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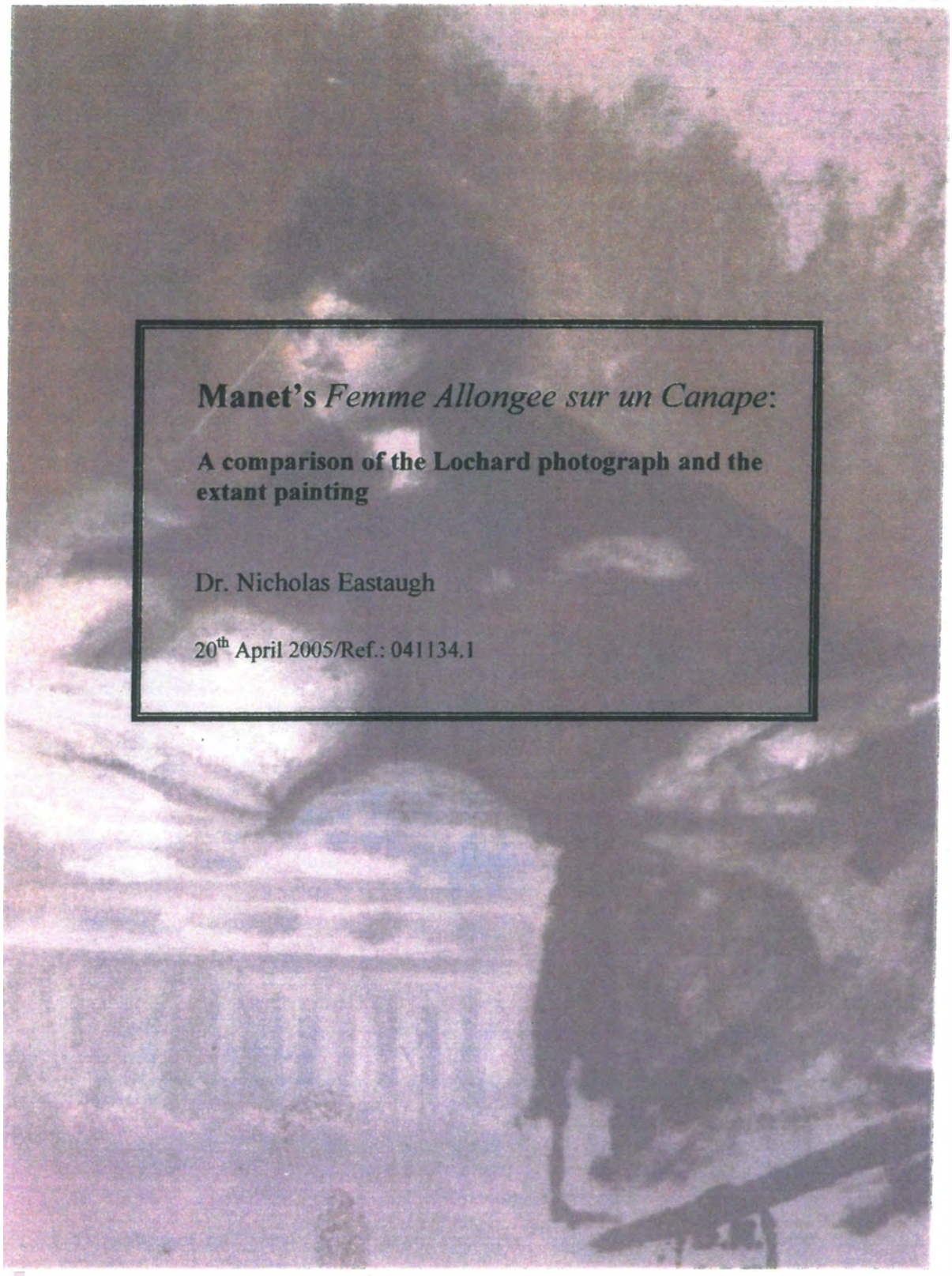

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Introduction

This report presents the results of a scientific study on painting considered to be by Manet, referred to as *Femme Allongee sur un Canape*.

An early photograph of the painting exists, taken by Ferdinand Lochard using the so-called 'wet-collodion' process. Taken in 1884, this image is held in the Bibliothèque nationale, Paris. A copy of this and various other Lochard photographs of Manet paintings were supplied to the author. Additionally, a prior technical report prepared by W.J. Young of the Research Laboratory, Museum of Fine Arts in Boston (ref. 78.93, 22/5/1979) was also made available.

