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Front cover: Veronese, *The Family of Darius before Alexander*; detail of Plate 11, p. 18

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Venice, San Sebastiano: Fig. 8, p. 20
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Analyses of Paint Media

Presented here, in tabular form, are the analytical results for paint media obtained from samples from National Gallery pictures. The information is derived from two principal analytical techniques: a preliminary examination of the paint fragment using a Fourier transform infra-red spectrometer coupled to an infra-red microscope (FTIR–microscopy), followed by a more detailed fingerprint, at the molecular level, using gas chromatography–mass spectrometry (GC–MS). A fuller account of the specific application of infra-red microscopy to actual paint samples as a routine method of analysis may be found within the present volume on pp. 73–84.

For the bulk of the results presented below, the analytical procedures for sample preparation (saponification and methylation) prior to GC–MS analysis remain as reported earlier.[1] However, some of the samples have undergone a new, single-stage and improved method of chemical derivatisation involving the use of m-trifluoromethylphenyl-trimethylammonium hydroxide. The reagent has proved most successful in trials conducted in the National Gallery Scientific Department and has shown itself amenable to the rapid and quantitative derivatisation of chemically sensitive terpenoid components found in natural resins. Further details will be published with the tabular paint media results in a future *National Gallery Technical Bulletin*.

Analyses of Paint Media

RAYMOND WHITE AND JENNIFER PILC

Artist	Picture	Date
Masaccio	*The Virgin and Child* NG 3046	1426
Follower of Fra Angelico	*The Annunciation* NG 1406	late 1450s?
Butinone	*The Adoration of the Shepherds* NG 3336	1480
David Ghirlandaio	*The Virgin and Child with Saint John* NG 2502	1480s
Domenico Ghirlandaio	*The Virgin and Child* NG 3937	1480s
Gerolamo da Vicenza	*The Death and Assumption of the Virgin* NG 3077	1488
Michelangelo	*Madonna and Child with Saint John and Angels ('The Manchester Madonna')* NG 809	*c.*1497
	The Entombment NG 790	1500/1
Francesco Morone	*The Virgin and Child* NG 285	*c.*1500
Garofalo	*An Allegory of Love* NG 1362	early 1500s
	The Holy Family with Saints John the Baptist, Elizabeth, Zacharias and (?)Francis NG 170	early 1500s
Andrea del Sarto	*The Madonna and Child with Saints Elizabeth and John the Baptist* NG 17	early 1500s
Raphael	*The Procession to Calvary* NG 2919	*c.*1504
Botticelli	*Four Scenes from the Early Life of Saint Zenobius* NG 3918	*c.*1505
	Three Miracles of Saint Zenobius NG 3919	*c.*1505

