5–7 µm.[a]	soda ash, some particles leached	11.5	3.5	2.3	67.5	0.5	2.7[d]	1.4	3.5	5.8	0.1	0.7	0.6

a. Analysis carried out on carbon-coated samples under high vacuum conditions, 200 pA, 25 kV, 60s livetime.
b. Analysis carried out on uncoated samples under variable pressure conditions, 200 pA, 25 kV, 60s livetime, 50 Pa, air as the chamber gas.
c. Particles that seem to be a pure form of silica, containing only small amounts of other elements, were also detected in this sample.
d. The apparent elevated sulphur concentration in this sample is probably not reliable and likely to result either from a sulphur-containing red lake pigment or, due to overlap of the sulphur peak with that from lead, a contribution to the spectrum from lead pigments around the glass.
e. Red lake pigments, especially those based on insect dyestuffs, often contain phosphorus. This could contribute to the apparent concentration in the glass, especially where the particles are small.
f. The binding medium of many of these paintings has been analysed by Gas Chromatography–Mass Spectrometry and identified as a drying oil. These analyses have generally been published in past issues of the *National Gallery Technical Bulletin*.
g. In this sample the glass particles are very small and are embedded in a matrix of red lake, with a substrate containing alumina. The interaction volume of the electron beam is likely to be larger than the glass particle and the apparent aluminium concentration too high.
h. The quantitative results quoted are from a particle in the priming layer, which does not contain red lake, or from a large particle in red lake paint; the high reported Al content is therefore reliable.
i. A dispersion of a paint sample allowed individual glass particles to be seen in transmitted light under the microscope. They could be seen to have angular edges and showed conchoidal fracture, confirming that they were glass, despite the rather low alkali content seen by EDX analysis, which is a result of severe leaching. See the Appendix in J. Dunkerton and H. Howard, 'Sebastiano del Piombo's *Raising of Lazarus*: A History of Change', *National Gallery Technical Bulletin*, 30, 2009, pp. 26–51.

Notes

1 M.P. Merrifield, *Original Treatises, dating from the XIIth to XVIIIth Centuries on the Arts of Painting*, London 1849, Vol. 1, pp. ccxl–ccxlii.

2 J.A. van de Graaf, 'The Interpretation of Old Painting Recipes', *The Burlington Magazine*, CIV (716), 1962, pp. 471–5.

3 M. Kirby Talley, *Portrait Painting in England: Studies in the Technical Literature before 1700*, Guildford 1981, pp. 94–7.

4 See 'Houten Beeldhouwwerk', *KIK/IRPA Bulletin*, 10, 1967/8, p. 210 (in a fifteenth-century polychrome sculpture group, in the relief mass of applied relief brocade); W. Fünders, 'Aktuelle Befunde zur Verwendung "vergessener" Pigmente in niedersächsischen Raumfassungen', in H. Möller (ed.), *Restaurierung von Kulturdenkmalen: Beispiele aus der Niedersächsischen Denkmalpflege, Berichte zur Denkmalpflege in Niedersachsen*, 2, 1989, pp. 44–8; U. Birkmaier, A. Wallert and A. Rothe, 'Technical Examinations of Titian's *Venus and Adonis*: A Note on Early Italian Oil Painting Technique', in A. Wallert, E. Hermens and M. Peck (eds), *Historical Painting Techniques, Materials, and Studio Practice*, Los Angeles 1995, pp. 117–26; R. Jones, 'The methods and materials of three Tudor artists', in K. Hearn (ed.), *Dynasties. Painting in Tudor and Jacobean England 1530–1630*, exh. cat., Tate Gallery, London 1995, pp. 231–40 (in a portrait by Cornelis Ketel from *c*. 1579–80); J. Dommermuth, '*The Castle Ashby Holy Family*: A technical investigation and comparison with the technique of Sebastiano del Piombo', *Hamilton Kerr Institute Bulletin Number 3*, Cambridge 2000, pp. 87–96. K. Fletcher, 'Marcus Gheeraerts' *The Countess of Bedford and her daughter*', *Hamilton Kerr Institute Bulletin Number 3*, Cambridge 2000, pp. 119–26; R.E. Straub, 'Einige technologische Untersuchungen am Tiefenbronner Magdalenaltar des Lukas Moser', *Jahrbuch der Staatlichen Kunstsammlungen in Baden-Württemberg*, VII, 1970, pp. 31–56, cited in K. Lutzenberger, H. Stege and C. Tilenschi, 'A note on glass and silica in oil paintings from the 15th to the 17th century', *Journal of Cultural Heritage*, 11, 2010, pp. 365–72. This last paper is the only one to report analyses of the glass; most of the other publications rely on microscopical examination of the particle shape.

