Microscopical techniques applied to traditional paintings

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For 50 years, conservators have made cross-sections using small samples from traditional paintings, in order to study the materials of painting. Conservation scientists have extended earlier examinations in visible light alone, to examination in ultraviolet fluorescence, on to studies of melting point (thermomicroscopy), and most recently advanced imaging techniques applied to the same cross-sections. Developments in these areas are presented. Two projects are presented as short case studies - cataloguing of 16th- and 17th-century paintings, and cataloguing of early 20th-century Camden Town paintings.

Cross-sections and pigment dispersions have been used to examine historical paint for many years: the seminal paper on the techniques most applicable to samples from paintings was published exactly 50 years ago (Plesters 1956). The ‘classical’ method of placing a (sub-) milligram paint sample in a half-filled mould of polyester resin, topping up the mould, and grinding down one face, is still used (Figure 1). Modifications include the use of pre-cast acrylic moulds to accommodate different sizes of sample (see www.easysections.com) and the use of cushioned silicone carbide paper for final polishing (Micromesh 2005). The latter has made possible the study of water-sensitive inter-layers based on plant gums and proteins. When samples were routinely prepared in water, such layers were rarely discussed in publications.
There are several reasons for using microscopy to study paintings. Many conservators make cross-sections to establish whether the artist has reworked a painting, whether paint was added to well-dried paint by a later (therefore restorer’s) hand, and whether the original varnish is present. If it is, it will have been partially absorbed by the drying paint. Later-applied varnishes may overlie a recognisable dirt layer. Further, more research-oriented reasons to use microscopy include: the generation of new knowledge about actual use of a material, as opposed to its date of invention; studies of a particular artist’s methods and materials; authentication studies based on such knowledge; and research to determine the presence and causes of colour change on the surface of the paint.

The ideal sample site is an edge protected by the frame - provided that this area is not already lost, or made complicated by damage and overpaint. Drying cracks also offer good sampling possibilities. The close examination of the surface for sample sites, typically at x7-x100 times, also builds up information about the artwork in question. Many conservation studios use a custom-built table with a gantry to support the microscope and fibre-optic lights (Figure 2).

A number of biological and fluorochrome stains have been applied to paint cross-sections over the years. Not all are successful and reproducible: it is always necessary to compare their effects on genuine materials of comparable age, and on a range of other possible materials of the same age. This is a serious problem in practice, and it is common to use paint samples from accelerated light and heat ageing as reference material. Old, naturally-aged samples of well-documented composition are disappointingly rare. We have found that the only reliable stains for historic paint, whose ageing history is always unknown, are for proteins: aqueous Acid Fuchsin and weakly acidic Amido Black.

The other classical technique for paint studies is polarising light microscopy (PLM). It is used as frequently today as it was 50 or 100 years ago. New compendia of reference material continue to be published (Eastaugh et al. 2004). The technique provides reliable and compound-specific particle identification, it is high-resolution in the sense that a single particle among hundreds of different ones may be identified accurately, and also selective. It is easy for the microscopist to ignore surface dirt, varnish, fragments of conservation material and anachronistic pigments from overpaint applied at a later date, while concentrating on the particles of genuine interest. For most instrumental methods of analysis, the presence of such foreign material would greatly confuse and complicate the interpretation of results. Since most pigments are inorganic materials, they have high refractive indices (RI), and the microscopical mountant of choice generally has an RI of 1.66.

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**Newer microscopical techniques used to examine paint**

Ultraviolet fluorescence microscopy is enormously useful for the study of paint cross-sections. Typical varnishes based on natural resins develop strong auto-fluorescence as they age, and can always be recognised as individual layers. Intermediate varnish layers, varnish running into small cracks, and original varnish soaking into drying paint are all recognisable, and give information about the artist’s technique. Many nineteenth-century paint formulations involved combinations of drying oil and different resins with yellow/white auto-fluorescence (Townsend et al. 1998; Townsend et al. 2004). Glue and egg in the paint medium has a strong blue/white auto-fluorescence, and wax in the formulation gives a milky auto-fluorescence. While this is never a definitive indicator of medium type, it can indicate likely paint formulations and thereby suggest the best preparation methods for later chromatographic analysis of the paint medium. With practice, it is easy to infer from the cross-sections which sample sites would offer the best possibility of successful analysis, and whether one chromatographic analysis is likely to be indicative of the medium used throughout the painting.

Only a small number of common pigments show significant auto-fluorescence, but they are interesting ones. Madder lakes have an intensity of fluorescence which depends on the mordant used (Eastaugh 1991; Townsend 1993) to fix the dye, and a mordant not based on aluminium usually leads to a pigment of poor lightfastness. The unlaked pigment Indian yellow also has a characteristic auto-fluorescence. Knowledge that either is present tells the conservator that the paint in question is likely to be more light-sensitive than typical oil paintings.

