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Front cover: Giampietrino, *Salome*; detail of Plate 1, page 4.

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Analyses of Paint Media

RAYMOND WHITE AND JENNIFER PILC

A detailed Table of analytical results is presented here (pp. 96–99), with accompanying notes. In addition, the Table is prefaced with an introductory overview of the results and there is also included a brief note on experimental procedure.

Examination of the paint media used by painters of the Italian Schools has revealed that there was a gradual change from the use of egg tempera to the use of drying oils from the middle decades of the fifteenth century onwards. Painters naturally varied in their approach to the adoption of a paint medium with very different handling, drying and optical properties to those of egg. It is not unusual to find examples of both media used in the same painting and there are several different ways in which they could be employed. Several of the paintings examined, all but one produced in Florence during the years between the 1420s and the end of the century, contain both egg and drying oil and illustrate different approaches to the use of the two together.

The earliest example is particularly interesting from an art historical point of view. Two panels examined, *Saints Jerome and John the Baptist* (NG 5962) and *Saints Liberius(?) and Matthias* (NG 5963), are at present attributed jointly to Masaccio and his slightly older contemporary, Masolino. They were originally the front and back of a single panel, part of a double-sided triptych formerly in the Colonna Chapel in the church of Santa Maria Maggiore, Rome, but now dismembered; the central panels from the altarpiece are in the Museo di Capodimonte, Naples and those forming the other wing are in the Johnson Collection, Philadelphia Museum of Art. The altarpiece may date from between 1423 and 1428 (when Masaccio died), although the precise nature of the presumed collaboration between the two artists is unclear.[1]

Stylistic differences between the two panels have led to the suggestion that Masaccio was largely responsible for *Saints Jerome and John the Baptist*, while *Saints Liberius(?) and Matthias* was mostly painted by Masolino. It was therefore particularly interesting that examination of the paint in several areas of the two panels revealed differences in the paint medium used. The handling of the flesh paint appeared markedly different and it was found that whereas egg tempera was used to paint Saint John's flesh, the paint of Saint Matthias's flesh contained egg enriched by the addition of a little drying oil. FTIR–microscopy indicated the presence of both protein and drying oil in discrete areas throughout the sample examined, suggesting that here an emulsion of drying oil in egg was used. Such a paint would have differed from ordinary egg tempera to the extent that it would be rather richer and could be manipulated more freely and with greater flexibility; it might allow a softer blending of individual brush strokes, if the artist so desired.

In the *Saints Jerome and John the Baptist* panel, Saint John's red cloak has been painted in egg tempera, possibly with a trace of drying oil added. In the companion panel, however, Saint Liberius's pinkish-cream cassock and Saint Matthias's olive-green robe have been painted in linseed oil. This is an extremely early instance of the use of linseed oil in a painting of any Italian School. The results as a whole may provide some corroborative evidence for the suggestion that the panels are by different hands, at least in part.[2] Masolino's presence in Florence is not recorded during the second decade of the fifteenth century and he is known to have been working in Hungary between 1425

and 1427.[3] If he had also had some contact with Northern European practice during his earlier period of absence, it is conceivable that he learned something of the use of drying oil at this time, if not later during his stay in Hungary.

The altarpiece of *The Trinity with Saints* (NG 727, 3162, 3230, 4428 and L15) was commissioned from Francesco Pesellino in 1455. On his death in 1457, Fra Filippo Lippi and his workshop in Prato completed the work by 1460. It is thought that Pesellino, who had probably trained in Lippi's workshop, was responsible for the overall design of the altarpiece and perhaps for the two figures on the left, while Lippi was responsible for the right-hand figures, the landscape and various other parts of the work, such as God's hands and the dove. The Lippi workshop is thought to have been responsible for the predella panels.[4] In the main panel, examination of paint from the left- and right-hand figures and parts of the sky and landscape showed that the medium used was egg containing an admixture of drying oil, similar to the paint used in the panel of *Saints Liberius(?) and Matthias* described above. The sky, however, was painted in egg tempera alone. In the paint used in the Trinity altarpiece for the robe of Saint Jerome (on the right), which was slightly richer in texture, the proportion of oil in the emulsion was correspondingly higher.[5] In this case, examination of the paint medium has thrown little light on the problems of attribution of the different parts of the picture: the same medium appears to have been used on the two sides of the painting, although not in the sky. The fact that the white paint of the rocks in the predella panel of Saint Jerome and the Lion (NG 4868.4) contains pure egg tempera may be significant, given that this part of the altarpiece is thought to have been produced by the Lippi workshop in Prato.

When egg tempera and drying oil are found in the same picture, it is perhaps most common to find egg tempera used for the underpaint with oil in the paint layers above, or egg used in certain areas of the painting – white, pale blue or flesh paint, for instance – and oil in others – reds and greens perhaps. The reason behind this may be purely visual: egg tempera gives a colder white, for example, and a paint surface with a slight sheen. The glazes of lake pigments and copper-containing green pigments used to model the shadows and folds of clothing are more effective in a medium of drying oil, however. A combination of the two methods of proceeding is found in *The Virgin and Child with Saint John* (NG 1412), painted by Filippino Lippi around 1475–80.[6] The pale blue sky was painted using egg tempera, while drying oils were used for the principal layers of the robes of Saint John and the Virgin. The Virgin's green sleeve lining, for which linseed oil was used, was underpainted in egg tempera, however. The red lake pigment (identified as lac lake)[7] used for Saint John's robe and the ultramarine used for the Virgin's robe are poor driers; accordingly the walnut oil used for the former and the linseed oil for the latter had both been heat pre-polymerised (partially, in the case of the walnut oil), presumably to assist drying.