Sample	Medium	P/S	Oil type	Note
1. Lilac paint of angel's garment, left-hand edge	Egg			
2. Light grey of moulding of plinth to throne	Egg			
1. Red of garden wall	Egg			
2. Grey paint of arch	Egg			
3. Pale blue of Virgin's robe	Egg			
4. Pink fold of angel's dress	Egg			
1. Blue paint of sky	Egg			1
1. Red glaze paint of carpet, bottom left-hand edge	Oil	1.3	Linseed	2
2. Red underpaint of sample 1	Egg			
3. Cool flesh paint of Saint John's left arm	Egg			
4. Virgin's blue dress, left shoulder	Egg			
5. Green trees above rock	Oil	1.5	Linseed	
1. Matt flesh paint of Christ's right hand	Egg			3
2. Discoloured principal layer of blue robe of Virgin	Oil	3.2	Walnut	
3. Ochre-yellow underpaint of sleeve of Virgin's robe	Egg			
4. Yellow cushion, left-hand edge	Egg			
5. Thick dark green paint of somewhat raised diamond pattern of rug	Oil	3.4	Walnut	
6. Rich red paint of rug, bottom edge of picture	Egg + oil	3.2	Walnut	
1. Blue sky to left of aureole	Egg + trace of oil?			4
2. Grey of moulding at base of Virgin's bier	Oil	3.0	Walnut	
3. Grey layer, over blue sky, to left of aureole	Egg			
1. Red lake paint of fold of the Madonna's red dress; below Christ's right instep	Egg + oil		Walnut	5
2. Greyish-blue sky, containing azurite; sampled from top edge	Egg			
3. Black hatching (undermodelling) of the Madonna's cloak; somewhat richer paint of fold	Egg			
4. Glaze or *imprimitura* on exposed gesso, left-hand unfinished figure	Background lipids			
5. Brownish-green grass, foreground	Egg + a little oil			
1. Discoloured (dark brown?) paint of Saint Joseph's cloak	Oil	1.3	Linseed	5
2. Cool-toned flesh paint of Christ's upper arm	Oil	1.4	Linseed	
3. Warm-toned flesh paint of Saint John's right calf	Oil	1.2	Linseed	
4. White *imprimitura* of Saint John's midriff	Egg			
5. Pale blue sky, beneath strip of old varnish on top edge, adjacent to crack	Oil	1.4	Linseed	
1. Green foliage in background, right-hand edge	Oil + trace resin	2.8	Walnut	6
2. Red of curtain	Egg			
1. White cloth	Oil	2.4	Walnut	7
2. Red of drapery, right-hand side	Oil	2.3	Walnut	
3. Green of foliage, centre (underpaint)	Oil	2.1	Walnut	
4. Brown glaze over yellow drape	Oil + pitch	2.2	Walnut	
5. Blue paint	Oil			
6. Green paint of foliage (leaves of trees in mid-ground)	Oil + resin	2.3	Walnut	
1. Brown-black outline paint of left-hand female saint's headdress	Oil + pitch		Walnut	
2. Transparent green paint of cloak from left-hand male saint	Oil + resin		Walnut	
3. Red glaze paint of shadow in fold of Virgin's dress	Oil		Walnut	
2. Yellow drapery of Saint Elizabeth	Oil	3.1	Walnut	8
3. Blue paint of sky, right-hand corner	Unsatisfactory			
4. Yellow paint from knee of Saint Elizabeth	Oil	3.2	Walnut	
1. Darker blue paint of distant hill, left-hand edge	Egg			9
2. Deep brownish red of fold of drapery, fifth figure from left	Egg			
3. Green dress, left-hand edge	Egg + some oil	3.0	Walnut	
4. Transparent dark green of left arm-band, figure on horse	Oil + trace of resin	2.9	Walnut	
1. Blue sky between buildings	Egg			10
2. Green carpet, foreground	Egg + a little oil	2.3	Walnut	
3. White paint of architrave	Egg			
1. Blue sky between buildings	Egg			
2. Pink glaze of man's cloak	Egg + some oil	2.5		
3. Orange-red glaze of man's garment	Egg + some oil	2.4		
4. White paint of highlight on robe of figure in central group	Egg			
5. Bright blue of garment of figure in central group	Egg			

Artist	Picture	Date
Cesare da Sesto	*Salome* NG 2485	*c.*1510
Altobello Melone	*Christ carrying his Cross* NG 6546	*c.*1516–18
Giampietrino	*Christ carrying his Cross* NG 3097	1520–50
Dosso Dossi	*The Adoration of the Kings* NG 3924	1530s
Caravaggio	*The Supper at Emmaus* NG 172	1602
	Salome receives the Head of Saint John the Baptist NG 6389	1607–10
Domenichino and Assistant(s)	*Apollo pursuing Daphne* NG 6287	*c.*1616–18
	Apollo killing the Cyclops NG 6290	*c.*1616–18
Anonymous **Italian** Painter	*The Adoration of the Shepherds* NG 232	1640s?
Master of the Saint Bartholomew Altarpiece	*Saints Peter and Dorothy* NG 707	*c.*1500
Lucas Cranach the Elder	*Johann the Steadfast* NG 6538	1509
	Johann Friedrich the Magnanimous NG 6539	1509
Hans Holbein the Younger	*A Lady with a Squirrel and a Starling* NG 6540	*c.*1527
	Jean de Dinteville and Georges de Selve ('The Ambassadors') NG 1314	1533
Johann Rottenhammer	*The Coronation of the Virgin* NG 6481	1596–1606
Jan van der Heyden	*A View in Cologne* NG 866	1660s
	View of the Westerkerk, Amsterdam NG 6526	1660s