5 R. Jones, 'Gainsborough's materials and methods', in S. Foister, R. Jones and O. Meslay, *Young Gainsborough*, exh. cat., National Gallery, London 1997, pp. 19–26. This survey of Gainsborough's early works found jagged colourless particles that were interpreted as glass in over 80% of the samples taken, through examination of dispersions in transmitted light. More recently it has been reported on a painting by Alexander Cozens, dating from *c*.1759–65. See www.tate.org.uk/servlet/ViewWork?workid=22590, accessed 20 January 2012.

6 A large number of occurrences in Italian paintings of the late fifteenth and early sixteenth centuries were first reported at the conference on Perugino's painting techniques held in Perugia in 2003, published in several papers in B.G. Brunetti, C. Seccaroni and A. Sgamellotti (eds), *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS Tech Workshop, Quaderni di Kermes*, Florence 2004.

7 M. Spring, 'Perugino's painting materials: analysis and context within sixteenth-century easel painting', in Brunetti et al. 2004 (cited in note 6), pp. 21–8. See also, in the same volume, E. Martin and J.P. Rioux, 'Comments on the technique and materials used by Perugino, through the study of a few paintings in French collections', pp. 43–56; C. Seccaroni, P. Moioli, I. Borgia, B.G. Brunetti and A. Sgamellotti, 'Four anomalous pigments in Perugino's palette: statistics, context, hypotheses', pp. 29–42; D. Cauzzi, 'The Madonna in Glory with Saints at the Pinacoteca Nazionale of Bologna', pp. 81–90.

8 M. Spring, 'Raphael's materials: Some new discoveries and their context within early sixteenth-century painting', in *Raphael's Painting Technique: Working Practices before Rome, Proceedings of the Eu-ARTECH workshop organised by The National Gallery and Eu-ARTECH, London November 11th 2004*, A. Roy and M. Spring (eds), *Quaderni di Kermes*, Florence 2007, pp. 77–86. See also, in the same volume, B. Mottin, E. Martin and E. Laval, 'Raphael's paintings in French museums: some new results from recent technical investigations', pp. 13–24; I. Borgia, B. Brunetti, P. Moioli, C. Seccaroni and A. Sgamellotti, 'Raphael in Perugia: the fresco of San Severo, the Baglioni Altarpiece and the Gonfalone of Città di Castello, pp. 35–44; B.H. Berrie, 'Raphael's Alba Madonna', pp. 101–8.

9 Spring 2007 (cited in note 8). See also M. Spring, 'Pigments in sixteenth-century painting of the German School', in *The Pictorial Technique of Grünewald and his Peers*, P. Béguerie-De Paepe and M. Menu (eds), Colmar 2007, pp. 136–144. Lutzenberger et al. 2010 (cited in note 4).

10 Merrifield 1849 (cited in note 1), p. cliv, p. ccxl and p. 503.

11 D.V. Thompson (trans.), *Cennino d'Andrea Cennini, The Craftsman's Handbook, The Italian 'Il Libro dell'arte'*, New York 1960, p. 29. This is cited in the discussion of pulverised glass in documentary sources given in Lutzenberger et al. 2010 (cited in note 4).

12 R. Haydocke, *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*, London 1598 (trans. of 1584 edn of Lomazzo), p. 101.

13 J.A. van de Graaf, *Het de Mayerne Manuscript als bron voor schildertechniek van de barok*, Mijdrecht 1958, p. 175.

14 Z. Veliz, *Artists' Techniques in Golden Age Spain*, Cambridge 1986, p. 72.

15 G. Field, *Chromatography; or, a Treatise on Colours and Pigments and of their powers in painting, &c.*, London 1835, p. 81. Eighteenth- and nineteenth-century references to powdered glass are discussed in L. Carlyle, 'Paint driers discussed in 19th-century British oil painting manuals', *Journal of the American Institute of Conservation*, 38 (1), 1999, pp. 69–82, and L. Carlyle, *The Artist's Assistant, Oil Painting Instruction Manuals and Handbooks in Britain 1800–1900*, London 2001, p. 50.