Giovanni Antonio Boltraffio's *The Virgin and Child* (NG 728) presents a very much more complex case altogether, discussed at length elsewhere in this *Bulletin* (pp. 13–17).[8] A blackish underpaint, present in certain areas of the painting, such as the Virgin's robe, the green cloth of honour and the dark blue water in the background, contained egg tempera essentially, but with a trace of oil added; the paint above (where it was the original paint and not later restoration) contained oil, identified as walnut oil in the flesh of the Christ Child. However, a reddish isolating layer or *imprimitura* beneath the blackish underpaint, exposed in places where the dark-coloured paint has shrunk away, was also found to contain walnut oil. The use of a richer oil-containing *imprimitura* under the leaner egg tempera-containing underpaint is probably responsible for the shrinkage.

Of the sixteenth-century Italian paintings found to contain an oil medium, *The Adoration of the Kings* (NG 640) by the Ferrarese painter Girolamo da Carpi, and dating from about 1545–50, was interesting in that components of the medium appear to have been responsible for the severe wrinkling and reticulated appearance of the paint in certain areas of the picture. The paint of a tree trunk in the background, for example, has a markedly 'crocodiled' appearance, caused by the presence of a softwood pitch, identified by the presence of pyrolysis products derived from abietatriene acids, mixed with the walnut oil. This gives a brown colour, rather similar to that of asphaltum; like asphal-

tum, it tends to cause wrinkling and similar paint defects because it is liable to inhibit drying of the oil.[9] A softwood pitch was found in an orange-brown glaze, used to model the folds of an apostle's yellow robe in Cima da Conegliano's altarpiece, *The Incredulity of Saint Thomas* (NG 816), but in this case the paint is in very good condition, showing no drying faults.[10] It must be assumed that Girolamo da Carpi incorporated too much pitch in his mixture; even though the walnut oil used had been heat bodied to improve its drying properties, the paint dried poorly. It is worth noting that Cima used the more strongly drying linseed oil for his glaze. In his treatise on painting, published in 1587, Giovanni Battista Armenini suggests the use of 'the smoke of Greek pitch' as one of the pigments suitable for shadows on flesh (mummy and asphaltum being others), but with verdigris being added: this would aid drying.[11]

A rather similar, although less pronounced, defect is apparent in the right-hand kneeling figure's green cloak. The paint was found to contain walnut oil, with a small amount of pine resin. Examination of a fragment of the paint by FTIR–microscopy showed that the resin had only reacted with the copper-containing green pigment in one or two isolated areas: it was present essentially as a component of the paint medium rather than in the form of 'copper resinate'.[12] Further examination showed that less reticulated areas of the paint contained rather less pine resin. This suggests that the painter stirred a proportion of pine resin varnish, *vernice commune*, into the green paint, a little generously and carelessly perhaps, but rather as Armenini described for painting and glazing green draperies.[13]

The drying oils most frequently encountered in both sixteenth- and seventeenth-century paintings are linseed and walnut. Poppy oil, which, like walnut oil, is a semi-drying oil strictly speaking, is rather rarely encountered, although it has been identified in the painted wings of an altarpiece dating from 1525–30 in the church of Saint Lambert, Neerharen, Antwerp.[14] In the compilation of recipes made by the physician Theodore Turquet de Mayerne between 1620 and 1646, the properties of poppy oil are mentioned several times: it is said to be very pale, so particularly good for white and blue, and it does not spoil the colours.[15] Philippe de La Hyre (writing at the beginning of the eighteenth century, but perhaps referring back to the procedures in use during the years around 1660, when he was training) describes poppy oil as being paler than walnut oil, but says it was used only for small works, where it could 'contribute to the beauty and vivacity of the colours'.[16] In the two seventeenth-century French paintings in the National Gallery collection in which it has been identified, it occurs in white or light coloured paint. In an earlier study, poppy oil was identified in the white ermine on the Cardinal's red robe in Philippe de Champaigne's *Cardinal Richelieu* (NG 1449), of about 1637.[17] The present examination revealed the presence of linseed oil in the paint of a shadow in the fold of the same red robe, but what could be either walnut oil or a mixture of linseed and poppy oils in the grey paint of the architecture. In the circumstances, the latter possibility is far more likely; probably the artist ground his lead white in poppy oil, but used linseed oil for other pigments, resulting in a mixture of oils in the grey paint. Poppy oil was also found used for the sitter's white cuff in the *Portrait of a Man* (NG 2929), attributed to Gabriel Revel, whereas linseed oil was found in the red glaze on the sleeve.

The National Gallery collection includes several paintings by Nicolas Poussin and by artists in his circle, those by Poussin himself dating largely from his two periods of activity in Rome, from 1624 to 1640 and again from 1642 until his death in 1665. He returned briefly to Paris in 1640–2. A notable characteristic of his studio practice is the care he appears to have taken over most aspects of his work; little appears to have been left to chance. This careful approach seems to have extended to his painting technique, which, as far as the paint medium used is concerned, appears very sound. The painter used linseed or walnut oil, often heat pre-polymerised (which gives the paint extra body as well as improving drying); heat-bodied linseed oil was used in the lime green paint of foliage on the right of *A Bacchanalian Revel before a Term of Pan* (NG 62), dating from about 1630–4, for example, while heat-bodied walnut oil was used for green foliage paint in *Landscape with a Man washing his Feet*

at a Fountain (NG 40), of about 1648. There appears to be no particular preference for employing walnut oil with white or blue pigments, for which it was traditionally used.

