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Organic Analysis in the Arts: Some Further Paint Medium Analyses

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In a previous report of some analyses of paint media in National Gallery paintings (1) we briefly outlined our method, based on fatty acid analysis, for distinguishing between egg-tempera and drying-oil media and for identifying the particular oil used in the latter case. We will here range a little more widely and give some account of the history of analysis of the organic materials used in art objects in general and of paint media in particular, what can now be accomplished but also what limitations yet remain on our ability to say with certainty that we have detected all the components of a particular paint sample.

The question of the use of egg-tempera or oil medium, particularly from the point of view of who 'invented' oil painting, is one which has interested the art historian ever since Vasari (2). In England, in the first half of the eighteenth century, the question was studied by the antiquaries George Vertue and Horace Walpole in the course of their researches on the history of painting in this country (3). Surviving records of royal expenditure (the Close Rolls) had many mentions of oil and varnish in connection with painting work already in the thirteenth century, implying that oil painting was practised here well before its supposed introduction by the Van Eycks in the fifteenth century. Recent analyses of samples from some paintings of that period have fully confirmed that this was so (as will be described in some future article) but in the eighteenth century there were of course no suitable methods of analysis. Walpole could only go by written records and by whether the painting 'looked' as if it were painted in oil. Nonetheless it would seem that persons might have been prepared to try tests of some sort for in speaking of 'The Wilton Diptych' (now No.4451: 1395 or later), which bears a label of some date later than 1639 stating that the painting is in oil (4), he says that 'the picture is too great a curiosity to have experiments made upon it'.

In the nineteenth century knowledge of the history of techniques of painting was greatly extended by the work of Eastlake and of Mrs Merrifield (5,6) on the documentary sources but, while organic chemistry of natural materials was beginning to take shape by this time, understanding of their complexities was only rudimentary and analysis was still impracticable. Nor was it sure that it ever would be since it was realized that organic materials were not of the durability of mineral or inorganic materials, such as most pigments were, but were subject to oxidation and change. Thus they might have changed to the point of being beyond recognition or even have disappeared almost entirely from the paint film.

At this point it is necessary to summarize briefly the classes of natural materials which are regularly or

occasionally incorporated into art objects, and paintings in particular. They are as follows:

Oils and fats. These are all basically similar chemically and consist of the esters of glycerol with various fatty acids i.e. triglycerides. As far as paintings are concerned the materials in this category are the drying oils, of course, and the fats present in egg-yolk. The chemistry of these materials has been summarized elsewhere (7).

Proteinaceous materials. Proteins are one of the main components of animals and plants. Compounds containing nitrogen as well as carbon, hydrogen and oxygen, they are complex polymers made up of a number of smaller compounds known as amino acids. Animal glue is a partially degraded protein which results from boiling animal protein for a long time with water. Egg-white consists almost entirely of the protein albumin and there is also a proportion of protein in the yolk. Casein is the protein in milk. All of these are important adhesives and binding media.

Polysaccharides. The plant gums and mucilages fall in this category. They are water-soluble polymers made up of a variety of sugar units. While not normally incorporated into easel paintings they are the usual binding medium of watercolours, miniatures, and illuminated manuscripts. Materials such as gum arabic (gum acacia) are of this type.

Natural resins. With the sole exception of shellac which is of insect origin all the natural resins come from trees or shrubs, from which they exude either naturally or on tapping. They mainly consist of complex mixtures of terpenoids and have recently been reviewed (8).

Waxes. These originate from insects (beeswax), plants (carnauba wax), or mineral deposits formed from long-decayed plant matter (earth waxes, petroleum waxes etc.). They contain long-chain hydrocarbons and esters and have recently been reviewed (9).