16 Veliz 1986 (cited in note 14), p. 73.

17 Merrifield 1849 (cited in note 1), p. 666, 'polvere di vetro ben pesta'.

18 Kirby Talley 1981 (cited in note 3), p. 380.

19 Van de Graaf 1958 (cited in note 13), p. 145 (no. 24).

20 Van de Graaf 1958 (cited in note 13), p. 165 (no. 41).

21 Van de Graaf 1958 (cited in note 13), p. 190 (no. 120a) and p. 146 (no. 25).

22 Merrifield 1849 (cited in note 1), pp. 818–19. 'Le cristal broyé mis dans les couleurs est trés bon pour les faire seicher', Brussels MS, 1635. Two much later English sources repeat almost exactly this instruction; *A Practical Treatise* (1795) and the *Compendium* (1808), again using the term 'cristal', which by this time is likely to have been taken for leaded glass, but which earlier might have meant 'cristallo', the glass made in Venice with purified ashes. These English sources are cited in Carlyle 2001 (cited in note 15).

23 In her preliminary observations on the sixteenth-century Marciana manuscript Merrifield lists, among the facts established by this source, 'That powdered glass was used as a dryer for lakes and other colours which dried slowly in oil' (Merrifield 1849 (cited in note 1), p. 606) but, as has already been pointed out by Seccaroni, it is not mentioned in the excerpts published by her and this statement in fact refers to the Paduan manuscript. See Seccaroni et al. 2004 (cited in note 7), pp. 29–41. A recent edition of the Marciana manuscript dates it to the second half of the sixteenth century and includes the recipe for a mordant for gilding referred to here. The ingredients are ground together and then heated over a slow fire. See F. Frezzato and C. Seccaroni, *Segreti d'arti diverse nel regno di Napoli. Il manoscritto It. III.10 della Biblioteca Marciana di Venezia*, Padua 2010, p. 155. This is also discussed, along with other references to powdered glass in Italian sources in the context of gilding, in C. Seccaroni, 'Polvere di vetro per dorare', *Kermes*, 77, 2010, p. 77.

24 E. Vandamme, 'Een 16e-eeuws Zuidnederlands receptenboek', *Jaarboek van het Koninklijk Museum voor Schone Kunsten Antwerpen*, 1974, pp. 101–13. It is not clear which pigment 'sinober' refers to. It could mean vermilion, but 'vermilloen' is used elsewhere in this book and it is close to 'sinople', which is used in the title for a red lake recipe.

25 Van de Graaf 1962 (cited in note 2).

26 G.B. Armenini, *On the True Precepts of the Art of Painting*, E.J. Olszewski (ed. and trans. of 1586 edn), 1977, p. 195.

27 These are the eleventh-century varnish recipes in Theophilus and those from around 1500 in the *Liber illuministarum*, which Van de Graaf considers to derive from the earlier source; Van de Graaf 1962 (cited in note 2).

28 Merrifield 1849 (cited in note 1), p. ccxxxix.

29 Veliz 1986 (cited in note 14), pp. 156–7.

30 I am grateful to Melanie Gifford, National Gallery of Art, Washington, DC, for allowing me to include the collaborative analysis of samples from the van Eyck *Annunciation*. Two wings by the Master of the Aachen Altarpiece in the Walker Art Gallery, Liverpool, which belong with a central panel in the National Gallery, were sampled by the author.

31 Kirby Talley 1981 (cited in note 3), p. 380.

32 Documentary sources relating to Venetian glass show that manganese-containing minerals were already being used as a decolouriser from at least 1290; M. Verità, 'L'invenzione del cristallo muranese: una verifica analitica delle fonti storiche', *Rivista della stazione Sperimentale del Vetro*, 1985, pp. 17–35.

33 These are included in Table 1: Pontormo (NG 6452), Bacchiacca (NG 1219), Bronzino (NG 5280 and NG 1323).

34 E. Buzzegoli, D. Kunzelman, P. Moioli, R. Scafè and C. Seccaroni, *Caratterizzazione di Pigmenti Tramite Indagine XRF su Dipinti Conservati presso La National Gallery di Londra*, unpublished report, ENEA, RT n.95/008, 1995.