Using a series of analytical techniques, the photograph has been compared in detail to the painting. Methods employed include surface inspection by optical microscopy, X-radiography, reflectance spectrophotometry, infrared imaging, pigment and media analysis, and study of layer structure from paint cross-sections. Digital image processing was also used extensively to study the similarities and differences between the painting, technical images derived from it and the Lochard photograph. Details of the specific methods used and results from them can be found in the appendices to this report, along with various images.

Various discussions of Manet's materials and techniques were also referred to during the preparation of this report[1], primarily to gain a better understanding of elements of the construction of the painting observed during the current research as they relate to Manet's known methods of painting.

It will be shown that from consideration of the behaviour of early photographic techniques, the main features of the Lochard photographs can be explained in relationship to their corresponding paintings. In the case of the *Femme Allongee sur un Canape*, a close match was found in terms of the position of detailed features (such as the form and location of certain brushstrokes). However, greater difficulty was encountered in explaining the lack of visibility of other features in the Lochard phtograph, such as the background and parts of the supporting divan.

Examination of the paint layers (from surface microscopy and paint cross-sections) shows that there is a stratum that corresponds to the preliminary design for the painting, and that this apparently corresponds with the more sketch-like appearance of the transmitted infrared images of the painting. At the same time, the overlying paint appears to be either in direct contact with underlying layers, or separated by an unpigmented varnish-like layer, without any discernable presence of dirt layers or material alteration such as yellowing.

Analysis has also shown a range of pigments to be present in the painting consistent with published examples of Manet's practice, in terms of both specific choices and complexity of mixtures.

[1] Among these we may specifically note: Bomford, D., Roy. A. "Manet's 'The Waitress': An Investigation into its Origin and Development" *National Gallery Technical Bulletin* 7 (1983) 3-19. Bomford, D.; Kirby, J.; Leighton, J.; Roy, A. "Edouard Manet. 1. Music in the Tuileries Gardens" *Art in the Making. Impressionism* National Gallery, London (1990) 112-119. Rioux, J.-P. ""La serveuse de bocks" de Manet: étude technique et comparaison avec des oeuvres apparentées" *Histoire de l'art* **5-6** (1989) 109-120.

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General description of the painting

The painting is on canvas, measuring 50cm (h) by 65cm (w). The size is apparently one of the standard French formats of the period (for example, a 'number 15 *paysage*' canvas of these dimensions is listed in a range available from Bourgeois *ainé* in 1888)[2]. The original canvas is a fine plain-weave type, although also interesting is the lining canvas, which has a herringbone pattern[3]. It is possible that this was applied fairly early in the life of the painting. There are a couple of more recent patches on the reverse of the painting supporting minor damages. The painting has not been cut down or otherwise altered in size.

A detailed surface examination was also carried out using low-power binocular microscopy. This revealed that there is a significant amount of seemingly recent restoration present on the painting, although this does not seem to represent a substantial alteration or distortion of the appearance of the primary paint layers.

UV fluorescence imaging was used to study the painting. However, it is not of particular value in the present instance as what restoration or alteration exists is beneath the varnish and therefore not subject to being revealed by this technique.

The Lochard image and early photographic processes

Key to the comparison of the Lochard photograph to the painting as it now appears is a basic understanding of the original photographic technology involved. Only by this can we see what factors affect the relative appearance of the two images and be in a position to reasonably infer how the two actually compare.

Invented in 1851, the wet collodion photographic process produced a glass negative and what are often referred to as 'beautifully detailed' prints. Preferred for the quality of the prints and the ease with which they could be reproduced, the method is known to have thrived from the 1850s until about 1880, when gelatine dry plates became available. It has been said that: "Within its limitations, the process produced prints which are arguably finer than anything from more recent photography, highly detailed and with superb tonality." Although gelatine dry plates replaced collodion for general photography in the 1880s, collodion apparently remained in use in commercial studios for copying and plate making for reproduction much afterwards.[4] Descriptions of early photographic techniques may be found in numerous publications, including early books such as Towler's *The Silver Sunbeam* of 1864[5].

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[2] Bomford et al., p.46.