A few seventeenth-century artists were in the habit of adding a small amount of pine resin to their paint, either for particular colours or in general, to add increased gloss and transparency to the paint.[18] This would be particularly effective in giving increased depth to areas of shadow or in glazing draperies and it is not uncommon to find an addition of resin to the paint for this purpose. Philippe de Champaigne added a little pine resin to the linseed oil used for the glaze of Cardinal Richelieu's red robe, while pine resin and mastic were present in the medium used in the glaze on the sitter's coat in the portrait attributed to Gabriel Revel. Poussin seems not to have followed this practice. The only exception is the early, and unfinished, *Nurture of Bacchus* (NG 39), dated about 1627, where a trace of pine resin was present in the cream-coloured sky above the horizon. Of the painters in Poussin's immediate circle, his brother-in-law, Gaspard Dughet, seems also to have used conventional linseed oil on the whole; only in the *Landscape in the Roman Campagna (Tivoli?)* (NG 161) were traces of pine resin also found. (Examination of the paint samples by FTIR–microscopy ruled out the possibility of contamination from an old varnish layer.) In view of Poussin's apparent preference for a simple drying oil medium, the results obtained from *Bacchanalian Festival with Silenus* (NG 42), dating from about 1635–6 and only attributed to the artist, were particularly interesting. Both the sky and foliage were found to have been painted in linseed oil, but in both cases a little resin had been added to the oil, pine resin alone in the case of the sky, mastic and pine resin in the foliage.

By the late eighteenth and nineteenth centuries, literary sources suggest that the incorporation of various types of varnish into drying oils was not uncommon.[19] The disastrous effects of the inappropriate or ill-considered use of some of these – the notorious megilp (essentially equal parts of linseed oil, prepared with lead driers, and mastic varnish shaken together) condemned by many writers – have been much discussed, ever since the contemporaries of Sir Joshua Reynolds lamented the results of his experimenting with his materials.[20] However, in more cautious hands, varnish-containing media gave perfectly stable and lasting paint films. Paul Delaroche used a medium consisting of heat pre-polymerised linseed oil mixed with mastic varnish for several areas of his painting *The Execution of Lady Jane Grey* (NG 1909), dated 1833, including the red glaze pattern of the brown brocade dress on the seated attendant's lap and the executioner's black coat. The paint of this coat has retained the brushwork to an extent that is not usually seen in black paint, the extra body being provided by the mastic-containing medium used. Other areas of the painting – the brown paint of the brocade dress, Lady Jane's white dress – were painted in ordinary drying oils, linseed oil for the former, walnut for the latter. One of the painting varnishes described by Mérimée in his book of 1830 is the so-called *vernis des Anglais*, which had a jelly-like consistency and consisted of mastic and linseed oil alone (without beeswax or any other additional components); possibly Delaroche used something of this type.[21] The picture is very thinly and carefully painted; despite the fact that, at one stage in its history, it suffered flood damage, the paint is sound and in remarkably good condition.[22]

J.M.W. Turner, Delaroche's contemporary, was a painter who could be described as throwing caution to the winds as far as his use of materials was concerned. He is reported as having used varnish mixtures, beeswax and spermaceti wax in his media as well as conventional drying oils;[23] he is also recorded as having worked extensively on his paintings on the so-called 'varnishing days' at the Royal Academy or British Institution, when artists were permitted to retouch or varnish their works immediately before the opening of the exhibition.[24] For this he is said to have used watercolours, or, according to John Ruskin, dry pigments applied in water, glue or whatever came to hand, then varnished.[25]

Turner's *The Fighting 'Temeraire' tugged to her last Berth to be broken up, 1838* (NG 524), the subject of a National Gallery *Making and Meaning* exhibition in 1995, has never been cleaned; the results of examination of the surface layers in some areas of the painting were therefore particularly interesting.[26] The salmon-pink paint of the sunset contained heat pre-

polymerised walnut oil (needless to say, Turner did not restrict his use of walnut oil to white or pale colours); the paint also contained Sumatra benzoin. From the sixteenth century onwards, recipes can be found for varnishes for delicate, decorative objects that will not be subjected to handling, using the alcohol-soluble benzoins.[27] The varnish dries almost immediately after painting and would thus permit the rapid application of layer upon layer of paint, applied very thinly, without picking up pigment from the layer below, as the artist sought to emphasise or to modify some aspect of the painted surface, perhaps so that it would not lose by the sudden comparison with the works of other artists that had come to hang nearby for the duration of the exhibition. During sampling it was suspected that more than one layer of paint was present; as it is unlikely that a benzoin-containing spirit varnish could be mixed satisfactorily with walnut oil, it seems that the varnish was used for the final touches of salmon pink, over the oil paint. It is less likely, although not impossible, that the artist worked without a conventional medium for these last touches, then applied the spirit varnish over the top.

Turner used walnut oil, sometimes heat-bodied, sometimes not, as his principal medium, but the results of analysis show a range of resins also present, with the oil, in different areas of the painting: pine resin and mastic in the brownish-black shadow of the buoy; pine resin and a dammar in the mustard-coloured reflection of the sun in the sea; a still unidentified triterpenoid resin in the white impasto of a cloud. These probably indicate the use of the various varnishes, megilp and other proprietary products, in which Turner showed a great interest and is also known to have purchased, mixed into the paint on the palette.[28] The presence of a non-drying fat in the white paint of the clouds suggests something (possibly tallow – the material could not be precisely characterised) added as a plasticiser to give some softness to their surface texture. Although there are occasional references to the addition of soap to oil paint, this could equally well be some other household material (like salad oil or dripping) Turner happened to have to hand.[29]

More technical and detailed information concerning the samples and their analyses can be found in the notes to the Table, below.

Note on an Improved Analytical Procedure

Most of the analytical results presented here have been obtained using a new, single-stage and improved derivatisation procedure. Reference was made to this in last year's *Bulletin*.

Thermal degradation of quaternary ammonium salts of carboxylic acids in the heated injection port of a gas-chromatograph has been known to produce *in situ* methylation of such acids and has been utilised for three decades. However, the method has a serious drawback in that with the usual reagents, tetramethyl- and trimethylphenylammonium hydroxides, thermolysis temperatures are high and the alkalinity of the reagents lead to base-induced isomerisations of the more labile functional features of a molecule (for example double bonds, hydroxyl groups and others).[30] The trifluoromethyl homologue of the latter reagent, that is, *m*-(trifluoromethyl)phenyl-trimethylammonium hydroxide, or trimethyl(α,α,α-trifluoro-*m*-tolyl)ammonium hydroxide – abbreviated to TMTFTH – has been tested in this laboratory and has been found to perform very well in the conversion of labile fatty and terpenoid acids to their methyl esters. In addition, this reagent is able to effect a conversion of glycerides to methyl esters of their component acids. This appears to be the result of the reduced alkalinity of this reagent, in comparison to those mentioned above, and the superior properties of dimethyl(trifluoro)toluidine as a leaving group, resulting in a lower thermolysis temperature.

