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Analyses of Paint Media

John Mills and Raymond White

We report here further analyses of paint media of National Gallery paintings carried out during the past year. Generally speaking such analyses are only made on samples from paintings which are undergoing restoration since it is only in such circumstances that the samples can conveniently be taken, free from varnish and with the assurance of being able to see exactly what is being sampled. This means that it is impossible to concentrate on any particular group of paintings and results of statistical significance can emerge only in the fullness of time. Trends in the results have been briefly indicated before (for example in [1]), in particular the predominant use of walnut oil in the earlier Italian oil paintings and the tendency for this to be replaced by linseed oil in the course of the sixteenth century, though without any numerical evidence for this being adduced. Enough results have now accumulated for this to be feasible.

The identification of the three different drying oils,

walnut, linseed, and poppyseed, in paintings is posited on the finding that in known samples of these oils the ratios of palmitic acid to stearic acid present (P/S ratios) fell within different, though overlapping, ranges. The question can therefore be asked: do the results from actual paint samples confirm such a trimodal distribution? There are too few examples of apparent finding of poppyseed oil so far to consider those but with the other two oils the results do in fact show a bimodal distribution. This can be shown when a histogram is constructed of the number of findings of each P/S ratio (to one point of decimals). To reduce the number of sources of other variation and so give a more clear-cut finding we show here the result for Italian paintings only in Fig.1a. Two peaks appear with median values of 1.7 (linseed) and 2.5/6 (walnut), and a trough in the 2.2, 2.3 region where the distribution curves for each oil must overlap.