Thermomicroscopy also offers useful information for the conservator (Townsend 2000). Controlled heating of a free paint fragment to 150-200°, while it is observed or filmed, will indicate whether any components of the paint layers or varnishes soften or melt out, or whether the whole paint layer has a sudden melting point due to its composition. While it is tedious to watch paint fail to melt during heating at 10°C per minute, the conservator is then informed whether mild heating is a safe treatment option for the artwork in question.

**Ultraviolet fluorescence microscopy is enormously useful for the study of paint cross-sections**

Scanning electron microscopy (SEM) has long been used to study surface defects in well-dried paint, while energy-dispersive X-ray analysis (EDX) has been applied to paint fragments and to cross-sections coated with carbon. SEM requires a moderately high vacuum, and any residual solvent or water would be extracted from the sample, destroying its morphology. The wider availability of low-pressure and environmental SEM has made it possible to examine the morphology of newly painted samples, and paint which has recently been swelled by varnish application, or the use of cleaning solvents. However, SEM/EDX is not a good method for the study of slow-forming deterioration products from pigments. The depth of sample analysed is 2-5 μm, depending on the accelerating voltage, whereas a coloured degradation product which can easily be seen by eye on the paint surface may in fact be of sub-micrometre thickness.

Even using windowless detectors that permit the detection of elements of low atomic number, and
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Fast area mapping, quantitative analysis of pigments is not easy. The most common white pigments include basic carbonates, oxides, sulphates and carbonates, while coloured inorganic pigments have a far wider range of compositions. Quantitative analysis is only interpretable when the pigment mixture is known and relatively simple, and reference standards of known proportions of these materials are available for analysis, presented in the same matrix (paint medium and embedding medium) as the unknown samples. The method has been evaluated for chalk/barium sulphate mixtures in the ground of van Gogh’s paintings (Haswell and Carlyle 2006) but would be unlikely to succeed for the full range of white pigments available throughout history, still less for the full range of coloured pigments.

Recent developments in the analysis of cross-sections

In recent years, research has been carried out into the composition and deterioration of 17th- to 19th-century paints, as part of the MOLART (1995-2002) and de Mayerne (2000-2005) projects, funded by the Dutch Organisation for Scientific Research (NWO). These have involved the evaluation and development of a number of techniques such as Fourier Transform infrared spectroscopy (FTIR) mapping and secondary ion mass spectrometry (SIMS) applied to existing cross-sections, to identify chemical compounds (Keune 2005; Keune et al. 2005).

Fig 3. Optical microscopy and FTIR mapping.
Fig 4. SIMS in positive ion mode. The analytical area is slightly different from Fig. 3.

Fig 5. SIMS in negative ion mode, with the same analytical area as shown in Fig. 4.
The first stage was a re-evaluation of the sample preparation methods used for traditional cross-sections. The human brain’s useful ability to ignore ‘foreign’ material in a sample is not matched by a sensitive surface analytical technique. FTIR mapping has a spatial resolution of a few micrometres, and comparable depth resolution, while paint layers range in thickness from 10-150 μm, with varnishes having a typical thickness of 10-20 μm. Thus, smearing of organic material (the paint medium) by a mere 10 μm could re-deposit some of it onto a neighbouring layer. Aggressive surface preparation techniques such as ion milling, which produce excellent cross-sections for SEM mapping, might remove paint medium to such a depth that only the pigment could be analysed. The solution was to use a polyester resin of appropriate hardness when fully cured, combined with dry polishing with cushioned silicone carbide paper to a much finer grit size than is required for optical microscopy.

The same preparation method was found to be applicable for SIMS. Coating with gold enhances the detectability of some compounds (Keune and Boon 2004). SIMS can be used in positive ion mode, to detect elements such as Ca in chalk (calcium carbonate), Pb (basic lead carbonate), Al (mordant for a red lake pigment) and Fe (present in ochres and umbers, and in negative ion mode, when light elements such as S in vermilion (mercuric sulphide), as well as organic compounds such as fatty acids with a chain length of 16 or 18), can be detected.

When FTIR mapping (Figure 3), SIMS (Figures 4 and 5), and EDX mapping (Figure 6) are carried out on the same cross-section, a great deal can be inferred about its original composition, as well as its present one. A mechanism has been proposed for the darkening of bright red vermilion in many historic paintings (Keune 2005; Keune and Boon 2005), and studies are still ongoing on the formation of transparent white spots in lead-based paints, and tiny surface spots which are visible on many older paintings (Noble et al. 2005).
An example is shown in Figure 3, which was taken from a yellow button on a crimson chair back, occupied by A Lady of the Grenville Family and her Son (Tate T03237, sample 9, oil on canvas, 741 x 608mm, Jackson, 1640). The yellow paint of the topmost layer includes Pb and Sn according to the EDX map, which means it is made from lead-tin yellow, while Pb is also present in the two lowest layers, which constitute the 2 preparatory layers on the canvas. The SIMS map confirms the presence of Pb in these layers. The FTIR map shows that the upper paint layer contain lead carboxylate but no carbonates. Only the ground layers can include lead white now, since they alone contain carbonates. The SIMS maps show that fatty acids, lead soaps and Pb are present in the upper layer. The original paint of the top layer would have included lead-tin yellow and oil. Optical microscopy does indicate to the experienced analyst that this layer has an unusual appearance, suggestive of lead-tin-yellow but with a strong UV fluorescence. This in combination with EDX would not have offered any explanation for the anomaly. The combined information of imaging-FTIR and SIMS lead to the conclusion that lead soaps have been formed in this layer. A reactive phase in the lead-tin yellow reacts with fatty acids derived from the oil to form lead soaps. The degradation mechanism has been described elsewhere (Keune 2005).