In 1850 were made some discoveries at Saint-Médard-des-Prés which included what appeared to be the equipment and materials of a painter in encaustic technique of the fourth century. The chemist Chevreul was able to demonstrate, within the limitations of simple tests of solubility and melting point, that some of the remains contained beeswax apparently chemically quite unaltered after 1500 years (10). Identifying organic materials was not, then, quite a hopeless business. We now know that waxes are in fact exceptionally stable materials because they are largely saturated compounds, i.e. they contain no double bonds, and are thus almost invulnerable to oxidation. That this was not true of all the above mentioned classes was indicated by some similar archaeological finds of painting materials of the third century (or perhaps of cosmetics;

opinions differed) which were found to contain a mixture of oxidized free fatty acids, presumably the products of decomposition (hydrolysis) of the original triglycerides of fats of some kind, though the other product of the supposed hydrolysis, glycerine, was not detected doubtless because, being water-soluble, it could be readily washed away over the years. Such observations as these were repeated on a number of occasions during the late nineteenth and early twentieth century and of course raised questions as to what might have happened to the oil medium of paintings but they showed that at least the decomposition products survived as an indicator of the fatty nature of the original material. (We now know that though hydrolysis of unpolymerized triglyceride molecules can occur naturally by chemical and perhaps bacterial action, this is less likely to occur to the *polymerized* triglycerides of dried drying oils.)

Findings such as these on archaeological materials gave valuable leads but of course the samples available for experimentation were fairly large, enormously larger than could be taken from paintings or most types of object. Even on the large samples the classical methods of organic chemistry usually gave only an indication of the class of material to which the sample belonged—fat, protein, resin etc.—but individual characteristic components were not identified and there was no way of pinning down what individual fat or resin was involved. In the first quarter of this century work concentrated on developing tests which could be carried out on small samples, either colour reactions for the general classes of compounds or perhaps the detection of characteristic elements such as nitrogen (which indicated the presence of proteins) or phosphorus (which would indicate the specific protein casein). Often however colour tests which were reliable on fresh materials no longer worked on aged ones or were confusing in the presence of other organic materials. Likewise tests for particular elements could be interfered with by the presence of certain pigments. Another approach which was examined was that of the preferential staining of oil or proteinaceous media by the use of different stains as had long been in use by biologists. This was first investigated by Wilhelm Ostwald, who showed a very clear-sighted view of the problem, and though his results were first published already in 1905 (11) they were not widely known until published in English translation in 1936 (12). Munich seems long to have been an important centre for studies of painting technique and one of the major figures in this field was Alexander Eibner, eventually Director of the 'Versuchsanstalt für Maltechnik' of the Technical High School. He published several substantial books on painting technique and related topics and made important contributions to analysis. Towards the end of his life he published an article on medium analysis (13) which stands as a valuable summary of the state of this art at that time (1932). Passing in review most of the methods indicated above he seemed to feel that they did permit the distinction between oil, glue, egg-white, and plant gums, but that oils and egg-yolk still presented difficulties of distinction. There was no way he could

foresee of distinguishing between different drying oils; resins were difficult even to detect let alone distinguish and of course mixtures of egg and oil would also be problematic.

Very little advance in methods took place for more than twenty years, nonetheless important additions were made to our knowledge of painters' techniques using the existing simple approaches (14,15). What truly revolutionized organic analysis in general and, after some delay, analysis of paint media was the discovery and development of the chromatographic methods for separating mixtures into their components: paper-chromatography in the mid-1940s, gas-chromatography in the early fifties and thin-layer chromatography some ten years later. These methods, and especially gas-chromatography, meant that instead of having to utilize the properties of natural materials as a whole (which are an average, as it were, of all the components which make them up) these natural materials could be analysed quantitatively into all their individual and perhaps characteristic components, and because of the sensitivity of the methods this could be carried out on very small samples. A chronological account of the application of these methods to paint media seems unnecessary here: we will rather try and describe the situation as it stands at present.