[3] This is probably the 'symmetrical' (or 'pointed') 2/2 vertical herringbone as one of the common weaves of the period by Callan (See: Callan, A.*The Art of Impressionism. Painting technique & the making of modernity* Yale University Press (2000) p.31.)

[4] http://photography.about.com/library/weekly/aa111802a.htm

[5] Towler, John. *The Silver Sunbeam*. Joseph H. Ladd, New York (1864). Electronic edition prepared from facsimile edition of Morgan and Morgan, Inc., Hastings-on-Hudson, New York. Second printing, Feb. 1974. See: http://photography.about.com/gi/dynamic/offsite.htm?site=http://albumen.stanford.edu/library/monographs/sunbeam/toc.html.

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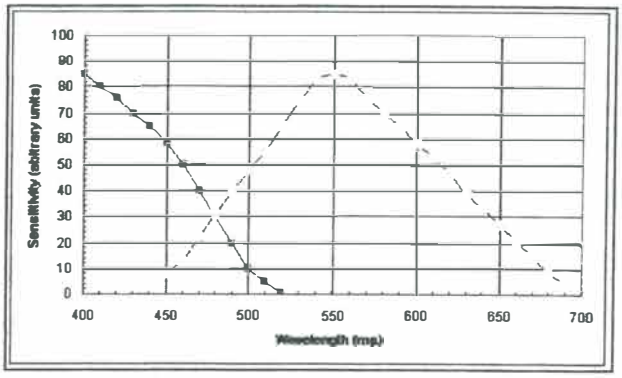
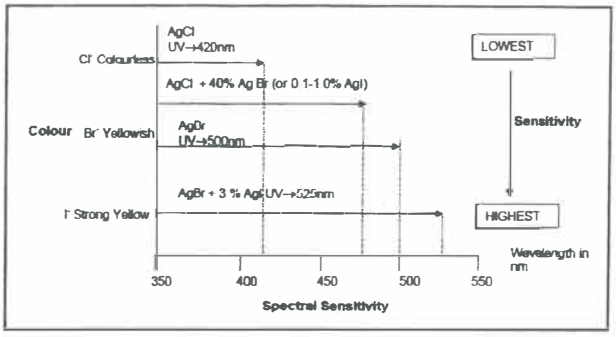
The radiation sensitivity of silver halides ends for all practical purposes at about 525nm. In the adjacent figure[6], the pink curve illustrates the spectral sensitivity of a typical silver bromo-iodide emulsion and the yellow curve illustrates the average human visual response. As these show, the maximum response of the eye is in the yellow-green near 550nm, which lies beyond the sensitivity range of the emulsion, which is much more sensitive to the violet and blue than the eye. However, the situation is a little more complicated still. Only three halides of silver have been used in emulsion-making – the chloride, bromide and iodide – and of these only chloride has been used extensively alone. Silver iodide emulsions are too insensitive for commercial use, and those containing silver bromide alone are rare. The three halides have different sensitivities to light (see diagram below[7]), so in practice historically various mixtures were used, with associated shifts in the peak sensitivity to the spectral distribution of light.



It is important to keep in mind that the image that results is dependent on the variation in sensitivity across the spectral range, not the upper limit of sensitivity. In any imaging process of this nature there are also in fact further contributions to the overall response as a result of the spectral distribution of the illumination system (sunlight, lamps), as well as any absorption from optical components in the camera; of these the former is the most crucial. In terms of the overall response of the imaging system, we can none-the-less make some conjectural observations about how a particular image might shift in appearance, especially when there is more detailed knowledge of the light reflectance properties of the materials that make up that object. With the painting of this report it was of course possible to directly measure the spectral reflectance at a number of locations, thereby gaining some indication of how the overall response might vary according to different conditions of illumination and silver halide composition (see below).



The contrast visible in an image (the density range of tonal values between black and white) is dependent on other factors to do with the grain size of the silver halide crystals. It is known for example that a narrow range of grain sizes leads to a higher contrast with fewer intermediate shades of grey, and *vice versa*. Density is in fact proportional to the amount of metallic reduced silver, this proportionality depending on the silver halide mean grain size, grain size distribution curve, silver halide concentration, sensitizers, and also on the properties of the developer, such as development agents, their concentrations, pH, and other species present in the developing solution. Therefore the preparation and development of the wet collodion plate can significantly affect the final contrast.

