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Analyses of Paint Media

John Mills and Raymond White

These paint media analyses were effected during a period in which samples were sometimes examined by gas-chromatography – mass-spectrometry as well as by gas-chromatography alone. Generally this was only done if the chromatogram suggested the presence of components additional to those from oil, but after it was found that resin components could sometimes be detected by mass-spectrometry even when present in amounts insufficient to yield a visible peak on the gas-chromatogram [1], we aimed to look at all important samples by this means if possible. This was not done for all the samples in the Table however so absence of resin may simply mean that it was not looked for as a trace component.

Notes to the Table

1. The samples from this painting by Duccio were low in lipid material and undoubtedly were painted in egg tempera. However, the brown sample showed a somewhat higher azelate peak than would be expected from egg alone. It is possible that the rather lean original paint had absorbed some oil from an old oil varnish.

2. This is an unusually high ratio for walnut oil, which nonetheless probably still lies within the limits of statistically possible bounds. With the higher P/S (palmitate/stearate) ratios the margin of error in measuring them becomes wider. Small errors in measuring the area of the small stearate peak have a large effect on the ratio.

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Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Duccio	The Annunciation No.1139	1308 – 11	1. Blue sky, top	Egg			1
			2. Brown floor	Egg			
			3. Gilding + bole	Egg			
Cima	The Incredulity of S. Thomas No.816	1502 – 4	1. Red robe of S. Thomas	Oil	1.5	Linseed	
			2. Green robe, R.H. side	Oil	1.8	Linseed	
			3. White tile	Oil	1.6	Linseed	
			4. Brown ceiling	Oil	1.4	Linseed	
Busati	The Entombment No.3084	c.1510 (?)	1. Blue sky	Oil	3.0	Walnut	2
			2. Green dress	Oil	3.4	Walnut	
			3. Red of S. John's robe	Oil	2.7	Walnut	
			4. White of Christ's loincloth	Oil	4.3	Walnut	
Pontormo	Joseph in Egypt No.1131	c.1515	1. Dark grey steps, L.H. corner	Oil	1.7	Linseed	
			2. Light grey, bottom	Oil	2.0	Linseed	
			3. Deep green curtain, top	Oil	2.1	Linseed	
			4. Blue sky, top edge	Oil	1.9	Linseed	
			5. Orange strip, L.H. side	Oil	1.5	Linseed	
Sassoferrato	The Virgin in Prayer No.200	1640s (?)	1. Ground	Oil	1.6	Linseed	
			2. White	Oil	1.5	Linseed	
			3. Blue robe	Oil	1.8	Linseed	
Salvator Rosa	Landscape with Mercury and the Dishonest Woodman No.84	1650s (?)	1. White cloud, L.H. edge	Oil	1.8	Linseed	
			2. Green highlight	Oil	1.7	Linseed	

continued overleaf

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Veronese	Allegory of Love, I No.1318	1570s(?)	1. White sheet	Oil	1.9	Linseed	3
			2. Green leaf	Oil	1.8	Linseed	
	Allegory of Love, III No.1325	1570s (?)	1. White sheet	Oil	2.7	Walnut	
			2. Pale yellow robe	Oil	2.9	Walnut	
			3. Red curtain, R.H. side	Oil	1.5	Linseed	
			4. Deep green sash	Oil	1.8	Linseed	
			5. Browned green of textile	Oil	1.7	Linseed	
	Allegory of Love, IV No.1326	1570s (?)	1. Bright green glaze of man's tunic	Oil + resin	1.8	Linseed	
			2. White dog	Oil	2.0	Linseed	
			3. Bright yellow cloak	Oil	1.9	Linseed	
			4. Deep orange sphere	Oil	1.5	Linseed	
			5. Red glaze, R.H. side	Oil	1.6	Linseed	
6. Palest yellow			Oil	2.6	Walnut		
Canaletto	Venice: The Feastday of S. Roch No.937	c.1735	1. Ground	Oil	1.8	Linseed	4
			2. White impasto	Oil	2.0	Linseed	
			3. Blue-white sky	Oil	2.4	?	
			4. Red robe	Oil	2.0	Linseed	
			5. Beige, top of awning	Oil	2.3	?	
Follower of Campin (see p.21)	The Death of the Virgin No.658	Early 16th cent. (?)	1. Pale yellow tile	Oil	1.9	Linseed	
			2. Red glaze, R.H. side	Oil	1.7	Linseed	
			3. Green robe	Oil	2.1	Linseed	
Aldorfer	Christ taking Leave of His Mother No.6463	1520	1. Blue sky	Oil	1.9	Linseed	5
			2. Black, bottom R.H. side	Oil + resin	1.6	Linseed	
			3. Green, bottom edge	Oil + resin	1.7	Linseed	
			4. Green, top	Oil + resin	1.8	Linseed	
Rubens	Samson and Delilah No.6461	c.1609	1. Yellow flame, L.H. edge	Oil	1.5	Linseed	6
			2. Purple curtain, top L.H. corner	Oil	1.4	Linseed	
			3. White, old woman's headdress	Oil + resin	1.7	Linseed	
			4. Brown, carpet stripe	Oil + resin	1.5	Linseed	
			5. Greenish glaze, old woman's robe	Oil	1.8	Linseed	
Cuyp	A Hilly River Landscape No.53	c.1655 – 60	1. Blue sky, top edge	Oil	1.8	Linseed	
			2. Red coat of man	Oil	1.5	Linseed	
			3. Grey-green leaf, top R.H. corner	Oil	1.3	Linseed	
Manet	The Waitress No.3858	1878/9	1. White impasto + green beneath	Oil	3.6	Poppy	7
			2. Pale blue, top edge	Oil	4.1	Poppy	
			3. Opaque red, top edge	Oil	3.6	Poppy	
			4. Pink, top edge, left	Oil + ?	4.1	Poppy	
			5. Yellow, top edge	Oil + ?	2.3	?	
			6. Greenish yellow, top edge, right	Oil + ?	1.6	?	