Sample	Medium	P/S	Oil type	Note
1. Green paint of tablecloth	Oil	3.3	Walnut	
2. Brownish green of sash	Oil	3.0	Walnut	
1. Red lake of Christ's robe, lower left-hand edge	Oil	2.3	Walnut	
2. Black paint of helmet of figure behind Christ, left-hand edge	Oil	2.4	Walnut	
1. Brown glaze craquelured toning, shadow beneath Christ's chin	Oil + resin	2.8	Walnut	11
2. Textured cool flesh paint, Christ's right-hand shoulder	Oil	3.0	Walnut	
3. Black background, above angle of cross	Oil	2.8	Walnut	
1. Blue sky, top edge	Oil	3.2	Walnut	
2. Grey paint of earth, bottom edge	Oil	3.3	Walnut	
1. White paint of highlight from tablecloth, centre, immediately beneath green leaf	Egg + some oil	2.9	Walnut	**12**
2. White of tablecloth, principal layer sampled from same area and after removal of sample 1	Oil	2.6	Walnut	
3. Green paint of Cleophas's sleeve, from elbow	Oil	3.1	Walnut	
4. Dark brownish-black background, mid-left-hand edge	Oil	2.8	Walnut	
1. White highlight of Salome's shawl	Oil + some egg	2.7	Walnut	
2. Lower white layer from same area	Oil	3.2	Walnut	
1. Foliage of tree: darker, richer green paint	Fresco			**13**
2. Underpaint of paler green foliage	Fresco			
1. Impasto of pink flesh paint from Apollo's neck	Fresco			
2. Darker flesh paint of Apollo's thigh	Fresco			
1. Brown paint of column, left	Oil	1.5	Linseed	14
2. Brownish flesh paint, face of right-hand woman	Oil	1.7	Linseed	
3. Dark, purplish-brown paint, to left of fowl's legs	Oil	1.5	Linseed	
Obverse				15
1. Green brocade	Oil			
2. White tile, right-hand edge	Oil			
Reverse				
3. White sky	Oil			
4. Green brocade, right-hand side	Oil			
5. Red glaze paint of Saint John's robe	Oil			
6. Red marbling, right-hand edge	Probably oil			
1. Green paint, background	Oil	1.7	Linseed	**16**
2. Black of robe, bottom edge	Oil	1.6	Linseed	
1. Green paint of sleeve, bottom edge	Oil	1.8	Linseed	
2. Rich red pattern on sleeve, bottom edge	Oil + resin	1.2	Linseed	
1. Turquoise-blue background, right-hand side	Oil	1.8	Linseed	
2. Green leaf, right-hand side	Oil + resin	1.6	Linseed	
3. Grey of shadow of drapery on shoulder, left-hand side	Oil	1.7	Linseed	
1. Grey *imprimitura*, beneath white of marble floor	Oil	1.7	Linseed	**17**
2. Red lake glaze paint of left-hand figure's left sleeve	Oil + resin	1.4	Linseed	
3. Deeper, translucent green of curtain	Oil + resin	1.5	Linseed	
4. Flesh paint of hand, left-hand figure	Oil	1.6	Linseed	
1. Pale yellow of aureole, top edge	Oil	1.3	Linseed	
2. Dark, bluish-green cloak of angel, near right-hand top edge	Oil	1.3	Linseed	
3. Red paint of lower left-hand figure's crimson mantle	Oil	1.5	Linseed	
1. Blue sky, top edge	Oil	1.3	Linseed	**18**
2. Greyish white of masonry	Oil	1.7	Linseed	
1. Yellow highlight of leaves, tree to right of church	Oil	3.2	Walnut	
2. Greenish-brown leaves, central tree	Oil + resin	1.4	Linseed	
3. Blue sky, lower layer	Oil	2.7	Walnut	
4. Green of reflection of door in water	Oil	1.8	Linseed	

Artist	Picture	Date
French or English School(?)	*'The Wilton Diptych'* NG 4451	1395–9
Nicolas Poussin	*Cephalus and Aurora* NG 65	*c.*1630–3
	The Triumph of Pan NG 6477	1636
	The Adoration of the Shepherds NG 6277	*c.*1637
Eustache Le Sueur	*Saint Paul preaching at Ephesus* NG 6299	*c.*1649
Maurice-Quentin de La Tour	*Henry Dawkins* NG 5118	*c.*1750
Vincent van Gogh	*Sunflowers* NG 3863	1888
Henri Matisse	*Portrait of Greta Moll* NG 6450	1908
Anthony van Dyck	*Lord John Stuart and his Brother Lord Bernard Stuart* NG 6518	1639
Sir Joshua Reynolds	*Captain Robert Orme* NG 681	1756
Johann Zoffany	*Mrs Oswald* NG 4931	early 1760s
Richard Wilson	*A View of Holt Bridge on the River Dee* NG 6196	*c.*1762
	The Valley of the Dee, with Chester in the Distance NG 6197	*c.*1762
George Stubbs	*The Milbanke and Melbourne Families* NG 6429	*c.*1769
Thomas Gainsborough	*Mrs Siddons* NG 683	*c.*1785
Sir Thomas Lawrence	*Queen Charlotte* NG 4257	1789
J.M.W. Turner	*Ulysses deriding Polyphemus* NG 508	*c.*1829