The approach based on fatty acid analysis has been adequately described in our previous articles. It provides a sure distinction between drying oil and egg-yolk media when these are used alone. It also gives strong indications for the use of these two materials in admixture when they are both present in similar proportions but it will not indicate the presence of small amounts of egg in oil. The conditions of workup of the sample and for the chromatographic separation are such that the procedure has the bonus of probably indicating the presence of any diterpenoid resins (i.e. those from conifers etc. (see 8)), though this has not often been observed. It will not indicate the presence of triterpenoid resins, for example dammar and mastic, which would have to be looked for in a separate procedure, but equally it is not interfered with by their presence. Likewise the presence of egg-white, glue, and plant gums does not interfere since they have no significant content of fatty acids but of course neither does the method give any indication of their presence. This fact is a particular instance of the rather general rule that because the various groups of natural materials encountered as paint media are so different chemically, quite different approaches have to be taken for their preparation for gas-chromatography and in actually carrying this out. Thus separate samples may be needed for the different procedures. A separate sample would indeed be required if one were going to follow up a fatty acid examination, which had seemed to suggest the presence of egg in addition to oil, by a study of the amino acid composition of the proteinaceous component of the suspected egg. This would be a desirable check in doubtful cases and we ourselves do this occasionally. The lengthy procedure is, however, discouraging involving as it does acid hydrolysis, ion-exchange to remove dissolved metal ions, two

stages of derivatization and then gas-chromatography.

Examination of proteinaceous media is more important in the case of murals, paint grounds and the like when different proteinaceous materials—egg, glue, casein—may be involved. Paper-chromatography was first employed for this purpose (16) while subsequent developments have been made in ion-exchange chromatography (17), thin-layer chromatography (18,19), and gas-chromatography (18,20). A procedure which shows promise in suggesting the presence of materials of all classes within a single sample is that of pyrolysis gas-chromatography (21) but so far this does not seem to have been followed up in actual practice. It seems worth mentioning here a simple colour test for glue, the modified Ehrlich test which was developed for quite another application (22) but can readily be scaled-down to provide a very sensitive test for very small paint samples. Such a test for glue is often very useful since it is, we believe, a rather common non-original component of many paintings through its use in glue relining, blister-laying etc. It is thus good to be able to check for it so that one does not interpret other positive simple tests for protein as necessarily being due to the presence of egg protein.

All the above tests demand care in sampling to ensure as far as possible that only one layer has been taken and thus avoid uncertainties as to distribution should one find more than one medium to be present. Because of this question of mixed media and of the use of different media in different layers, the use of staining techniques originated by Ostwald has received renewed attention in recent years (23–26). We also have sought to use these techniques in this Department especially in cases when the gas-chromatography results have suggested the presence of both egg and oil. Some of the resulting findings are included in the 'Notes' which follow the Table of gas-chromatography results (see p.75). Our general feeling is, however, that the method really should be used in conjunction with chromatographic techniques since it can give results which will otherwise be wrongly interpreted.

There is one further point to be made about the limitations of our ability fully to define the nature of an artist's oil medium. Drying oils can be prepolymerized by heating them or exposing them to sunshine for a prolonged period. The resulting 'stand oil' has many improved qualities from the point of view of handling, lower yellowing, and permanence of the resulting dried oil film and it is known from the early manuscripts that such thickened oils were indeed in use by artists. This pretreatment in no way affects, however, the final fatty acid composition of the dried oil film (so far as we know) and therefore our fatty acid analyses give no indications on this point. This is a sad limitation but one for which there is no foreseeable solution.