[6] After: http://www.cheresources.com/photochem.shtml
[7] After: http://www.wmin.ac.uk/ITRG/IS/DPI/HIW/PM1notes.pdf

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Given the extreme range of possible conditions the most that can probably be achieved in terms of modelling the process is to study the effect of altering what is known as the 'gamma' of the images[8].

A series of experiments was carried out on images of various Manet paintings and the associated wet-collodion photographs[9], including those of the painting under discussion here. Although a relatively crude method, it was straightforward to show that by taking the blue channel of an RGB image of a painting, converting to greyscale and increasing the contrast (reducing the range of grey levels), images of the paintings comparable to the photographs was possible. (An example of this is included for reference at the end of this report.)

However, it proved significantly more difficult to achieve correspondence in the case of the *Femme Allongee sur un Canape*. In particular it was not possible to explain the light background of the Lochard photograph, or the absence of the blue divan. Other features, such as the full extent of the drapery of the skirt, were also dark in modelled images of the painting.

Further research was carried out on the painting to study what might be expected of an imaging system that is highly sensitive to light at the blue end of the spectrum. This can be done by measuring the spectral reflectance of the painting and then either calculating or estimating the likely response overall (fibre-optic reflectance spectrophotometry). What one can simply show though is that for an area to appear light in the final image there must be an appreciable relative reflectance at the blue end of the spectrum. It was found that while areas of the blue paint of the divan did (as one would expect) strongly reflect blue light, other areas within the general locus did not. For example, there are various darker details within the divan that have a low blue reflectance. This is also the case with the background. Judging from the photograph, we would expect an area surrounding the head and back of the woman to have low blue reflectance, while outside this zone it should be significantly higher. This was not the case in the spectrophotometry results. Such findings are consistent with the simpler imaging studies exploiting manipulation of digital images as described above.

Positional correspondence of the painting and the Lochard image

In addition to the studies of spectral response and imaging of apparent surface and sub-surface elements of the structure (discussed below), another approach is the confirmation of the alignment of visible features in the Lochard photograph with the extant painting. For example, by identifying features in both images and checking the relative positions should show that they are directly related. In practice this is more difficult to achieve than might be at first apparent. Almost all common imaging techniques suffer from various aberrations, notably here the lens effects that can distort the recorded image. In addition, there may be slight errors in placement that can lead to perspectival alterations.

However, as with the spectral analysis, one may make reasonable conjectures. A possible approach for example is to take a series of common features between the two images and use these for scaling purposes (that is, adjust one image so that a series of points coincide). If this correctly maps the images, other points not used in the scaling should then be expected to coincide if the images are of the same object. Detailed image processing of this kind is complex and properly requires specialised

[8] The gamma is defined as the slope of the central portion of the relationship ('characteristic curve' or 'H-D curve') between the density of the image and the exposure; a high gamma gives high-contrast images, a low gamma low-contrast images. See for example: http://photography.about.com/library/glossary/bldef_characteristic.htm.
[9] These were supplied to the present author in a dossier.

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software to implement it, though an approximation can none-the-less be developed through application of simple spatial processes (scaling, rotation, perspective distortion, etc.). This was attempted here with the available image of the Lochard photograph, a colour photograph of the painting and the transmitted infrared image of the painting, digitised images being manipulated using common tools[10]. Example results are presented at the end of this report, but it is perhaps sufficient to report here that the probability is very high that the Lochard image is of the same painting – it was found that overlay images of the Lochard photograph scaled remarkably well to match the painting.

Comparison of the transmitted infrared image with the wet-collodion image

A composite mosaic created from transmitted infrared images was prepared. This is broadly similar in principle to a previous image taken during the Boston MFA research, although the technical details differ[11]. The image that results from transmitted infrared will be dependent upon the presence within the paint structure of materials that are relatively infrared-absorbent. Typically these are pigments such as carbon-based blacks (which absorb IR very strongly), although others, such as Prussian blue, are also strongly IR absorbent. In consequence it is also useful to know about the detailed composition of paint layers as part of such studies. Such matters have been addressed in later sections of this report.