How can one demonstrate the transition from

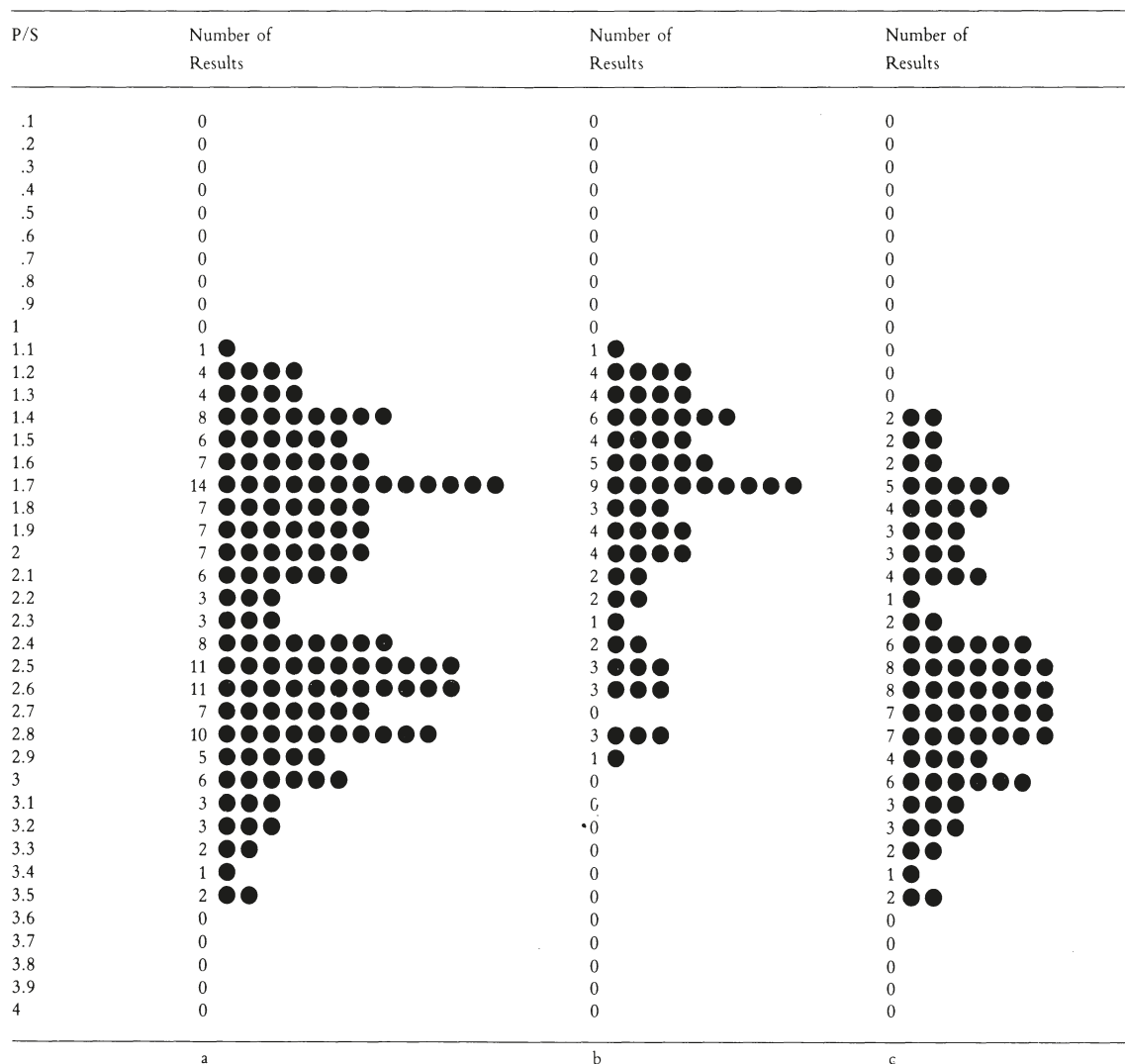


Figure 1
Distribution of the palmitate/stearate ratios for Italian oil painting samples.
(a) 1400 - 1800
(b) 1521 - 1800
(c) 1400 - 1520

walnut to linseed oil? There was no sudden change and a dividing line must be to some extent arbitrary but there is a way of finding a date such that the two groups of results which it forms (those before and those after) show maximum homogeneity within themselves (minimum within-group variance) combined with maximum difference one from the other (maximum between-group variance), as measured by the ratio of these two quantities (the variance ratio). This analysis of variance is a common statistical technique described in textbooks (for example [2]) and need not be entered into here. The variance ratios could be simply computed, from stored analysis results, for different dates as the dividing line. They are shown in the Table below.

Dividing date	Variance ratio
1490	3.3
1500	7.9
1510	31.6
1520	56.5
1530	55.4
1540	49.6
1550	65.3
1560	61.3
1570	42.0
1580	11.1

For reasons which are not clear two maxima are shown, around 1520 and 1550. Probably this simply reflects an inadequate number of results for the period to yield a smooth curve. At all events it may be said that taking any of the dates from 1520 to 1570 as a dividing line produces two groups which are, statistically speaking, very significantly different and unlikely to have arisen as a chance result. The histograms for the results within the two groups produced by a dividing date of 1520 are shown in Figs. 1b and 1c. The predominance of walnut oil before, and linseed oil after is evident.

Notes to the Table

1. The use of two different oils here seems fairly certain but it cannot be rationalized. Sample three had a rather low azelate peak and there may have been some egg present, perhaps as undermodelling.
2. A third sample, of black background, containing layers of probable repaint showed the presence of both egg and oil.
3. A medium of linseed oil for these two paintings accords with a similar finding for the *Virgin and Child with SS. and a Donor*, No.1432 of the 1500s [3]. An early work of David, probably of the 1480s, the *Christ Nailed to the Cross*, No.3067, was found to be in walnut oil in an analysis carried out some ten or more years ago [1]. Looking again at the relevant chromatograms gave no reason to doubt that result.

4. Sample 2 was taken from a strip along the edge of the painting to see if it showed any indication of being a later addition. It was not significantly different from the other sample.

5. Sample 2 was a translucent brown glaze which had developed a network of fine cracks. It showed only a weak azelate peak, only about half the height of the palmitate, suggestive of a mixture of egg and oil as the medium.

6. The problem of the Stubbs's medium is dealt with in a separate 'Research Note' on p.64.

7. The chromatograms given by all four samples from this painting by Claude all showed high proportions of azelate, in the case of Sample 4 exceptionally so, and there is consequently no reason to suspect the presence of any additional fatty ingredient such as egg fats. The multilayered structure of many areas in this painting mean that probably more than one layer was included in Samples 2 and 3 at least. The almost certain use of poppyseed oil for the white paint means that results for the other three samples could be interpreted as resulting from a mixture of linseed and poppy but walnut oil alone seems more likely.