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Giovanni Bellini	The Blood of the Redeemer No.1233	Late 1460s?	1. Blue sky 2. White tile	Egg Egg			1
Carlo Crivelli	The Vision of the Blessed Gabriele No.668	1489/90	1. White sky 2. Black foliage R.H.S. 3. Green/blue, top edge 4. Pale brown, lower R.H.S.	Egg + oil Egg + oil Egg + oil Egg + oil			2
Michele Giambono	A Saint with a Book No.3917	2nd quarter 15th cent.?	1. Grey paint beneath old retouching 2. Blue background	Egg Egg			3
Luca Giordano	Homage to Velasquez No.1434	c. 1692	1. Lilac-grey dress 2. Black, lower R.H. figure 3. White paint	Oil Oil Oil	1.5 1.6 2.1	Linseed Linseed ?	4
Giovanni di Paolo	SS. Fabian and Sebastian No.3402	3rd quarter 15th cent.	1. Red glaze of S. Fabian's robe 2. Flesh of S. Sebastian's arm	Egg Egg			5
Fra Filippo Lippi	S. Bernard's Vision of the Virgin No.248	1447?	1. Dark grey, bottom edge 2. Salmon-pink underlayer L.H. edge 3. Grey of Saint's robe 4. Dark background, R.H. edge	Egg Egg Egg (some oil) Egg (some oil)			6
Filippino Lippi	Moses Brings Forth Water Out of the Rock No.4904	c.1500	1. Lighter blue of sky 2. Darker blue of sky 3. Red of smock, third figure from left (+ some red undermodelling)	Oil Oil Oil + some egg	2.7 3.5 1.7	Walnut Walnut Linseed	7
	Worship of the Egyptian Bull-God, Apis No.4905	c.1500	1. Red smock of R.H. figure 2. White of dress sixth figure from right 3. Blue sky 4. Green smock L.H. figure 5. Dark blue of smock 6. Pale orange undermodelling of red smock	Oil Egg + trace oil Oil Oil Oil Egg	1.4 2.9 1.9 2.5	Linseed Walnut Linseed Walnut	
Roman School	Saint Cecilia No.5284	c.1630	1. White cloud 2. Brown shadow of cloak 3. Dark green drape 4. Flesh of neck	Oil Oil Oil Oil	1.6 1.3 1.4 1.9	Linseed Linseed Linseed Linseed	
Palma Vecchio	A Blond Woman No.3939	c.1520	1. Black background R.H.S. 2. Brown hair 3. Green robe 4. White sleeve	Oil Oil Oil Oil	2.3 2.4 2.7 2.7	Walnut Walnut Walnut Walnut	
Paolo Veronese	The Family of Darius before Alexander No.294	1570s?	1. White masonry, top edge 2. Flesh of hand 3. Dark blue collar of figure in green dress, L.H.S. 4. Red-brown tunic, figure on balcony, upper L.H.S. 5. Dark brown shadow of blue train, woman in centre (two samples)	Oil Oil Oil Oil Oil Oil	2.6 1.9 1.8 1.6 1.9 2.1	Walnut Linseed Linseed Linseed Linseed Linseed	
Van Dyck	Lady Elizabeth Thimbleby and Dorothy, Viscountess Andover No.6437	1630s	1. Yellow highlight of silk dress bottom edge 2. White sleeve of dress 3. Dark brown background, lower L. edge 4. Green drape	Oil Oil Oil Oil	1.8 1.9 1.7 1.8	Linseed Linseed Linseed Linseed	
Francois-Hubert Drouais	Madame de Pompadour No.6440	1763/4	1. White lace, inner canvas 2. White lace, outer canvas 3. Yellow ormolu, R.H.S. 4. Pink ribbon, bottom 5. Red-brown drape L.H.S.	Oil Oil Oil Oil Oil	5.2 4.1 3.3 2.8 2.5	Poppy Poppy ? ? ?	8

Notes to the Table

Incorporating some results on the staining of cross-sections by **Jo Kirby** and **Ashok Roy**

Unless noted otherwise staining tests were carried out on thin cross-sections. For full details of procedures see the references already given (23–26). The paint fragments were fixed in formalin to which 0.5% CaCl_2 aq. had been added, for 48 hours, washed with alcohol, and impregnated and embedded in polyester resin. The sections cut were 6–10 μm in thickness. The protein stains used were the Amido Black reagents described by Martin (26) together with Acid Fuchsin and Light Green. Lipid stains used were Sudan Black B and Oil Red O. Staining was sometimes supplemented by observing the effects of heating the section on a microscope hot-stage as described by Gay (23).

1. Both samples from the Bellini indicated the presence of a small quantity of oil in addition to egg. It is most probable that this originates from traces of later re-paint remaining in them and that the medium of the original is egg alone.