We may none-the-less remark that it is quite striking how similar details of this image are to the Lochard photograph. Neglecting for the moment the areas discussed above as being difficult to model from the reflectance data, the areas rendered particularly well in comparison to the Lochard image are the upper torso and much of the skirt. For example, the definition of the dress against the pillows of the divan follow very closely, as do lines across the waist of the dress and the bulk of the skirt laid out to the right (sitter's proper left). The woman's head is also quite similar in form and volume. However, the comparison appears to break down in the fall of the skirt at the bottom centre of the painting. It is clear that there is a greater density of paint in this region, much as has been found from the other imaging experiments described to this point. Additionally the darker background running around the top and back of the woman is only weakly present in the infrared image, whereas is a very noticeable feature of the Lochard image (in the IR, it is possible to make out some of the shading in the right-hand section). Close examination of the painting under low-power binocular microscopy suggests that the reason for this is likely to be that the shading is based on relatively IR-transparent brown pigments, as opposed to the black pigments that show most strongly in the dress. Conversely, the blue of the divan to the left also shows up poorly, though we might have anticipated this to be of greater IR density; the explanation here is likely to be the relative thinness of the paint.

To enable easier comparison of the Lochard image and the IR transmittography, an overlay diagram has been prepared (see Plate 7).

X-radiography

In addition to the infrared imaging discussed above, the painting was also examined using conventional X-radiography. These are standard techniques within the field and are substantially

[10] Work was carried out in Adobe Photoshop version 7 with extensions from FoveaPro version 2. It was found that by altering the transparency of the Lochard photograph, areas such as the face and details of the skirt could be made to coincide, with other elements also coming into close correspondence.
[11] In fact the main difference is the relative spectral responses, with the technique used here sensitive further into the infrared part of the spectrum.

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complementary in terms of the types of material that they may image[12]. Trivially, the image resulting from X-radiography is often dictated by the presence and distribution of X-ray dense pigments (such as those based on lead) and their physical thickness. Infrared imaging (reflectography and transmittography) on the other hand is suited to determination of features where there is an inherent IR contrast, such as with a drawing based on an infrared absorbing material overlying an infrared reflective substrate beneath paint layers that are of greater transparency in the infrared part of the electromagnetic spectrum (one of these pigments is, interestingly, lead white).

The radiograph was prepared in the present case to make specific study of the upper paint layers. This was so that an evaluation could be made of whether there was any evidence of substantial additions to the painting. In such a study, one typically looks for evidence of damage or alteration that could be underlying, such as where there are specific losses or craquelure that have become in-filled with later paint applications. However, the radiograph of the painting is dominated by the ground (because it contains lead white) rather than the upper paint layers (which, by and large, do not contain significant amounts of X-ray dense pigments). Consequently the X-ray image is largely composed of an image of the canvas support (because the ground penetrates into the interstices of the fabric) and some elements of the pictorial composition such as the white and lighter blue paint on the divan and (more weakly) the woman's face.

However, detailed examination of the X-ray plates shows that there are some very minor damages and a fine craquelure across the painting, there apparently penetrating the ground and paint layers. By study under magnif ication it is possible to see that there is no evidence (especially where there are denser layers present such as the white/lighter blue noted above) of either in-filled or overlain cracks. Consequently there is no evidence for later additions of paint from this[13].

The pigments

Pigments were identified from a series of samples taken from a wide range of locations so as to determine whether there were consistent similarities or differences across the painting.

The principle pigments identified optically in the paint samples were lead white (presumably lead carbonate hydroxide), the chromium oxide hydrate known as viridian, Prussian blue, (synthetic) ultramarine, a red 'lake' and various iron oxide/hydroxide based pigments (perhaps as a range of both naturally and synthetically derived pigments). Additionally, elemental analysis showed the further presence of cobalt blue (determined by joint presence of aluminium and cobalt), lead antimonate ('Naples yellow'; from the presence of small amounts of antimony in addition to lead) and zinc white (zinc oxide); the further identification of low levels of arsenic in one sample might imply the inclusion of 'emerald green' (copper acetate arsenite).

All such pigments identified to this point appear to be consistent with those that might have been used in France in the 1880s. None are of types with known dates of introduction post-1883.

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[12] A good introduction to the principles and practice of radiography of historical artefacts can be found in: Lang, J.; Middleton, A. (eds.) *Radiography of Cultural Material* Butterworth-Heinemann (1997). No equivalent single-volume introduction to infrared reflectography of paintings exists although the following (and references therein) form a reasonable general starting point: Bomford, D. (ed.) *Art in the Making. Underdrawings in Renaissance Paintings* National Gallery Co. Ltd. (2002).