35 R. Bellucci, M. Cetica, R. Coppola, C. Silvestri, P. Moioli, P. Poggi, and C. Seccaroni, 'Indagini su Raffaello, La Fornarina, Analisi non distruttive a confronto', *Kermes*, 49, 2003, pp. 64–72.

36 Martin and Rioux 2004 (cited in note 7).

37 Seccaroni et al. 2004 (cited in note 7). The presence of colourless glass in paint samples has subsequently been confirmed on six of the paintings examined by XRF in this study; see Cauzzi 2004 (cited in note 7) and C. Ricci, I. Borgia, B.G. Brunetti, C. Miliani, A. Sgamellotti, C. Seccaroni and P. Passalacqua, 'The Perugino's palette: integration of an extended in situ XRF study by Raman spectroscopy', *Journal of Raman Spectroscopy*, 35(8–9), 2004, pp. 616–21.

38 Mottin et al. 2007, Borgia et al. 2007, Berrie 2007 (all cited in note 8). I. Borgia, D. Cauzzi, B. Radicati and C. Seccaroni, 'Raphael's Saint Cecilia in Bologna: New Data about its Genesis and Materials', in Roy and Spring 2007 (cited in note 8), pp. 93–9. Bellucci 2003 (cited in note 35).

39 Seccaroni et al. 2004 (cited in note 7). S. Nerger, P. Moioli and C. Seccaroni, 'L'altarolo bifronte del Parmigianino nella Galleria Doria Pamphilj, *Kermes*, 51, 2003, pp. 65–70. P. Moioli and C. Seccaroni, 'Analisi non distruttive di fluorescenza X', in *L'Adorazione del Mistero*, A. Costamagna (ed.), Rome 2004, pp. 61–4 (Fra Bartolomeo, *Adorazione del Bambino*, Rome, Galleria Borghese); P. Moioli and C. Seccaroni, 'Le analisi XRF', in *Angeli, santi e demoni. Otto capolavori restaurati per Santa Croce*, M. Ciatti, C. Frosinini and C. Rossi Scarzanella (eds), Florence 2006, pp. 213–24 (Agnolo Bronzino, *Giudizio Universale* and Giuseppe Salviati, *Deposizione*, both in the Museo di Santa Croce, Florence). Lutzenberger et al. 2010 (cited in note 4) reports another example of a painting by Andrea del Sarto, as well as one by Parmigianino, in which colourless glass has been used.

40 For example Lotto's *Madonna delle Grazie* (State Hermitage Museum, Saint Petersburg) painted in Venice in 1542, where glass was found in the priming; K.B. Kalinina, I. Bonaduce, M.P. Colombini and I.S. Artemieva, 'An analytical investigation of the painting technique of Italian Renaissance master Lorenzo Lotto', *Journal of Cultural Heritage*, available online 20 December 2011, doi:10.1016/j.culher.2011.11.005, in press.

41 Michelangelo's *Entombment* (NG 790) is listed in the table and in addition XRF analysis has suggested that glass is present in his *Doni Tondo* (Uffizi Gallery, Florence); see E. Buzzegoli and R. Bellucci, 'Michelangelo's 'Doni Tondo' investigated with non-invasive analytical techniques', in *Studying Old Master Paintings, Technology and Practice, The National Gallery Technical Bulletin 30th Anniversary Conference Postprints*, M. Spring (ed.), with H. Howard, J. Kirby, J. Padfield, D. Peggie, A. Roy and A. Stephenson-Wright, London 2011, pp. 52–8.

42 Glass has also been reported in Francia's *Calvary with Saint Job at the Foot of the Cross* (Musée du Louvre, Paris). XRF analysis has also indicated its use in other paintings by Lorenzo Costa; see Martin and Rioux 2004 (cited in note 7). For Costa, see note 37 in this article, where unpublished reports on XRF analyses by ENEA are cited.

43 Claudio Seccaroni, personal communication, 9 February 2011.

44 See Birkmaier 1995 (cited in note 4).

45 Lutzenberger et al. 2010 (cited in note 4).

46 Lutzenberger et al. 2010 (cited in note 4).

47 Lutzenberger et al. 2010 (cited in note 4).

48 S. Dietz, H. Autzen, U. Baumer, P. Dietemann, I. Fiedler, C. Krekel, A. Schönemann and A. Stange, 'Studying the 'Graue Passion' by Hans Holbein the Elder', in Spring et al. 2011 (cited in note 41), pp. 89–94.