Sample	Medium	P/S	Oil type	Note
Left-hand panel, reverse (Shield with Arms of Edward the Confessor, impaled with those of the Kingdom).				19
1. Red glaze, over gold of lion motif on shield	Egg			
2. Section of fleur-de-lis motif of shield	Egg			
3. Mordant from fleur-de-lis motif	Egg			
4. Black paint from outline of lion	Egg			
Right-hand panel, obverse (Virgin and Child with eleven Angels)				
5. White paint of angel's wing-tip	Egg			
6. Greenish-black foliage, bottom edge	Egg			
7. Intense blue paint from right-hand edge of angel's gown	Egg			
Left-hand panel, obverse (Richard II, Saints John the Baptist, Edward the Confessor and Edmund)				
8. Light green paint from robe of Saint Edmund	Egg			
Right-hand panel, reverse (White hart, lodged)				
9. Greenish-black foliage of background, by hart and near frame's edge	Egg			
1. Brownish-red sheet	Oil	1.7	Linseed	20
2. Grey sky	Oil	2.0	Linseed	
1. Blue sky, top edge	Oil	1.7	Linseed	
2. Olive-green foliage, top edge	Oil	1.3	Linseed	
1. Blue robe, right-hand edge	Oil	1.7	Linseed	
2. Brownish red of cow, right-hand edge	Oil	1.5	Linseed	
1. Blue drapery of figure behind Saint Paul	Oil	1.4	Linseed	21
2. Greyish-blue paint of drapery from figure behind kneeling man	Oil	1.5	Linseed	
1. Red lake paint of jacket, from turnover edge	Gum			22
2. Faded red lake of jacket	Gum			
3. White paint of cuff	Gum, probably			
4. Dark background	Gum			
5. Size on blue paper support	Glue			
1. Pale yellow impasto of background	Oil + trace of beeswax	2.8	Walnut	23
2. Exposed ground from damage, top left-hand corner	Oil	1.5	Linseed	
3. Brownish-yellow impasto of top sunflower	Oil + non-drying oil/fat + trace of beeswax	2.0	Linseed	
1. Blue paint, beneath ochre wash, top edge	Oil	4.8	Poppy	
2. Grey ground, top, left-hand turnover	Oil	1.4	Linseed	
1. Brownish-black paint of background, left-hand edge	Oil + birch pitch	1.8	Linseed	24
2. Yellow brocade wrap over upper arm of left-hand figure	Oil + birch pitch	2.3	Walnut	
3. Red-brown lining of drape, lower arm of left-hand figure	Oil	1.8	Linseed	
4. White highlight stroke of right-hand figure's grey silk sleeve	Oil	2.5	Walnut	
5. Black shadow in fold of silk jacket of right-hand figure	Oil + birch pitch	1.4	Linseed	
6. Blue paint of cloak, right-hand figure	Oil	1.7	Linseed	
1. White outline of florets in background foliage, right-hand side	Oil	5.3	Poppy	25
2. Red background, near sample 1	Oil	1.3	Linseed	
3. Blue paint from edge of coat, near thigh	Oil	1.3	Linseed	
4. Green foliage, right-hand side, beneath rebate of frame	Oil + resin	1.7	Linseed	
1. White highlight of frill on hat	Oil	4.8	Poppy	
2. Caramel brown of distant hill, to left of hat	Oil	1.8	Linseed	
1. Heavily 'crocodiled', brownish green of tree trunk	Oil			26
2. Rich dark green/black of leaves	Oil + larch resin	1.7	Linseed	
3. Pale blue sky, between clouds, upper section	Oil	1.8	Linseed	
1. Heavily 'crocodiled', blue-green of water, just below bridge	Oil + some resin	3.0	Walnut	
2. White paint of clouds, non-'crocodiled'	Oil	2.6	Walnut	
1. White cloud, top edge	Oil	3.3	Walnut	
2. Dark green of bough of tree	Oil	1.7	Linseed	
1. Black plume of hat	Oil	1.7	Linseed	
2. Red glaze of dress	Oil	1.3	Linseed	
3. White highlight of dress	Oil	5.7	Poppy	
1. White impasto on fringe of outer skirt, right-hand side	Oil	1.5	Linseed	
2. Black of right-hand drape, from edge	Oil	1.6	Linseed	
3. Red paint of brown foliage	Oil	1.8	Linseed	
1. Red from right-hand edge of ships	Oil + some mastic	1.3	Linseed	27
2. Yellow highlight of wave, bottom edge	Oil + some mastic	1.4	Linseed	