[13] It is however to be understood that paint layers added early in the life of the painting could crack with, and in a similar manner to, any prior underlying layers.

From a more specific perspective, comparison with the handful of analyses of paintings by Manet provides an interesting point of reference, even though these tend to relate to more elaborated works. In particular, we might compare Manet's *Corner of a Café-Concert* (National Gallery, London; NG 3858; also known as *The Waitress*), a complex picture in that it was much altered by Manet, but not greatly dissimilar in date (1878)[14]. Additionally, the less-altered but somewhat earlier *Music in the Tuileries Gardens* (also National Gallery, London, dated 1862; NG 3260) provides further comparison[15].

Both of the National Gallery paintings contain a wide range of pigments. The *Café-Concert* was analysed to show the presence of cobalt, ultramarine and cerulean blues, red lake and vermilion, lead antimonate yellow, chrome yellows and oranges, chromium oxide hydrate, lead white and 'ivory' black. In the *Tuileries Gardens* a range of pigments was identified encompassing Prussian and cobalt blues, vermilion, lead antimonate (as well as an apparently manufactured 'shade' version), lead chloride oxide ('Merimées yellow'), yellow lake and yellow ochre, chrome orange, chromium oxide hydrate as well as copper acetate arsenite and 'Scheele's green' (copper arsenate compounds), lead white and 'ivory' black.

Several points may be drawn from this information. First, both lists are quite extensive, with multiple pigments of each broader colour range – between the two paintings four distinct blues have been used for example, while the *Tuileries Gardens* sports five yellows alone. In fact, when one studies the analyses closely, it is also clear that Manet would also mix numerous pigments together to obtain a shade he wanted – so, not only did he have a complex palette, he also mixed colours in a complex way[16].

Returning to the *Femme Allongee*, we can now see that the extensive number of pigments identified within the structure of the painting woul no be surprising for Manet and that, rather, we should expect and anticipate this. urther, the individual samples show mixtures that are not necessarily simple – not as many as with some samples from the *Café-Concert* perhaps, but none-the-less indicative of an artist using multiple pigment mixtures to achieve specific colours.

There was also no discernable pattern such that some areas had significantly different composition in terms of pigments used. That is, there were no obvious instances of similar colours in different parts of the painting having been executed using markedly different combinations of pigments.

Paint media

Study of the paint media was, in this case, targeted less at determining the type of binding medium used (such as linseed oil) than at establishing whether there was any discernable or determinable difference between a range of areas on the painting. The supposition here was that by comparing similar types of paint (that is, containing broadly similar pigments) one might expect to find different levels of components within the binding media if they had been applied at widely differing dates. Presentation of the full interpretation of the chromatograms and associated mass spectra is outside the scope of the present repo rt in that it is highly complex; therefore only a brief summary will be given here. In essence, no significant differences were found among the four samples analysed – all were

[14] See: Bomford and Roy (1983).
[15] See: Bomford *et al* (1990).
[16] This is not untypical of this group of artists.

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largely consistent in terms of the ratios of principle components of fatty acids and presence of minor compounds. Such differences as were detected are likely to be due to normal statistical variation or localised effect of particular pigment mixtures involved.

Stratigraphy

Study of the paint layer stratigraphy is relevant to this case in that it is necessary to show whether or not there are significant identifiable additions to the structure. Normally one is looking for key features within a layer structure that might indicate the passage of significant amounts of time (that is, years rather than months or days) between successive strata. The most frequently identified features of this type are usually intermediate dirt layers, discoloured varnish, lacunae or other forms of surface deterioration occurring within a sequence.

Initially four samples were removed from the painting and prepared as cross-sections. At least one of these contained the entire sequence from canvas fibres to the uppermost varnish layer extant on the picture; therefore the ground and some primary paint layer structure can be described with confidence. The locations for these four samples were not ideal in some respects (for example, the examination of the stratigraphy in areas difficult to interpret by the imaging discussed above did not coincide with convenient losses) but, despite the potential for additional information, it was felt that the invasive nature of cross-section sampling could not be justified ethically.

Again, there is a series of points that can be made. In none of the samples taken was there evidence of dirt layers or other such clear indications of discontinuity. Typically, if a surface is left exposed for any significant period of time, then various alterations can take place, from build-up of atmospheric particulate dirt to physical and chemical alteration of the upper surface of an exposed film. With varnishes this is often visible as yellowing and cracking; with oil paint films differences are sometimes visible with ultraviolet fluorescence microscopy as diffuse surface bands. None of these specific phenomena could be discerned in the samples.

