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Analyses of Paint Media

John Mills and Raymond White

This article continues our series summarizing the results of analyses of the media of National Gallery paintings. Both gas-chromatography alone and combined gas-chromatography–mass–spectrometry [1] have been used to obtain them, but we now more and more tend to use just the latter method since it is more sensitive and provides the added benefit of sure identification of minor components. The peak areas (used for calculation of the P/S ratios) with this method are obtained by summing the ion counts for the scans making up the particular peaks, and so could conceivably be different from areas of peaks yielded by the hydrogen flame detector used for gas-chromatography alone. Comparative tests, however, show the results to be comparable and unlikely to lead to significant error.

The standard chromatography conditions used now for all samples are: 25 m wide-bore (0.52 mm) quartz capillary column with methyl silicone–equivalent bonded phase; on-column injection; helium carrier gas at 37 cm/sec. linear velocity; temperature programming from 130 to 290°C at a rate of 5°C/min.

Notes to the Table

1. The palmitate/stearate ratios for this painting fall in the overlap region for linseed and walnut oils and one cannot be sure which has been used here. All of the samples contained significant amounts of pine resin (by GLC–MS; presence of dehydro- and 7-oxo-dehydroabiatic acids), a considerable amount in the case of the green which was presumably of the ‘copper resinate’ type. As usual with the medium of copper greens, the oleate peak was strong (larger than the stearate).
2. Only samples 2 and 7 were also examined by GLC–MS. The former showed the presence of small amounts of pine resin; the latter of some beeswax (see [2]), but this seems unlikely to have been an original component. Egg is clearly the principal medium but one cannot be certain whether the apparent presence of small amounts of oil in three of the samples is original or due to later contamination; the presence of both media in two paintings by Crivelli, No.807 [3] and No.668 [4], has been noted earlier. Discussion of results on some further samples, taken from the predella frame in the course of its restoration, will be postponed until a future article on this topic.
3. In contrast to the preceding, results for this painting did not suggest the presence of any oil. Only one sample (the green, sample 6) was examined by GLC–MS. It showed no trace of resin components.
4. Only insignificant traces of resin were shown (by GLC alone) even in the green sample.
5. A distinctly low azelate peak in both samples suggested the probable presence of egg fats in addition to drying oil. This makes identification of the oil less certain but it was probably walnut. Amounts of resin were small.
6. Samples 1 and 2 showed a fair amount of pine resin and since both were semi-transparent glazes it seems likely that an oil–resin varnish medium was used in each case. We have discussed elsewhere [1] the possibility of distinguishing heat bodied oils (as would be formed in the preparation of oil–resin varnish by traditional methods) and raw oils. This involves the ratio of the C9 to C8 dicarboxylic acid esters, higher proportions of the C8 ester being formed on drying from the bodied oils. Higher proportions of C8 ester were indeed present in samples 1 and 2, C9/C8 being roughly 3.5 for sample 1 (green) and 2.6 for sample 2 (red) as compared with 5.6 for each of the straight oil samples 3 and 4, but it must be noted that these are apparently walnut oil, whereas the work cited above was on linseed oil. A similar possibility of the use of bodied oils has been discussed in connection

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Bordon	Daphnis and Chloe No.637	c.1540(?)	1. Flesh, Chloe's knee	Oil	2.1	?	1
			2. Red robe	Oil	2.0	?	
			3. Blue, Daphnis's garment	Oil	2.3	Walnut?	
			4. Blue, Chloe's dress	Oil	2.2	Walnut?	
			5. Green, top left	Oil + resin	2.8	Walnut	
Carlo Crivelli	Virgin and Child with SS. Jerome and Sebastian No.724	After 1490	1. Red robe	Egg. Some oil?			2
			2. Brown glaze on flower pot	Egg			
			3. White marble, L.H. edge	Egg			
			4. Green book	Egg. Some oil			
			5. Brown marbling, R.H. edge	Egg			
			6. Virgin's blue robe, upper layer	Egg. Some oil?			
			7. Green marbling on predella frame	Egg + wax			
Carlo Crivelli	The Immaculate Conception No.906	1492	1. White scroll	Egg			3
			2. White architecture	Egg			
			3. Blue of Virgin's robe	Egg			
			4. Red of Virgin's dress	Egg			
			5. Brown glaze on marble	Egg			
			6. Green inside mantle	Egg			
Palma Vecchio	Portrait of a Poet No.636	c.1515–16	1. Grey ground	Oil	2.8	Walnut	4
			2. Red robe	Oil	2.3	Walnut	
			3. Green leaf	Oil	2.1	?	
			4. White shirt	Oil	2.7	Walnut	
Solari	A Man with a Pink No.923	before 1495(?)	1. Pale blue sky	Oil + egg + resin	2.5	?	5
			2. Red robe, lower R.H. side	Oil + egg + resin	2.4	?	
Tura	An Allegorical Figure No.3070	c.1460	1. Green of inside robe	Oil + some resin	1.4	Linseed	6
			2. Red glaze on robe	Oil + some resin	1.4	Linseed	
			3. White band at bottom	Oil	2.5	Walnut	
			4. Dark blue sky	Oil + trace resin	2.0	Mixture?	
			5. Red underlayer of robe	Egg			
			6. Pale green underlayer, base of throne	Egg			
			7. Green underpaint of dress	Egg			
			8. Green underpaint of green of masonry	Egg			