A case study: Tudor Stuart paintings
Artists of the Tudor Stuart period were born during the reigns of Henry VII to Queen Anne. Tate has 108 such paintings in its collection, with dates ranging from 1545 to 1735. This corresponds to the Dutch Golden Age of Rembrandt and Rubens, whose paintings have been studied and published extensively. Many Tudor Stuart artists were trained or born in the Low Countries (modern Belgium and the Netherlands), and there should be many interesting points of comparison between countries.

The most interesting finding to date is that almost half of the paintings in this group exhibit the type of deterioration and changed optical properties seen in the top layers of Figure 3, taken from a Tudor Stuart painting. Since the paintings span 150 years, were painted by over thirty artists with varied training and sources of supply, and have not shared a common storage and display history, the phenomenon is clearly widespread, and not specific to any artist’s technique. The spots of transparent paint seen in Figure 3 sometimes migrate to the surface in large numbers, where they are recognisable as white spots of approximately 0.5-2 mm diameter. Quantities of them on a black costume, for example, lower contrast and suppress the delicately-rendered detail of lavish needlework and costly fabrics which the artists sought to portray realistically. In Figure 7, the costume appears strangely plain in comparison to the elaborate lace of the collar, and the seeming absence of lace cuffs is unusual. But Figure 8, a detail of the proper right wrist, shows that the white cuff was painted over the black fabric. Numerous white spots are now eclipsing it.

The systematic making of cross-sections, use of PLM and EDX/SEM, and protein staining, contribute to the artistic equivalent of epidemiological studies on materials use in different countries, as well as to appreciation of artists’ techniques, and a better understanding of suspected alterations in surface appearance. Very few of these paintings survive in pristine condition. There have been some surprises during this survey: less fading of red lake pigments,
and indeed less variety of red dye types than expected. There are perhaps fewer faded yellow lakes than expected - though microscopical techniques are not always suitable for rendering colour loss noticeable - and rather few examples of any green pigments.

**An ongoing case study: Camden Town paintings**

Many of the artists who formed the Camden Town group studied at the Slade School of Art, London, at the end of the 19th century. Their choice of local urban landscapes and interiors as subject matter gave the group its name. Their painting techniques are very simple in comparison to artists of the Tudor Stuart period. The Camden Town artists used paint straight from the tube (17th-century artists had mixed and ground their own) and applied it to canvases with light-coloured or white grounds. Low-powered stereomicroscopy is sufficient to answer any remaining queries about their technique. The paintings are not quite so old that major conservation treatment has been deemed necessary to preserve them - thus it will be possible to compare canvas fibre type, and the materials used in their ground layers, to their state of deterioration now. Microscopical techniques such as optical and ultraviolet fluorescence microscopy of cross-sections, protein staining, and EDX of the few layers present have yielded sufficient information to make the comparison. For this study, the decision was made to select only the canvases whose maker was identifiable by a stamp or label. The analytical results can then be correlated with surviving trade and price literature. Several points of interest have emerged already.

**Strengths and limitations of optical microscopy applied to paintings**

Optical microscopy is capable of resolving the coarse to fine (50-2 μm) particles found in historic paint, thus they can be identified unambiguously in most cases. This size range affects surface appearance. It follows that the thinnest of applied paint layers can also be resolved easily. Thus, artists’ techniques including colour mixing, planned use of opaque and transparent layers, and deliberate selection of very coarse particles to give the most intense surface colours, or fine particles or low RI which bulk out the paint without affecting...
its colour, can all be detected. Foreign components can be ignored readily.

Increased industrialisation in the 19th century led to great use of machine grinding of pigments, while milling of pigments into paint superseded hand-grinding, in the same period. By the end of the 19th century, pigment particles had routinely become so small that they cannot be resolved with the optical microscope. EDX/SEM or instrumental methods of analysis have to be used instead.

While it takes time – and a good set of reference materials - to gain experience in the examination of historic paint, the time spent in sample preparation and interpretation is very low, once it has been gained. Occasional users can make effective observations, and create useful images, even with limited experience. The best way to examine an ‘unknown unknown’ and decide how to analyse it, is to use an optical microscope first. On occasion the sample remains mystifying, but generally microscopy will yield at least one point of useful information.

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References
Micromesh is available in the UK (2005) from DEP Fabrications Ltd, Unit 33, Cam Centre, Wilbury Way, Hitchin, Herts., SG4 0TW. T: 01462 441414, F: 01462 442110, Contact: Alan Cox.
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