One of the cross-sections (sample 13) did however contain an unpigmented layer consistent with a varnish between the lower blue and upper green layers. As already commented, detailed examination did not reveal clear indications of extended time intervals as having occurred between the applications of these strata. On the other hand, if the unpigmented 'varnish' and green layers had been added sufficiently early in the life of the painting, then there might not have been sufficient time for alteration phenomena to have become manifest.

Other direct comparisons of stratigraphy with the *Café-Concert* and the *Tuileries Gardens* are less justifiable, the former because of the major nature of the alterations, the latter because of the significantly different date. At the same time, we might note Manet's working method as described from the latter of these paintings. It is clear in the *Tuileries Gardens* that Manet sketched out his figures with 'a few thin lines and washes of dark colour which [...] are still partly visible'. Bomford *et al* also note that after Manet lay-in the initial figures, specific likenesses were added[17]. This approach would seem to be paralleled in the *Femme Allongee*, where an initial simple sketch has evolved into a more detailed portrait.

[17] Bomford *et al* (1990) 117

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In addition to this examination of paint cross-sections, extensive study of the surface of the painting was carried out using low-power binocular microscopy (already alluded to in previous discussions here). The function and purpose of this was multifold, in that it was both a prerequisite to the sampling described above, a means of establishing the location and distribution of later restoration and a functional method of resolving some of the questions regarding the sequence and manner of evolution in the painting. A group of indicative surface microphotographs has been included in this report (Plates 9a-p).

Briefly, it was clear from the examination that there was evidence for a relatively modern, but extremely localised, restoration intervention. However, close examination of critical areas where there are perceived differences between the Lochard photograph and the painting as it currently stands indicated that there are also other qualitative differences in the paint, seemingly more integral to the composition. In particular we might note the numerous areas in the painting where there are thinly applied paint layers lying over the ground, often exhibiting what looks like abrasion (though could be original, through 'wiping-off'); these must correspond to the earlier phases of the design. On top of this are thicker layers of paint, which none-the-less show forms of deterioration consistent with the earlier strata (for example, the craquelure and other lacunae pass directly through all these layers, without the upper layers lying over them). This confirms the findings from the paint cross-sections, which seemingly imply that the preliminary paint layers are essentially continuous with the upper layers, bar the few much later interventions specifically noted. Rather, the conclusion should be that the painting was to all intents and purposes produced continuously without significant later alteration. (Reconciling this observation with the apparent differences between the Lochard photograph and the extant painting will be touched upon in the following summary.)

It is difficult in practice to place an upper limit of the length of time that could have elapsed between the application of the lower and upper layers in the painting; however, the seeming continuity and the apparent absence of intermediate dirt layers or suchlike probably suggest a relatively short period, perhaps days to a few years rather than decades.

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Conclusions

From the various investigations reported above we can now draw together a series of points regarding the likely evolution of the painting and the position of the Lochard photograph vis-à-vis forming a historical record of the painting. At the outset of this summary though we must underline that there are remaining questions concerning the performance of Lochard's photographic technique. The analyses and conclusions that relate to how, for example, the *Femme Allongee* might notionally appear in a Lochard photograph, are based on reasoned, but none-the-less conjectural, interpretations of responses. However it has been possible to demonstrate that there are basic features of the painting's composition that align very precisely with the Lochard image. Specifically, we might highlight the numerous details of the figure that coincide exactly with features picked up through techniques such as the infrared transmittography.

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APPENDICES

A1. Samples

All samples were taken following standard approaches.

Table 1. Summary of samples and analyses

#	*Sample Description*	*Location*	*PLM*	*CSA*	*EDX*	*Other*[18]
1	Blue/green	102/255	* (1)		* (1)	UV-Vis-NIR
2	Green	94/238	* (2)		* (2)	
3	Pale blue	92/219	* (3)		* (3)	
4	Dark blue	23/186	* (4)		* (4)	UV-Vis-NIR
5	Pink (of hand)	125/263	* (5)		* (5)	
6	Dark pink	139/289	* (6)		* (6)	
7	Pink (of neck)	238/312	* (7)		* (7)	
8	Pink (of face)	220/340	* (8)		* (8)	
9	Brown	111/323	* (9)		* (9)	
10	Brown	187/323	* (10)		* (10)	
11	Green			* (C)		
12	Blue			* (D)		
13	Green			* (E)		
14	Blue			* (F)		

[18] GC-MS = gas chromatography/mass spectrometry; UV-Vis-NIR = UV-visible-near infrared transmission microspectrophotometry.