TMTFTH is commercially available and is readily made in the laboratory in methanolic solution by a slight modification of the method reported by MacGee and Allen.[31] Experimental details appear below.[32]

Analyses of Paint Media

Artist	Picture	Date
EARLIER ITALIAN SCHOOLS		
Lorenzo Monaco	*Adoring Saints* NG 216	probably 1407–9
	The Coronation of the Virgin NG 1897	probably 1407–9
Attributed to **Masaccio** and **Masolino**	*Saints Jerome and John the Baptist* NG 5962	probably between 1423 and 1428
	Saints Liberius(?) and Matthias NG 5963	probably between 1423 and 1428
Follower of **Fra Angelico**	*The Annunciation* NG 1406	probably about 1450
Francesco Pesellino	*The Trinity with Saints* NG 727	1455–60
	Predella of the Trinity with Saints Altarpiece NG 4868.4	1455–60
Filippino Lippi	*The Virgin and Child with Saint John* NG 1412	1480
Giovanni Antonio Boltraffio	*The Virgin and Child* NG 728	probably about 1493–9
Leonardo da Vinci	*The Virgin of the Rocks (The Virgin with the Infant Saint John adoring the Infant Christ accompanied by an Angel)* NG 1093	about 1508
After **Luini**	*Saint Catherine* NG 3936	early 16th century
Vincenzo Catena	*Portrait of the Doge, Andrea Gritti* NG 5751	probably 1523 to 1531
Girolamo da Carpi	*The Adoration of the Kings* NG 640	probably about 1545–50

Sample	Medium	P/S	Oil type	Note
1. Red lake paint of left-hand saint's robe	Egg			33
2. Mordant of lost gilding of pattern of Saint Peter's robe	Egg, possibly glue			
1. Blue of Christ's robe	Egg			34
2. Faded paint of Mary's robe	Egg			
1. Red shadow of fold of Saint John's cloak	Egg (+ trace of oil?)			35
2. Flesh paint of Saint John's right shoulder	Egg			
1. Pinkish-cream paint of Pope's cassock	Oil	1.7	Linseed	36
2. Olive-green paint of the cloak of Saint Mathias	Oil	1.2	Linseed	
3. Pale flesh paint from the back of Saint Mathias's neck	Egg + some oil			
1. Adhesive or mordant of gilding, trimmings of Virgin's right sleeve	Glue			37
2. Flesh paint of angel's neck	Egg			
3. Pale pink of angel's dress	Egg			
1. Green of trees on horizon	Egg + some oil			38
2. Yellow of inside of cloak of left-hand saint	Egg + some oil			
1. White rocks , upper right-hand corner	Egg			
1. Pale blue sky	Egg			39
2a. Green lining of Virgin's sleeve, principal layer	Oil	1.5	Linseed	
2b. Underpaint to above	Egg			
3. Red lake glaze of Saint John's cloak	Oil	2.5	Walnut	
4. Blue of the sleeve of the Virgin's robe	Oil	1.2	Linseed	
1. Red paint of Virgin's right sleeve	Oil + egg			40
2. Blue-black water in background, rocky scene, left side.	Oil			
3. Flesh paint, Christ Child's left leg	Oil	3.1	Walnut	
4. Black contracted underpaint, exposed at left-hand edge of green backcloth	Egg + oil			
5. Red-brown underpaint, exposed on Virgin's finger	Oil	2.1	Walnut	
6. Exposed black underpaint from edge of cuff of Virgin's right arm	Egg + oil			
1. Brownish-black paint of rocks, right-hand side	Oil	2.2	Walnut	41
2. Red-brown *imprimitura* layer (beneath sample 1)	Oil	2.1	Walnut	
3. Blue-black of angel's robe	Oil	2.5	Walnut	
4. Green leaf, lower edge	Oil	2.5	Walnut	
5. Pale bluish-green sky, between rocks at top	Oil	2.5	Walnut	
1. Brown paint of shadow of wheel	Oil	1.9	Linseed	
2. Dark green background	Oil	2.0	Linseed	
3. Red paint of Saint Catherine's right, upper sleeve	Oil	1.9	Linseed	
1. Dark red glaze of cap	Oil	1.6	Linseed	42
2. Flesh paint of neck	Oil	1.8	Linseed	
3. Yellow brocade, highlight of fold	Oil	1.6	Linseed	
4. Flesh paint of left forefinger	Oil	1.8	Linseed	
1. Brownish-black, heavily 'crocodiled' paint of tree trunk, mid-background scene	Oil + softwood pitch	2.7	Walnut	43
2. Green glaze-like paint of cloak of right-hand kneeling figure	Oil + pine resin	2.1	Walnut	