Notes to the Table

1. Examination was carried out by means of a Nicolet Fourier Transform infra-red spectrometer coupled to a Nic-Plan infra-red microscope (FTIR-microscopy) only.
2. Samples of cool flesh paint, blue of the Virgin's dress and red underpaint of the carpet were all identified as containing egg tempera by GC–MS. A rich red glaze paint over the red underpaint was found to be in linseed oil medium, as was the green foliage paint from trees above Christ's head.
3. GC–MS and FTIR indicated the use of egg tempera binder in samples of flesh paint, yellow underpaint of the Virgin's sleeve and a yellow paint from a cushion. Egg tempera, with drying oil mixed, was determined in a richer red paint from the rug, while walnut oil alone was identified by GC–MS in areas of discoloured blue of the Virgin's robe and a thick dark green paint of a raised pattern on the rug. The latter paint showed evidence of having undergone partial heat-bodying, but no resin could be detected.
4. Sample 1, taken from blue sky paint, appeared to be essentially egg tempera. However, an azelaic/palmitic ester (A/P) ratio of 0.35 seemed to suggest that some oil – probably walnut oil – might be mixed with the egg tempera.
   A sample of grey paint appeared to contain walnut oil only.
   Sample 3, a grey, unpigmented layer, possibly representing the remnants of a varnish, was identified as glair (egg white) by infra-red analysis. GC–MS confirmed low levels of non-drying lipids as might be expected from such proteinaceous material. Further confirmation was by staining with amido black.
5. From NG 790 samples of flesh paint, scarlet drapery and undermodelling had been examined by GC alone, some time ago. The results have been reported.[1] The present set of samples were examined by FTIR-microscopy and GC–MS.
   In the case of NG 809, a surface scraping of exposed gesso from an unfinished area of the painting (sample 4) was examined by GC–MS. Background levels of non-drying fats were all that could be detected.
6. Both samples were examined by FTIR-microscopy, but only sample 1 was large enough for GC–MS investigation.
7. White and red paints were identified as containing walnut oil. A cross-section sample of blue sky was examined by FTIR-microscopy and seemed to contain drying oil. Two samples of green paint of foliage were investigated, consisting of a green underpaint and a green transparent glaze paint above. The underpaint was based on partially heat-bodied walnut oil and appeared not to contain resin. The upper, more transparent green consisted of heat-bodied walnut oil with some pine resin (dehydroabietic and 7-oxodehydroabietic acids were detected). FTIR-microscopy suggested the presence of 'copper resinate' in this layer.
   Sample 4 consisted of a brown glaze over a yellow drape. Walnut oil was the principal component, but GC–MS revealed evidence of dehydroabietic and 7-oxodehydroabietic acids, together with some retene (M^+ m/z = 234, B^+ m/z = 219). This would seem to indicate the inclusion of some softwood pitch within the drying oil medium.[2]
   These additional results for NG 170 supplement those reported earlier (see References, note 1).
   Sample 1 exhibited signs of a heavy craquelure and the paint binder proved to be walnut oil, while the presence of dehydroabietic, 7-oxodehydroabietic acids and retene suggests the inclusion of a softwood pitch.
   Transparent green paint, sample 2, was based on a walnut oil medium and some 7-oxodehydroabietic acid, suggesting an addition of resin, probably pine resin, to the medium.
   Sample 3, a red glaze paint, also proved to be walnut oil, which had been partially heat-bodied.[3]
8. The analysis of blue paint, sample 2, was unsatisfactory owing to loss during derivatisation.
9. A blue paint sample from a distant hill, identified as containing an egg medium by GC–MS, was somewhat leaner in binder than the other samples examined.
   Sample 3, from a green dress, contained predominantly egg tempera, but with a little drying oil. The palmitate/stearate ester ratio of 3.0 would point to walnut being the source of the drying oil. The medium of a rich dark green area of an arm-band on one of the mounted figures appeared to be based on walnut oil, together with a little pine resin (some dehydroabietic and 7-oxodehydroabietic acids present). FTIR-microscopy did not indicate the use of 'copper resinate' pigment as such, but rather verdigris.
10. In NG 3918, the paint medium of samples 1 and 3 seemed to be based on egg tempera from both FTIR and GC–MS evidence. There appeared to be no addition of either diterpenoid or triterpenoid resins. Traces of wax, from previous conservation treatment, was identified by FTIR-microscopy and was removed prior to GC–MS. Sample 2, when examined by FTIR, also appeared to contain mainly egg tempera, but possibly with a little oil incorporated in the medium. GC–MS indicated the presence of egg tempera lipids and, in addition, a methyl azelate content (approximately 35% of the amount of methyl palmitate), which would seem to confirm the presence of a little drying oil.