2. All four samples from this painting by Crivelli had azelate peaks at about half the level of the palmitate peaks, suggesting the presence of both egg and oil. Staining tests indicated that this generally resulted from the use of a mixed medium. Four samples were stained, not all from the same areas as those used for GLC. In addition to all having a gesso–animal-skin glue ground they showed the following:

(a) Pale blue of sky. Lead white with azurite in an emulsion of a little oil in egg. Result supported by heating test.

(b) Beige of path. Lead white with scattered red and black pigment particles. Emulsion of oil in egg.

(c) Flesh of the Saint's foot. Lead white with occasional vermilion particles. Probably egg alone but oil cannot be ruled out entirely.

(d) Green foliage, R.H.S. Black underpaint in egg; opaque green paint (verdigris and lead white) in egg and oil; brownish-green glaze probably in oil alone.

3. The first sample was from an area which had been overpainted with oil paint but this had not affected the composition of the original paint beneath.

4. Probably linseed but just possibly walnut oil.

5. This painting is treated in a separate article (p.64).

6. This painting evidently has a long history of conservation treatment and overpainting behind it. Clearly it is predominantly painted in egg medium and this was confirmed by staining tests, but these did not show clearly whether the oil found in two of the samples by GLC was in a thin surface layer or present with the egg in the main paint layer. There was a similar ambiguity with the staining of cross-sections from grey areas of the Saint's and the Virgin's faces (the latter a thick section). All the modelling in the painting seems to have been carried out in a thin

superficial layer of grey paint but the thinness and darkness of this made interpretation of its staining almost impossible.

7. Of the two paintings by Filippino Lippi, one, No. 4904, had been transferred to canvas, acquiring a new pink ground in the process. It was thus of interest to see if this affected analytical results at all. It does not seem to have done so and the results reveal a careful and fairly complicated use of different media. Staining of a sample of red tunic from No.4904 showed, above the new pink oil ground and the old gesso–glue ground, undermodelling or drawing very rich in medium containing scattered pigment particles (egg-yolk); a layer of vermilion paint (oil); a glaze containing red lake pigment (hard to interpret but probably oil).

In the companion painting No.4905 staining and heating tests generally confirmed the GLC results and supplemented them somewhat as follows:

(a) Flesh of knee of figure in blue. Above the gesso–glue there was a very thin scattering of ultramarine particles in no apparent medium; lead white with a few particles of vermilion (egg-yolk); translucent yellowish–green–green earth (egg-yolk); a pink layer of lead white with vermilion etc. (egg-yolk).

(b) Light green of landscape below hill, R.H.S. Above the gesso–glue ground came two thin layers of lead white with charcoal and azurite (oil); a thick greenish translucent layer including verdigris and lead tin yellow (oil); a thinner similar layer (oil).

(c) Blue of sky. Above the ground there seemed to be two layers in lead white and azurite and lead white and ultramarine (both oil).

Returning to the Table one sees that apparently two different oils were used. Regarding sample 3 of No.4904 (Filippino Lippi), one would not normally assign an identity to an oil when contaminated with egg because the latter will change the P/S ratio. It raises that of linseed oil however and this sample must therefore be linseed oil since it is still within the linseed oil range. Summarizing the findings one can say that undermodelling was done in egg; areas which were to show as flesh or white and needed the least yellowing medium were finished in egg; pale colours such as blue were ground in walnut oil; darker colours such as green and red, where any yellowing would not be important, were ground in linseed oil.

8. In the Drouais work we have a further example of the (so far) rare occurrence of poppyseed oil. Once again it is in a French painting and would appear to have been used for the whites because of its lower degree of yellowing. It occurs both on the main canvas and on the small inset canvas which was used to paint the sitter's head and shoulders. Once poppyseed oil has been identified in a painting it makes interpretation of other samples with P/S ratios in the walnut oil range uncertain. They *could* be walnut oil but equally they could result from mixtures (chance or deliberate) of linseed and poppyseed oils.

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