Artist	Picture	Date
FRENCH SCHOOLS		
Nicolas Poussin	*The Nurture of Bacchus* NG 39	about 1627
	A Bacchanalian Revel before a Term of Pan NG 62	1630–4
	The Adoration of the Golden Calf NG 5597	by 1634
	Landscape in the Roman Campagna with a Man scooping Water NG 6390	about 1637–8
	Landscape in the Roman Campagna NG 6391	about 1639–40
	Landscape with a Man killed by a Snake NG 5763	1648
	Landscape with a Man washing his Feet at a Fountain NG 40	about 1648
	The Annunciation NG 5472	1657
Attributed to **Nicolas Poussin**	*Bacchanalian Festival with Silenus* NG 42	1635–6
After **Nicolas Poussin**	*The Holy Family with Saints Elizabeth and John* NG 1422	after 1710
Philippe de Champaigne	*Cardinal Richelieu* NG 1449	about 1637
Gaspard Dughet	*Landscape in the Roman Campagna (near Albano?)* NG 68	about 1670
	Landscape in the Roman Campagna NG 98	about 1670
	Landscape in the Roman Campagna (Tivoli?) NG 161	about 1670
Attributed to **Crescenzio Onofri**	*Landscape with Figures* NG 2723	probably 1670–1712
Attributed to **Gabriel Revel**	*Portrait of a Man* NG 2929	about 1675
Pierre Mignard	*The Marquise de Seignelay and Two of her Children* NG 2967	1691
Paul Delaroche	*The Execution of Lady Jane Grey* NG 1909	1833
BRITISH SCHOOLS		
Joseph Mallord William Turner	*The Fighting 'Temeraire' tugged to her last Berth to be broken up, 1838* NG 524	before 1839

Sample	Medium	P/S	Oil type	Note
1. Dark grey of added(?) strip	Oil	2.2	Walnut	44
2. Cream paint of distant sky	Oil + resin	1.6	Linseed	
1. Lime-green impasto paint of leaf, right-hand corner	Oil	1.6	Linseed	45
2. Blue sky, same area	Oil			
1. Blue robe of left-hand female figure	Oil			46
2. Yellow highlight of sleeve, woman seated with child	Oil			
1. Pinkish-white sky	Oil	2.2	Walnut	
2. Brownish-green leaves	Oil	1.7	Linseed	
1. Peach-coloured rock	Oil	1.7	Linseed	
2. Brownish-green leaf	Oil	1.7	Linseed	
1. Blue sky	Oil	1.4	Linseed	
2. Green foliage	Oil	1.8	Linseed	
1. Blue sky	Oil	1.5	Linseed	47
2. Green foliage, right-hand edge	Oil	2.3	Walnut	
1. White of angel's hem	Oil	2.4	Walnut	48
2. Yellow of Mary's shawl	Oil	2.2	Walnut	
1. Pale blue sky	Oil + some resin	1.6	Linseed	49
2. Green foliage	Oil + some resin	1.2	Linseed	
1. Light brown floor in background	Oil			50
1. Grey paint of moulding of plinth of enjoined pilaster	Oil	2.7	Poppy + Linseed?	51
2. Wine-red shadow of fold of robe	Oil + resin	1.5	Linseed	
1. Brown-green foliage	Oil	1.5	Linseed	52
2. Blue sky	Oil	1.5	Linseed	
1. Blue sky	Oil	1.8	Linseed	
2. Mustard highlight in path	Oil	1.5	Linseed	
1. Blue sky	Oil + some resin	1.8	Linseed	
2. Lime-green foliage	Oil + some resin	1.7	Linseed	
1. Pale blue sky	Oil	2.4	Walnut	
2. Cream-coloured paint of cloud	Oil	1.2	Linseed	
1. Red glaze paint of sitter's right sleeve	Oil + resin	1.2	Linseed	53
2. White of sitter's right cuff	Oil + resin	3.8	Poppy	
1. Pale cream paint of distant sky	Oil	3.0	Walnut	54
2. Red glaze paint of fold of drape, right-hand side	Oil	3.1	Walnut	
3. Blue sky	Oil	2.4	Walnut	
1. Upper, pale ground	Oil	2.4	Walnut	55
2. Lower, darker ground	Oil	1.8	Linseed	
3. White paint of Lady Jane's left sleeve	Oil	2.5	Walnut	
4. Black paint of executioner's right sleeve	Oil + resin	1.4	Linseed	
5. Brownish background colour of patterned dress over lap of fainting attendant	Oil	1.8	Linseed	
6. Red lake paint of pattern of dress on left-hand female attendant's lap	Oil + resin	1.7	Linseed	
1. Impasto paint of white cloud	Oil + resin	3.0	Walnut	56
2. Salmon-pink sunset	Oil + benzoin	3.0	Walnut	
3. Brownish-black buoy	Oil + resin	3.2	Walnut	
4. Mustard reflection of sun on sea	Oil + resin	2.6	Walnut	