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3. The results from Veronese's four 'Allegories' (those from number II were reported earlier) do not present a completely consistent picture of the use of different oils for light and dark pigments. Linseed oil seems to have been principally used but in three samples, the pale yellow in numbers III and IV and the white in III, the ratio is sufficiently high to suggest walnut oil. However, the white paint in numbers I and IV does not seem to be in walnut oil. Pine resin, detected earlier in the bright green of number II [1,2], was found again in the bright green of the man's tunic in number IV, yet it was not evident (from the chromatogram only) in the deep green sash in number III. This well-preserved green paint showed no difference, chromatographically, from the browned green paint of a textile in the same painting (which showed bright green below its surface) and the difference in their behaviour with time is inexplicable from the point of view of medium.

4. Probably this painting is entirely in linseed oil: the two higher P/S ratios of 2.3 and 2.4 are in the overlap region for linseed and walnut oils.

5. Methyl dehydroabietate, from pine resin, was detected in the last three samples, the first not having been examined by GLC – MS. The quantities were very small, insufficiently large to give a significant peak on the gas-chromatogram, but unlikely to have come from the remains of old varnish. This suggests the possibility that the medium used was an oil varnish of the boiled oil plus resin type. Such materials still consist predominantly of oil, and dry to a hard insoluble paint film like oil alone, but they often have the advantage, in the early days of their life at least, of not becoming so matt as pure oil paint and so not requiring to be varnished. We have mentioned in a previous article [1] an attempt to distinguish between the use of fresh oil and bodied oil in paint by measuring the ratio of the C9 and C8 dicarboxylate esters. The results reported were based on too few samples for confidence that they would remain consistent for others, but their trend is probably correct, namely a lower C9/C8 ratio for bodied oils than for raw oils. The results in the Table have been examined in this way to see if they gave any identification on this point, and it must be admitted that generally the ratio was found to be at some intermediate position between the values found for the experimental samples, and therefore ambiguous. The four samples from the Altdorfer however gave values averaging about 3.8, that is, at the lower end of the range, and so might be construed as supporting the theory of heat-bodilying of the oil medium in this case, as in the preparation of an oil – resin varnish, but such an interpretation is only very tentative.

6. Regarding resin content, similar remarks apply here as in the case of the Altdorfer. Significant amounts were present in samples 3 and 4; only traces in sample 2; none was convincingly detectable in sample 5, whilst sample 1 was not examined by GLC – MS. The C9/C8 ratios averaged about 5.8 and so offer no support to the idea of use of a heat-bodied oil in this case.

7. There were some anomalous features in the results for this painting. While samples 1 – 4 are clearly in poppyseed oil medium, numbers 4 – 6 had rather low azelate (C9 dicarboxylate) peaks, and consequently appeared not to be in oil alone but to have been diluted with more saturated fats, such as egg or animal fats, which would boost the amounts of palmitate and stearate relative to azelate. These materials also have low palmitate/stearate ratios and so would lower that ratio for poppy oil if they had been added to it. The low P/S ratios of samples 5 and 6 could be explained in this way yet sample 4, which also had a low azelate peak, still has a high P/S ratio. These samples are all from the top edge of the painting and so could be of later additions although other information gained from examination of the picture indicated that this was not the case (see p.17). The anomaly cannot be resolved at present but the important point is the predominant use of poppyseed oil, as has usually been found in other analyses of French Impressionist paintings.

References

1. MILLS, J.S. and WHITE, R., 'Organic Mass-Spectrometry of Art Materials: Work in Progress', *National Gallery Technical Bulletin*, 6 (1982), pp.3 – 18.
2. MILLS, J.S. and WHITE, R., 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 5 (1981), pp.66 – 7.