8. The three samples from this painting all showed distinctly lower proportions of azelate than the preceding one. Egg present?

9. This sample from an unblanched area seemed quite normal in composition for oil paint, with the usual high proportion of azelate. Another sample taken from an area of blanched green paint could not be interpreted. It showed additional unidentified peaks on the chromatogram arising either from unknown constituents in the paint or, more probably, from contamination of some kind. Unfortunately there was no opportunity to repeat the sampling. The problem of 'blanching' in paintings by Claude is discussed on p.49.

10. Walnut or poppyseed oil or perhaps a mixture.

References

1. MILLS, J.S. and WHITE, R., 'The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Painting by Fatty Acid Analysis', in N. Brommelle and P. Smith (eds.), *Conservation and Restoration of Pictorial Art*, Butterworths (London 1976), pp.72 – 7.
2. TIPPETT, L.H.C., *The Methods of Statistics*, 4th revised edition (London 1952), p.167.
3. MILLS, J.S. and WHITE, R., 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 3 (1979), pp.66 – 7.

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Bacchiacca	The History of Joseph II No.1219	c.1515	1. Green cloak	Oil	1.7	Linseed	1
			2. Red cloak	Oil	2.7	Walnut	
			3. Grey architecture	Oil	1.8	Linseed	
Pontormo	Pharaoh with his Butler and his Baker No.6452	c.1515	1. Red glaze, seated centre figure	Oil	2.2	Walnut	
			2. Grey stairs	Oil	2.5	Walnut	
Style of Reni	S. Mary Magdalene No.177	17th cent.	1. Red robe	Oil	1.5	Linseed	2
			2. Green-grey flesh	Oil	1.6	Linseed	
Gerard David	The Deposition No.1078	After 1515	1. White shroud	Oil	1.4	Linseed	3
			2. Green sleeve	Oil	1.7	Linseed	
			3. Blue of Virgin's sleeve	Oil	1.7	Linseed	
	The Adoration of the Kings No.1079	After 1515	1. Red robe of King	Oil	1.5	Linseed	
			2. Blue of Virgin's robe	Oil	1.5	Linseed	
			3. Brown of kneeling King's sleeve	Oil	2.2	?	
Style of Schongauer	The Virgin and Child in a Garden No.723	15th cent.	1. Pale blue sky	Oil	2.3	Walnut	4
			2. Blue sky, another area	Oil	2.6	Walnut	
Rembrandt	Portrait of an 83-year old Woman No.775	1634	1. Black dress	Oil	1.8	Linseed	
2. Light fawn background	Oil	1.9	Linseed				
Follower of Murillo	S. John the Baptist in the Wilderness No.3938	17th cent.	1. Sky R.H.S.	Oil	2.0	Linseed	
			2. Red of robe	Oil	1.8	Linseed	
			3. Grey neck of robe	Oil	1.6	Linseed	
Francisco de Zurbaran	S. Francis in Meditation No.230	1630s?	1. White sleeve	Oil	1.8	Linseed	5
			2. Brown shadow on hand	Oil	1.5	Linseed	
George Stubbs	Lady and Gentleman in a Carriage No.3529	1787	1. Pale sky L.H.S.	Oil + ?			6
2. Tree highlight L.H.S.	Oil + ?						
Claude	Seaport: The Embarkation of the Queen of Sheba No.14	1648	1. Dark blue-green sea	Oil	2.4	Walnut?	7
			2. Red-brown cloak of figure R.H.S.	Oil	2.1	Walnut?	
			3. Brown gunwales of boat	Oil	2.3	Walnut?	
			4. White foam at bow of boat	Oil	4.7	Poppy	
A Seaport No.5	1644	1. Red-brown ground	Oil	2.5	Walnut	8	
		2. Brown paint	Oil	2.2	?		
		3. Blue (blanched)	Oil	1.8	?		
Claude	Marriage of Isaac and Rebekah No.12	1648	1. Green foliage	Oil	1.2	Linseed	9
Monet	Bathers at La Grenouillère No.6456	1869	1. Light blue sky	Oil	3.9	?	10
			2. Green foliage R.H.S.	Oil	3.4	?	
			3. White highlight	Oil	3.7	?	