Notes and References

1. J. Dunkerton, S. Foister, D. Gordon and N. Penny, *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, New Haven and London 1991, pp. 252–4; P. Joannides, *Masaccio and Masolino: A Complete Catalogue*, London 1993, pp. 72–9, 414–22.
2. In one of the two panels in the Johnson Collection, Philadelphia, *Saints Peter and Paul* (cat. 23), egg tempera appears to have been used for the hands and feet while an egg-oil mixture was used elsewhere: see C. Strehlke and M. Tucker, 'The Santa Maria Maggiore Altarpiece, new observations', *Arte Cristiana*, LXXV, 719, March/April 1987, pp. 105–24; Joannides, ibid., p. 420.
3. For Masolino's early training and period in Hungary, 1425–7 (of which little is known), see Joannides, ibid., pp. 25–6, 31–2, 37–45, 153.
4. M. Davies, *National Gallery Catalogues: The Earlier Italian Schools*, London 1961 (1986 reprint), pp. 414–9; J. Ruda, *Fra Filippo Lippi: Life and Work, with a Complete Catalogue*, London 1993, pp. 449–52.
5. The analysis of this paint, and that from several other areas of the painting, was reported in an earlier issue of this *Bulletin*: see J. Mills and R. White, 'Paint Media Analyses', *National Gallery Technical Bulletin*, 13, 1989, pp. 69–71.
6. J. Dunkerton and A. Roy, 'The Materials of a Group of late Fifteenth-century Florentine Panel Paintings', in this *Bulletin*, pp. 21–31.
7. J. Kirby and R. White, 'The Identification of Red Lake Pigment Dyestuffs', in this *Bulletin*, pp. 56–80, especially p. 80.
8. L. Keith and A. Roy, 'Giampietrino, Boltraffio and the Influence of Leonardo', in this *Bulletin*, pp. 5–19, especially pp. 14–15.
9. R. White, 'Brown and Black Organic Glazes, Pigments and Paints', *National Gallery Technical Bulletin*, 10, 1986, pp. 58–71, especially pp. 65–7.
10. J. Dunkerton and A. Roy, 'The Technique and Restoration of Cima's "The Incredulity of S. Thomas"', *National Gallery Technical Bulletin*, 10, 1986, pp. 4–27, especially p. 17.
11. G.B. Armenini, *De' veri precetti della pittura*, Ravenna 1587, p. 124: '... il fumo di pece greca, il quale perche egli non hà corpo, s'incorpora benissimo col verderame ben macinato con oglio prima, del quale vi se ne mette un terzo & due di fumo ...' Armenini also recommends the addition of a little varnish, probably the *vernice commune* (essentially a varnish made with pine resin and oil) to which he refers elsewhere (p. 126). Some recipes for *vernice commune* include Greek pitch as an ingredient: see, for example, L. Fioravanti, *Del compendio dei secreti rationali...*, Venice 1564, p. 172. The resulting varnish would undoubtedly be very dark in colour.
12. J. Pilc and R. White, 'The Application of FTIR–microscopy to the Analysis of Paint Binders in Easel Paintings', *National Gallery Technical Bulletin*, 16, 1995, pp. 73–84, especially p. 82.
13. Armenini, 1587, cited in note 11, p. 126.
14. J. Sanyova, 'Etude scientifique des techniques picturales des retables anversois', *Antwerpse retabels, 15de–16de eeuw*, exhibition catalogue, edited by H. Nieuwdorp; 2 vols. (Vol. I. Catalogue; Vol. II. Essays), Antwerp 1993, Vol. II, pp. 151–64, especially p. 155.
15. T. T. de Mayerne, *Pictoria, sculptoria, tinctoria et quae subalternarum artium spectantia*, 1620–46 (British Library (British Museum) MS. Sloane 2052): edition annotated by J.A. van de Graaf, *Het de Mayerne Manuscript als Bron voor de Schildertechniek van de Barock*, diss., Utrecht 1958, no. 86a p. 178; no. 90, p. 180.
16. P. de La Hyre, 'Traité de la pratique de peinture', *Mémoires de l'Académie Royale des Sciences depuis 1666 jusqu'à 1699*, IX, Paris 1730, pp. 637–730, especially p. 707: 'mais ce n'a été que pour de petits ouvrages, où ils ont recherché tout ce qui pouvoit contribuer à la beauté et à la vivacité des couleurs'.
17. J.S. Mills and R. White, 'The Gas Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis', *Conservation and Restoration of Pictorial Art*, edited by N. Brommelle and P. Smith, London 1976, pp. 72–7.
18. R. White and J. Kirby, 'Rembrandt and his Circle: Seventeenth-Century Dutch Paint Media Re-examined', *National Gallery Technical Bulletin*, 15, 1994, pp. 64–77, especially pp. 71–3.
19. See, for example, J.F. Watin, *L'Art du peintre, doreur, vernisseur*, 3rd edn., Paris 1776 (1st edn. 1772), pp. 187–314; J.-F.-L. Mérimée, *De la peinture à l'huile*, Paris 1830 (facsimile reprint, Puteaux 1981), pp. 65–91 (the English edition of this book was published in 1839); L. Carlyle, *A Critical Analysis of Artists' Handbooks, Manuals and Treatises on Oil Painting Published in Britain between 1800–1900: With Reference to Selected Eighteenth Century Sources*, Ph.D. dissertation, Courtauld Institute of Art, University of London, 1991, pp. 42–189; L. Carlyle, 'Varnish Preparation and Practice 1750–1850', *Turner's Painting Techniques in Context*, 1995, edited by J.H. Townsend, London 1995, pp. 21–8.
20. L. Carlyle and A. Southall, 'No Short Mechanic Road to Fame: The Implications of Certain Artists' Materials for the Durability of British Painting: 1770–1840', in R. Hamlyn, *Robert*

Vernon's Gift: British Art for the Nation 1847, exhibition catalogue, London 1993, pp. 21–6; A. Southall, 'Turner's Contemporaries: Their Materials, Practices and Opinions', *Turner's Painting Techniques in Context, 1995*, ibid., pp. 12–20; M.K. Talley, '"All good pictures crack"; Sir Joshua Reynolds's practice and studio', in *Reynolds*, edited by N. Penny, exhibition catalogue, Paris/London 1985–6, pp. 55–70, especially pp. 55–6, 62–4, 67–8.