49 Martin and Rioux 2004 (cited in note 7), note 36.

50 Samples from many of the works in Table 1 have been analysed by gas chromatography – mass spectrometry confirming the presence of a drying oil in the paint. Many of these results have been published. There is not space here to give a reference for each analysis, but many of the results can be found in the *National Gallery Technical Bulletin*. Analyses of the German and Netherlandish paintings are published in Volume 18.

51 GC–MS analysis has identified both heat-bodied linseed oil and heat-bodied walnut oil in Lorenzo Costa's *Concert* (NG 2486) and walnut oil in his altarpiece for the Oratory of S. Pietro in Vincoli at Faenza (NG 629). The medium of the altarpiece by Costa and Maineri (NG 1119) has not been analysed, but the painting has extensive drying cracks which suggests an oil binder. The two *Scenes from the Story of Moses* (NG 3103 and NG 3104) are glue size paintings.

52 Seccaroni 2004 (cited in note 7).

53 Carlyle 1999 (cited in note 15) notes that manganese is mentioned in Merimee's book of 1830 as a drier. For general information on the effect of manganese on the drying of oil, see J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn, Oxford 1994, p. 38, and references therein.

54 Lutzenberger et al. 2010 (cited in note 4).

55 Martin and Rioux 2004 (cited in note 7), p. 52.

56 H. Pinheiro de Melo, J. Sanyova, A.J. Cruz, 'An unusual glazing technique on a Portuguese panel painting from the second half of the 16th century: materials, technique and reconstructions', *ICOM-CC 16th Triennial Conference, Lisbon 19–23 September 2011, Postprints*, Almada 2011, paper 105. Modern leaded glass was used for these reconstructions, which the authors considered to be on too small a scale to reach conclusions about its effect on drying rate.

57 Other published examples where glass is present in a mordant can be found in a painting by Lukas Moser (Lutzenberger et al. 2010, cited in note 4) and Hans Holbein the Elder (Dietz et al. 2011, cited in note 48).

58 Martin and Rioux 2004 (cited in note 7).

59 A list of paintings with a priming of lead white and a little lead-tin yellow is included in J. Dunkerton and M. Spring, `The development of painting on coloured surfaces in sixteenth century Italy', *Painting Techniques: History, Materials and Studio*

Practice, Preprints of the IIC Congress, Dublin 1998, A. Roy, P. Smith (eds), 1998, pp. 120–35. It was not appreciated that some of these also contain colourless powdered glass, however, until the samples were reanalysed for this study.

60 Bellucci 2003 (cited in note 35).

61 Martin and Rioux 2004 (cited in note 7).

62 Kalinina et al. 2011 (cited in note 40).

63 P. Riitano and C. Seccaroni, 'Attorno all'imprimitura', in *Raffaello: la rivelazione del colore. Il restauro della Madonna del Cardellino della Galleria degli Uffizi*, M. Ciatti, C. Frosinini, A. Natali and P. Riitano (eds), Florence 2008, pp. 95–103.

64 Lutzenberger et al. 2010 (cited in note 4); Pinheiro de Melo et al. 2011 (cited in note 56).

65 J. Kirby, M. Spring and C. Higgitt, 'Insight into the Technology of Red Lake Pigment Manufacture through Study of the Dyestuff Substrate', *National Gallery Technical Bulletin*, 26, 2005, pp. 71–87.

66 The whole of the first part of this section on glass in Italian paintings relies on Verità 1985 (cited in note 32), and M. Verità, 'Venetian innovations in glassmaking and their influence on the European glass history', *Les innovations verrières et leur devenir. Actes du deuxième colloque International de l'association verre et histoire, Nancy 26–28 Mars 2009*, published online http://www.verre-histoire.org/colloques/innovations/pages/p201_01_verita.html (accessed 9 February 2011).