Some remnants of an old varnish, which were well 'keyed-in' to the white paint of sample 3, were analysed by GC–MS and found to consist of heat pre-polymerised linseed oil with pine resin (7-oxodehydroabietic acid) and mastic resin (moronic acid, molecular ion (M^+) m/z = 468, base peak (B^+) m/z = 189).

Pure egg tempera was found in two shades of blue paint and in a white highlight from NG 3919. Sample 2, a pink glaze paint, was shown by FTIR-microscopy to contain mainly egg tempera. GC–MS confirmed the presence of egg tempera overall, but an azelaic/palmitic ester ratio of 0.4 indicated the use of some drying oil component as well; perhaps this was intended to enhance the transparency of this paint layer. No resin was detected in this sample. A similar result was obtained for an orange glaze paint, sample 3.

11. There was no evidence of a softwood pitch in sample 1, as no retene or similar components were detected. 7-oxodehydroabietic acid suggested some pine resin. The walnut oil did not appear to have undergone heat pre-polymerisation. The textured flesh paint (sample 2) appeared to have retained the shape of individual, fine brushstrokes. The walnut oil used in this instance would seem to have been heat-bodied.
12. The paint medium of the white highlight on the tablecloth was identified as mainly egg tempera, but with some drying oil, using GC–MS. A fragment of highlight was given a preliminary examination by FTIR-IR microscopy and the absorption bands suggested the presence of oil medium. The spectrum did contain very minor bands, which were likely to be from an input of proteinaceous medium, but it was not possible to give an unambiguous assignment. Further infra-red work on other fragments of the white highlight paint showed some areas with weaker oil bands and stronger, clearer protein bands, with others exhibiting the opposite pattern. On balance, the combined GC–MS and FTIR evidence would suggest that the white highlight paint, above the principal layer of white paint of the tablecloth, consisted of a mixture of, principally, egg tempera with an addition of drying oil. The chromatogram revealed a palmitic ester/stearic ester ratio little changed from that which might be expected of egg medium itself, though with an augmented azelaic acid component confirming the presence of some drying oil. As a result one may postulate that the oil addition is probably from walnut, since linseed would have been expected to lower the P/S ratio somewhat.

    By contrast, in the *principal* white paint layer of the tablecloth, sampled immediately below the material removed for sample 1, oil alone was established by FTIR analysis and the results from GC–MS. The latter technique revealed the use of walnut oil, which had undergone heat pre-polymerisation. Care was taken to sample and discard material well into this layer, to prevent contamination from paint of the highlight itself. Sample 4 of dark, brownish-black background was found to be based on a medium of partially heat-bodied walnut oil, using GC–MS. The presence of oil, alone, was confirmed by FTIR examination.

    In NG 6389, the medium of a white highlight of Salome's shawl was based on drying oil. Although no clearly discernible protein bands were resolved in the FTIR spectrum, GC–MS indicated the inclusion of a small amount of non-drying egg fats, which have slightly diluted the drying lipids. Some ninhydrin-positive material (protein) was present. The drying oil component was identified as walnut oil which gave indications of having undergone partial heat pre-polymerisation.