21. Mérimée, 1830, cited in note 19, pp. 70–1.
22. J. Kirby and A. Roy, 'Paul Delaroche: A Case Study of Academic Painting', *Historical Painting Techniques, Materials and Studio Practice*: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995, edited by A. Wallert, E. Hermens and M. Peek, Malibu 1995, pp. 166–75, especially p. 172.
23. See, for example, J.H. Townsend, 'Painting Techniques and Materials of Turner and Other British Artists 1775–1875', *Historical Painting Techniques*, ibid., pp. 176–85; J.H. Townsend, 'Turner's Use of Materials, and Implications for Conservation', *Turner's Painting Techniques in Context, 1995*, cited in note 19, pp. 5–11; M. Odlyha, 'The Role of Thermoanalytical Techniques in the Characterisation of Samples from Turner's "The Opening of the Wallhalla", ibid., pp. 29–34; J.J. Boon, J. Pureveen, D. Rainford and J.H. Townsend, '"The Opening of the Wallhalla, 1842": Studies on the Molecular Signature of Turner's Paint by Direct Temperature –resolved Mass Spectrometry (DTMS)', ibid., pp. 35–45.
24. There are several references to Turner's activities on varnishing days in M. Butlin and E. Joll, *The Paintings of J.M.W. Turner*, 2nd edn., London and New Haven 1985.
25. Ibid.; see also Townsend, 'Turner's Use of Materials, and Implications for Conservation', cited in note 23, p. 10.
26. J. Egerton, *Making and Meaning: Turner,'The Fighting Temeraire'*, with a technical examination of the painting by M. Wyld and A. Roy, exhibition catalogue, London 1995, pp. 121–3, 132.
27. *Segreti diversi*; the Marciana manuscript (Venice, Biblioteca Marciana, MS Ital. IV 48, sixteenth century) in M.P. Merrifield, *Original Treatises dating from the XIIth to the XVIIIth centuries on the Arts of Painting*, London 1849 (Dover reprint, New York and London 1967), Vol. II, nos. 394, 396–7, pp. 628–31; P.F. Tingry, *The Painter and Varnisher's Guide* ..., 2nd edn., London 1816, pp. 2, 59 (the material is mixed with other resins in this recipe); A.-M. Tripier-Deveaux, *Traité théorique et pratique sur l'art de faire les vernis*, Paris 1845, pp. 27–9. It should be said that benzoin is barely mentioned in sources at this time; it may have featured anonymously in one of the proprietary products available (see Carlyle, 1991, cited in note 19, p. 116) or the artist may have prepared it himself.
28. Townsend, 'Turner's Use of Materials, and Implications for Conservation', cited in note 23, pp. 7–10. For the use of Canada balsam see Carlyle, 1991, cited in note 19, pp. 114–15.
29. For the use of soap see Carlyle, ibid., pp. 157–8.
30. K. B. Anderson and R. E. Winans, 'Nature and Fate of Natural Resins in the Geosphere. 1. Evaluation of Pyrolysis-Gas Chromatography/Mass Spectrometry for the Analysis of Natural Resins and Resinites', *Analytical Chemistry*, 63, 1991, pp. 2901-8.
31. J. MacGee and K. G. Allen, 'Preparation of Methyl Esters from the Saponifiable Fatty Acids in Small Biological Specimens for Gas-Liquid Chromatographic Analysis', *Journal of Chromatography*, 100, 1974, pp. 35-42.
32. A 10 or 20 microlitre aliquot of a 5% methanolic solution of TMTFTH is added to the paint fragment in a 100 microlitre tapered reaction vial. The vial is sealed and heated to 60° Celsius for 5 hours; it is then allowed to stand for 2 hours after centrifugation. A 1 microlitre aliquot is injected onto a quartz HT5 (mixed carboranesiloxane stationary phase) capillary column, with an injection port temperature of 200° Celsius. Slow injection is not required and the chromatogram yields information on both combined and free acids in the form of their methyl esters. The first run of the day should be an aliquot of the methanolic reagent alone to condition both injector and column.
33. The mordant appeared to be proteinaceous and was contaminated by some paint beneath. The result of analysis by GC–MS indicated the presence of egg tempera lipids, mainly from the orange-yellow paint itself. A fragment of reasonably pure mordant showed little more than background lipids by GC–MS and indicates the use of glue. For materials and techniques of early Italian gilding, see D. Bomford, J. Dunkerton, D. Gordon and A. Roy, with contributions from J. Kirby in *Art in the Making: Italian Painting Before 1400*, exhibition catalogue, London 1989/90, pp. 21–4, 43–8.
34. The sample was taken from a relatively thick spot of paint; a cholestadien-7-one component (m/z = 382 (M^+), m/z = 174 (B^+)) derived from cholesterol originally present, which usually disappears with the passage of time, was still just detectable.
35. Both paints from this work were bound with egg tempera; there was some indication that sample 1 might also contain a minor addition of drying oil.
36. Pinkish-cream and olive-green paints were found to contain oil, with no evidence for the presence of egg tempera medium. Sample 3, flesh paint,

contained essentially egg tempera medium, but also some drying oil. These results point to an unusually early use of oil medium for Italy.