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Tura	The Virgin and Child Enthroned No.772	1470s(?)	1. Green pilaster, R.H. edge	Oil	3.2	Walnut	7
			2. Red glaze of pilaster, L.H. edge	Oil + some resin	3.1	Walnut	
			3. Pink underlayer of sample 2	Egg			
			4. Brown capital, L.H. side	Egg			
Zoppo	Pietà No.590	3rd quarter 15th C.	1. Light grey of sepulchre	Egg			8
Ascribed to Campin	A Man No.653a	2nd quarter 15th C.(?)	1. Blue of robe, L.H. edge	Oil + egg + resin	1.5	Linseed	9
			2. Red paint on reverse	Oil + egg + resin	1.4	Linseed	
	A Woman No.653b		1. Purple of robe, bottom L.H. edge	Egg + oil trace resin			
Hoogstraten	A Peepshow No.3832	3rd quarter 17th C.	Numerous samples	Oil and egg			10
Greuze	Portrait of a Man No.6500	1763(?)	1. Mixed colours, bottom edge	Oil	3.0	Mixture?	11
			2. Mixed colours, R.H. edge	Oil	3.6	Mixture?	
			3. White ground	Oil	4.0	Poppy	
Købke	Northern Drawbridge to the Citadel in Copenhagen No.6507	1837	1. Blue sky	Oil	1.6	Linseed	
			2. Black, lower edge of rushes	Oil	1.3	Linseed	
Gainsborough	Dr Ralph Schomberg No.684	c.1770	1. Green-blue bushes, L.H. edge	Oil	1.8	Linseed	12
			2. White impasto of stocking	Oil	3.6	Poppy?	
Reynolds	Lady Cockburn and her three Eldest Sons No.2077	1773	1. White of child's sleeve	Oil	3.5	Poppy?	13
			2. Red drape, upper L.H. side	Oil + resin	2.3	Walnut or mixture	
			3. Black shadow on preceding area	Oil + resin + bitumen	1.8	Linseed	
			4. Orange-yellow drape	Oil + resin	1.8	Linseed	
			5. Grey-white of dress, bottom edge	Oil	1.9	Linseed	
Van Gogh	A Cornfield, with Cypresses No.3861	1889	Several samples	Oil +			14

with an Altdorfer painting (No.6463) [5]. No.3070 is discussed at length on p.5ff.

7. A fortunate opportunity arose for taking a few samples from the edge of this painting by Tura for comparison with the preceding one. The results were gratifyingly clear-cut and, as can be seen, indicated a similar use of both egg tempera and oil media. The red and green glazes are used very thickly in some areas of the painting to render embossed details, and it can be seen in these that the paint has tended to sag towards its lower edge and must have been rather fluid. These thick details were in too good condition to allow sampling, but samples 1 and 2 appear to be the same paint used more thinly. The oil is clearly walnut and the proportion of resin is low; essentially absent in the case of the green. The C9/C8 ratios were high (about 6.0 and nearly 10, respectively) which would indicate that it was not a boiled oil varnish but, as was said above, we have not experimented on heat bodied walnut oil and are not sure of its behaviour.

8. Only one sample could be taken from this very small, thinly painted picture.

9. These two small panel paintings were in such good condition that sampling could be justified only in one or two places along the sides where paint had gone over the slightly raised lip of the ground at the edge. Azelate peaks were about half the size of palmitate for the first two, indicating dilution with saturated egg fats, while the single sample from No.653b was clearly largely in egg medium with just a little oil present. Despite the presence of egg, the P/S ratios for the first two samples are sufficiently low for one to be sure that the oil was linseed. Pine resin was present in all the samples, especially the first two. Unfortunately for lack of further samples the significance of these results cannot be certainly elucidated: that is, whether they represent the use of a different medium in different layers, or a mixed medium. On the basis of staining of cross-sections for protein, the presence of emulsion media, as well as the individual use of tempera and oil, have been reported in Early Netherlandish paintings [6,7].

10. The complicated results from this painting are discussed on p.85.

11. Apart from the white it proved impossible to take samples of single-pigment paint. Clearly poppy oil has been used for the white but the lower P/S ratios of the other two samples could result from admixture of either walnut or a smaller amount of linseed oil.

12. The white seems most probably to be prepared in poppy oil but a ratio of 3.6 may also be just within the range given by walnut oil. Repeated sampling would be needed for certainty. This painting will be the subject of an article in a future issue of the *Technical Bulletin*.

13. Again, the white is most probably in poppyseed oil but may just be walnut. Presence of bitumen in sample 3 indicated by detection of hopanoid triterpanes with base peak at mass 191 [8,9].

14. The results for this painting by Van Gogh are discussed at length on p.59.

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