    Walnut oil (without signs of heat pre-polymerisation) was detected by GC in the white paint below. No resin was found and there was no evidence for egg tempera by FTIR or GC–MS.
13. These two Domenichino wall paintings appear to be in true fresco, essentially. There seems to be some contamination from a beeswax conservation adhesive. Certainly there was no evidence of any oil-based or resinous binder within the areas sampled, using GC–MS. FTIR-microscopy gave little indication of any organic-based binding agent within the samples, save for the presence of a little protein in sample 1 of NG 6287 and sample 1 of 6290. This most probably represents residues of a glue facing-adhesive.
14. The paints examined in this study appeared to be rather leanly bound with oil medium.
15. Only FTIR-microscopy was carried out on these samples.
16. Sample 2 (NG 6538) of black paint from the sitter's robe contained linseed oil, as for sample 1. GC–MS indicated the presence of very minor diterpenoids attributable to pine resin. However, these were so minor that they were thought to represent possible residual traces of old varnish. Indeed, examination of a fragment of the paint sample by FTIR-microscopy did reveal traces of varnish contamination.

    In NG 6539, green paint was identified as containing linseed oil medium only, by means of GC–MS. A rich red paint from the pattern of a sleeve was shown to contain linseed oil together with some pine resin. Here, unlike the black paint mentioned above, FTIR examination indicated that the resin was incorporated within the body of the paint and did not originate from the presence of residual varnish on the surface.

17. Using FTIR-microscopy and GC–MS, grey underpaint, beneath white paint of the patterned marble floor in NG 1314, was identified as being rather leanly bound with linseed oil.
A richer red glaze paint from the left-hand figure's left sleeve was shown also to have been executed in linseed oil. In this case, GC–MS showed the medium to be partially heat pre-polymerised and the presence of pine resin was suggested by detection of some dehydroabietic and 7-oxodehydroabietic acid components in the paint medium.
Sample 3, the deep, translucent green of the background curtain was identified as containing a little pine resin in with the principal component, linseed oil, which did not appear to have been heat-bodied. Despite the suggestion, from its overall appearance, that this green paint might contain 'copper resinate', FTIR analysis gave no support for this assumption.
In NG 6540,[4] sample 2 (green paint of a leaf) was established as being bound with linseed oil, by GC–MS. In addition, dehydroabietic and a minor amount of 7-oxodehydroabietic acids pointed to the inclusion of some pine resin. Moreover, FTIR-microscopy would seem to indicate that the sample consisted of a deeper transparent green layer over a more dense, but less transparent, yellow layer. Comparison of infra-red spectra from these two layers pointed to a preponderance of oil in the lower, yellowish layer, though it did seem to contain bands associated with a resin input. The upper layer of transparent green paint contained quite strong resin carboxylate bands and would suggest the inclusion of some copper resinate pigment.
Greyish paint (sample 3) was rather leanly bound with linseed oil.
18. Samples from some areas of NG 6526 deserve some additional comment.
The paint of sample 1 consisted of discrete 'blobs' of paint, which seem to have shown no tendency to run or to shrink on drying. Heat-bodied walnut oil was identified as the binding agent. A bodied oil of this kind would be expected to lend itself to the retention of the original shape of the brush stroke. Moreover, given the lower scope for peroxy and alkoxy linkage-formation in drying oil (a proportion of cross-linking having already been induced by carbon-carbon bond formation during the bodying process) such a paint should exhibit less tendency to shrinkage, during drying and ageing.
Linseed oil was established as the medium in sample 2. GC–MS provided some evidence for the presence of 7-oxodehydroabietic acid within the medium and so we may conclude that some pine resin has been incorporated. However, FTIR did not give any indication that the green pigment was likely to be that known as 'copper resinate'.
19. Some paint samples were examined earlier from the reverse of NG 4451.[5]
20. Heat-bodied linseed oil appeared to have been used as binding agent in both samples of NG 6477, but non-heat-bodied linseed oil was found in the other samples. Although sample 2 (grey paint) of NG 65 had a P/S ratio of 2.0, this probably indicates the use of linseed oil once again.
21. Sample 2 contained a somewhat grey ultramarine and was bound more leanly than sample 1. Linseed oil was the medium in each case.
22. All samples, except for the paper size, sample 5, gave an indication of background levels of glycerides and other lipids. FTIR-microscopy indicated the presence of a polysaccharide binding agent and this was confirmed by positive results from an application of the furfural test.
23. A trace of beeswax was detected in the extract from a fragment of sample 1, but it would seem to be a very minor component. GC–MS of the residues, after they had undergone saponification and methylation, produced a chromatogram which suggested the use of a drying oil. The palmitic/stearic ester ratio was 2.8 and would seem to indicate the use of walnut oil. The azelaic ester component is a little deficient, probably as a result of limited ageing and the thickness of the paint. Certainly no protein (such as egg tempera) was present. Little in the way of higher methyl esters remained and so it seems unlikely that the relative quantities of azelaic, palmitic and stearic esters have been significantly distorted by the presence of a trace of beeswax. There was no history of treatment of the painting with wax-based lining adhesives. Waxes are known to have been added in commercially prepared paints to act as plasticisers and anti-settling agents at this period. This may be the case here.
An area of exposed ground was sampled and found to be bound, rather leanly, with linseed oil. No beeswax was detected here.
Sample 3, a rich brownish impasto, proved to contain a little beeswax. GC–MS of the residues of a benzene-extracted fragment revealed the presence of a drying oil binder. Here, however, the methyl azelate/palmitate ratio was only 0.7 and the palmitic/stearic ester ratio was 2.0. On balance, the depressed methyl azelate component, coupled with a P/S ratio intermediate between linseed and walnut oils, can be most plausibly interpreted as suggesting the presence of linseed oil medium containing some non-drying oil, presumably as a plasticiser. In view of the low level of higher fatty acids in these residues, it seems unlikely that sufficient beeswax remained to distort the P/S ester ratio to any significant extent. The non-drying lipids