67 Kirby Talley 1981 (cited in note 3), p. 380; Merrifield 1849 (cited in note 1), pp. 818–19.

68 S. Cagno, K. Janssens and M. Mendera, 'Compositional analysis of Tuscan glass samples: in search of raw material fingerprints', *Analytical and Bioanalytical Chemistry,* 391(4), 2008, pp. 1389–95; S. Cagno, M. Mendera, T. Jeffries and K. Janssens, 'Raw materials for medieval to post-medieval Tuscan glassmaking: new insight from LA-ICP-MS analyses', *Journal of Archaeological Science*, 37 (12), 2010, pp. 3030–6.

69 Although the K_2O content is greater than the 3% expected for Levantine ash in some of the samples, this higher potassium content cannot be convincingly ascribed to the use of barilla ash from Spain because the red lake matrix in these cases contains a significant amount of potassium due to unreacted alum (potassium aluminium sulphate) from the lake-making process.

70 E. Basso, B. Messiga and M.P. Riccardi, 'Stones from medieval glassmaking: a suitable waste product for reconstructing an early stage of the melting process in the Mt Lecco glass factory', *Archaeometry*, 50 (5), 2008, pp. 822–34. The authors concluded that here (unlike the glass in the Tuscan study), Al was not correlated with Si content and therefore did not originate from the silica source, so was not an indicator of use of a feldspar-rich sand.

71 Cagno et al. 2008 (cited in note 68).

72 M. Verità, 'Italian window glass chemical composition from the Roman time to the 18th century', *Verre et fenêtre de l'antiquité au XVIII^e Siècle, Actes du premier colloque international de l'association verre et histoire, Paris 13–15 Octobre 2005*, published online http://www.verre-histoire.org/colloques/verrefenetre/pages/p203_01_verita.html (accessed 9 February 2011).

73 E.S. Welch, 'Foppa, Vincenzo', in *Grove Art Online. Oxford Art Online*, http://www.oxfordartonline.com/subscriber/article/grove/art/T028910 (accessed 16 February 2012).

74 Lutzenberger et al. 2010 (cited in note 4).

75 K.H. Wedephol and K. Simon, 'The chemical composition of medieval wood ash glass from central Europe', *Chemie der erde*, 70, 2010, pp. 89–97; K.H. Wedephol, K. Simon and A. Kronz, 'Data on 61 chemical elements for the characterisation of three major glass compositions in late antiquity and the Middle Ages', *Archaeometry*, 53 (1), 2011, pp. 81–102.

76 K. Janssens, I. Deraedt, F. Adams, J. Veeckman, 'Composition of 15–17th century archaeological glass vessels excavated in Antwerp, Belgium', *Microchimica Acta Supplementum*, 15, 1998, pp. 253–67.

77 J. Barrera and B. Velde, 'A study of French medieval glass composition', *Archéologie Médiévale,* XIX, 1989, pp. 81–130.

78 J. Caen, O. Schalm and K. Janssens, '15th century stained glass windows in the former county of Flanders; a historical and chemical study related to recent conservation campaigns', *AIHV Annales du 17e Congrés*, 2006, pp. 459–66; O. Schalm, K. Janssens, H. Wouters, D. Caluwé, 'Composition of 12–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings', *Spectrochimica Acta Part B*, 62, 2007, pp. 663–8.

79 O. Schalm, D. Caluwé, H. Wouters, K. Janssens, F. Verhaeghe and M. Pieters, 'Chemical composition and deterioration of glass excavated in the 15th–16th century fishermen town of Raversijde (Belgium), *Spectrochimica Acta Part B*, 59, 2004, pp. 1647–56; B. Velde, 'Wood ash glass compositions in northern France for the period 13th–17th centuries', http://194.250.166.236/siteverre/francais/NOUVEAUTES/article%20bruce.htm (accessed 18 November 2003).

80 Mills and White 1994 (cited in note 53).

81 Samples from red lake-containing paint on the Westminster Retable, painted in the late thirteenth century, have been analysed by SEM–EDX at the National Gallery, but no glass was found.

82 For the methodology of quantitative analysis of glass under variable pressure conditions, and experiments carried out to optimise the conditions, see M. Spring, V. Kugler and S. Bean, 'Quantitative energy dispersive X-ray analysis of the blue pigment smalt in the variable pressure scanning electron microscope', in *SEM2010: SEM & Microanalysis in the study of historical technology, materials and conservation*, N. Meeks, C. Cartwright, A. Meek and A. Mongiatti (eds), London, forthcoming.