37. These results represent further sampling during the course of conservation treatment on this work. Previous media results were reported in R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 16, 1995, pp. 86–7.
38. Both green and yellow paints gave indications of egg tempera medium, but with a little drying oil. There was no suggestion that the oil and tempera were other than in the same paint layer. These results confirm the general conclusions reached in an earlier study reported in J. Mills and R. White, 'Paint Media Analyses', *National Gallery Technical Bulletin*, 13, 1989, pp. 69–71.
39. The red glaze paint of Saint John's cloak (sample 3) was identified as containing partially heat-bodied walnut oil, by GC–MS. Similarly, sample 4 (blue robe) was found to contain heat-bodied linseed oil.
40. In general, the layer structures of the paints sampled from this work were rather complex. FTIR–microscopy and GC–MS of partially separated layers of sample 1, red paint from the Virgin's right sleeve, indicated the presence of a dark underpaint in egg with, possibly, some drying oil too. Above this there appeared to be a red lake paint in drying oil (walnut oil, not heat-bodied). Above this was a resinous layer (mastic resin) and finally a red lake overpaint bound, essentially, by mastic resin. Sample 2 of blue/black water was similarly complex. It was not possible to separate the layers for GC–MS. The result obtained represents an average for both the dark underpaint and blue/black paint layers. FTIR would suggest that there is egg tempera in the dark, blackish underpaint (possibly with a little oil), while a thin reddish-brown isolating layer and a blue paint are in oil medium. A sample of flesh paint from Christ's leg did not appear to have any black underpaint and was found to contain walnut oil, there being no evidence for egg tempera. A sample of the black underpaint itself, from an area of the backcloth where the principal paint layer had flaked away, appeared to contain a mixture of egg tempera and some drying oil. This layer seemed to have undergone shrinkage and exhibited a very coarse craquelure. A reddish-brown *imprimitura* beneath the black underpaint, sampled from an area where it had been exposed as a result of shrinkage of the black paint above, contained walnut oil alone. For a fuller account see Keith and Roy, cited in note 8, pp. 14–15.
41. GC–MS indicated the use of heat-bodied walnut oil in each sample from this work.
42. GC–MS indicated the use of heat-bodied linseed oil in each sample from this work.
43. Brownish-black paint was identified as containing heat-bodied walnut oil, together with abietatriene acids and their pyrolysis products, such as retene and nor-abietatrienes. The latter components point to the inclusion of a softwood pitch or resin tar within the drying oil medium; much as in the case of asphaltum or bitumen, these have contributed to the paint film defects observed. Sample 2, green glaze-like paint, which exhibited some measure of 'reticulation', was found to contain heat-bodied walnut oil with some pine resin. FTIR–microscopy gave no indication that the pigment was 'copper resinate', although in some isolated areas there had been some interaction between the copper pigment and the resinous addition to the drying oil medium. Interestingly, a sample taken from a less reticulated area of the green paint, though based on the same components, appeared to have a somewhat lower proportion of resin present
44. GC–MS gave indications of heat pre-polymerisation in the case of grey paint from the added strip. The cream sky paint contained a little pine resin in addition to the linseed oil.
45. The linseed oil employed as binder for the lime-green paint had been heat-bodied. FTIR–microscopy indicated that a fragment of blue sky paint, inadvertently sampled with the green leaf paint, was bound with drying oil.
46. Gas-chromatographic results for the medium of samples examined earlier were reported in J. Mills and R. White, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 3, 1979, pp. 66–7. Two further fragments were sampled in the current study for examination by FTIR–microscopy. Both contained drying oil as paint binding medium.
47. GC–MS showed that the green paint of the foliage contained heat-bodied walnut oil as binder.
48. Both samples appeared to contain heat pre-polymerised oil; the yellow paint's binding medium appeared to have undergone partial heat-bodying, or was a mixture of bodied and non-bodied oils.
49. The green foliage paint, though based on linseed oil, also contained a little pine and mastic resins, but there was no indication of the use of 'copper resinate' here. The blue sky contained a minor addition of pine resin alone.
50. FTIR–microscopy was used for this examination only.
51. An earlier study, using GC, was reported in Mills and White, 1976, cited in note 17. In view of the use of poppy oil and the presence of linseed oil in the red fold of the robe, it seems likely that the palmitic/stearic ester ratio for the grey paint results from the admixture of poppyseed and linseed oils, rather than from the use of

walnut oil. The red lake paint also contained a little pine resin.

52. In the case of NG 161, a minor addition of pine resin to the linseed oil binder was detected; FTIR–microscopy established that this was not due to contaminating fragments of varnish. This may account for the slightly more transparent quality of the paint in areas of this work.
53. The red paint, bound in pre-polymerised linseed oil essentially, was found to contain both pine and mastic resins in addition. These resins were also present in the medium of the white cuff paint, which consisted principally of heat-bodied poppy oil.
54. In the case of the cream and red paints the walnut oil had been heat-bodied.
55. See Kirby and Roy, 1995, cited in note 22. Of the two ground layers, the lower, darker one is probably a commercial ground prepared with linseed oil; its darker colour is solely due to wax/resin lining of the canvas. The upper, lighter ground was prepared using walnut oil and is likely to be a studio-prepared ground. The white paint of Lady Jane's left sleeve contained walnut oil; there was no evidence for resin within the body of the medium, unlike the rich, 'bodied' black paint of the executioner's coat, bound with heat-bodied linseed oil into which a little mastic resin had been mixed. The paint showed no signs of the usual drying problems that frequently accrue with black paint and GC–MS indicated the absence of bitumen, asphaltum and heavily 'pitched' softwood. The cochineal lake glaze of the brocade dress on the attendant's lap also contained a mixture of heat-bodied linseed oil with the addition of some mastic resin.
56. See Egerton, 1995, cited in note 26. Sample 1 (white impasto) contained a trace of a triterpenoid resin in addition to walnut oil; the source is uncertain, but it is probably a Dipterocarpaceous resin and certainly not from the genus *Pistacia*. Some non-drying fats – probably tallow – were also present. Sample 2 (salmon-pink sunset) proved quite unusual. FTIR–microscopy indicated the presence of some drying oil, but other bands suggested that some form of resin might be present. GC–MS revealed the presence of walnut oil. The drying components did not appear to have suffered any dilution by non-drying oils or fats in this case and the oil had been heat pre-polymerised. Other minor components were also present. Some of these were identified as derived from benzoic acid, methoxy analogues and cinnamic acid isomers; others, although not identified completely, gave spectra which were almost certainly indicative of higher homologues of cinnamic esters. Such components might well be anticipated to result from compounds to be found among resin products from the Styracaceae and, possibly, the Fabaceae. Utilisation of resinous material from the latter botanical subfamily is unlikely, in this instance at least: resins derived from plants of this group, such as *Myroxylon balsamum* (L.) Harms var. *balsamum* (Tolu balsam) and var. *pereira* (Royle) Harms, are brownish in colour and thus probably unsuitable for general use in painting, particularly in a passage of this colour. In fact, the material detected is more likely to derive from *Styrax tonkinensis* (Pierre) Craib ex Hartwich (Siam benzoin), or *Styrax benzoin* Dryander (Sumatra benzoin); of the two, the latter seems more likely in view of its more pronounced content of cinnamic acid and derivative components. Such material would normally be employed in a spirit base. It is not at all likely that a benzoin resin could be incorporated satisfactorily with a drying oil to form a homogeneous medium and, indeed, more than one layer of paint appeared to be sampled. The brown-black shadow paint of the buoy (sample 3) contained heat-bodied walnut oil as principal binder, together with some pine and mastic resins. In the case of the mastic, in addition to the usual moronic acid component, the presence of norolean-18-ene components was quite pronounced and may be the result of tarring. Sample 4, mustard-coloured paint, contained walnut oil, a little pine resin and a triterpenoid resin, probably a dammar.