cannot result from an addition of egg tempera as no protein was detected by an application of the ninhydrin test.

For media analyses carried out on NG 3861, the reader may refer to an earlier article.[6]

24. Sample 1, consisting of brownish-black background paint was from an area showing some slight signs of shrinkage. Linseed oil was detected as the principal component of the paint medium. There was no evidence for heat pre-polymerisation. In addition, there were small amounts of components in the triterpenoid region of the chromatogram; the main component was identified as betulinic acid (as its methyl ester) by mass-spectrometry.

These results were supported by FTIR-microscopy. The yellow brocade was bound with walnut oil and some betulinic acid was identified, once again. The latter is not a usual component of diterpenoid and triterpenoid resins. Its precursor alcohol, betulin, occurs in substantial amounts within the bark of species of birch tree, particularly *Betula alba*. Thus this alcohol is an important component of bistre and pitch produced by the controlled pyrolysis. Betulinic acid is the natural oxidation product of the betulin and its presence in an old exposed film, such as in this case, would strongly indicate the toning of the layer with birch bark pitch or bistre. Sample 5, based on linseed oil – this time heat-bodied – also contained betulinic acid.

White paint of a highlight on a satin sleeve contained only walnut oil; a brownish-red paint of a drape contained linseed oil.

25. Red paint, sample 2, suggested the use of partially heat-bodied oil, from the reduced azelaic/suberic ester ratio.

Paint from green foliage (sample 4) was shown to contain heat-bodied linseed oil by GC–MS as well as some pine resin, in view of the moderate amounts of dehydroabietic and dehydroabietic esters. There was no indication from the FTIR examination that this resin content represented the presence of 'copper resinate' pigment.

26. Sample 1, from NG 6196, was examined by FTIR-microscopy only, by virtue of its limited size.

Sample 2 was from an area that exhibited partial 'crocodiling' of the paint and was examined by GC–MS. There was evidence for the use of a pre-polymerised linseed oil paint medium. In addition, identification of larixol labdanoids gave clear evidence of the incorporation of Venetian turpentine (Larch resin) with the oil.[7]

In contrast a sample of blue sky (sample 3) was found to be bound by heat pre-polymerised linseed oil.

In NG 6197, blue-green paint of the river was sampled from an area exhibiting pronounced shrinkage. Walnut oil was identified, together with some pine resin. White paint of some clouds, which exhibited no paint defects, appeared to contain a heat-bodied walnut oil.

27. FTIR suggested the presence of some resin, as well as drying oil in samples 1 and 2. The linseed oil in the red lake paint appeared to have been partially heat-bodied, with an azelaic/suberic ester ratio of 5.4. Moronic and oleanonic esters in the chromatogram pointed to the inclusion of some mastic resin. Similar results obtain for sample 2, except there was no evidence of heat pre-polymerisation of the oil in this case.

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