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A2. Analytical methods.

Polarised light microscopy: The polarising microscope is a versatile instrument for the study of most of the materials encountered in paintings. Paint samples are dispersed in media of known refractive index for examination, and the microscopist then characterises a material, mixture, or compound on the basis of a series of morphological and optical properties which include size, shape, cleavage, homogeneity, colour, transparency, pleochroism, refractive index and birefringence. This last property accounts for the exquisite interference colours observed with the polarising microscope.

Sample fragments were dispersed in Cargille Meltmount$^{(C)}$ of refractive index 1.66 and analytical methods developed by the present author and others were employed to aid identification[19]; additional comparisons were made to well-characterised reference material in the authors' collection. A Leica DMRX microscope with magnifications in the region of 100x to 1000x was used. PLM identification of the materials discussed was straightforward and was based on both observed morphology and comparison to reference samples. Also, PLM is not generally regarded as a technique providing definitive identification and therefore the analysis should be considered provisional unless or until confirmed by other methods.

Table 2. PLM Results

Sample	*Sample Colour*	*Identification*
1	Blue/green	Lead white, synthetic ultramarine, chromium oxide hydrate
2	Green	Prussian blue, chromium oxide hydrate, iron oxide, lead white
3	Pale blue	Lead white, calcite, trace of Prussian blue, iron oxides/hydroxides (hematite and goethite)
4	Dark blue	Prussian blue
5	Pink	Lead white, an iron oxide-based pigment, traces of chromium oxide hydrate and ultramarine
6	Dark pink	Iron oxide-based pigment, red lake, ultramarine
7	Pink	Lead white, iron oxide-based pigment
8	Pink	Lead white, iron oxide-based pigment
9	Brown	Probably a brown ochre with lead white
10	Brown	Probably a (different) brown ochre

Cross-sectional analysis: The study of paint layer structure is a powerful means of analysis which can not only assist in elucidating the sequence of application of paint but also permit analysis of pigments and media. Paint cross-sections - "thick cross-sections" - typically consist of small fragments of material embedded in a synthetic resin block which is then cut and polished to reveal the edge-on layer structure. The resulting sections are then viewed using reflected light under a suitable microscope, either with ordinary light or else with ultra-violet light (UV). Media-specific stains and other reagents may be applied to give topographical identification and localisation of components within the structure. For the present study a fragment was taken from each of the samples removed from the object and mounted in a polyester setting resin. These embedded specimens were then ground using successively finer grades of abrasive paper (400 to 800 grade) to reveal the layer structure; specimens were finally polished with 4000-12,000 grade abrasives to achieve as optically flat a surface as possible. Specimens were examined by both light microscopy and ultra-violet fluorescence microscopy on a Leica DMRX microscope with magnifications in the region of 100x to 1000x.

UV/Visible/near-IR spectrophotometry: This technique was used to perform direct colour measurement on the painting as well as to confirm some PLM identification. This technique involves capturing transmission or reflectance spectra in the ultra-violet to infrared range of the electromagnetic spectrum, in this case around 350-850nm. From comparison of the spectra to known standards it is possible to differentiate a number of pigments. By mounting the spectrophotometer on a microscope it is further possible to analyse individual pigment particles down to sub-micron size. Equipment used for this work was an Ocean Optics S2000 spectrometer connected via fibre-optic cable to a custom modification of the camera port of a Leica DMRX microscope. Analyses were principally carried out using a 100x oil-immersion objective lens. Output from the spectrometer was digitised through a National Instruments DAQ-700 PCMCIA card into a Sony Vaio PCG-Z600LEK computer running SpectraWin v.5.0 software.

Scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX): In the practical application of the SEM-EDX technique the sample (and therefore the composite atoms of the sample) is excited by a source of energetic radiation, in this case the electrons from the microscope beam. X-rays are released during subsequent de-excitation that are

[19] Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *The Pigment Compendium. Optical Microscopy of Historical Pigments* Elsevier (2004).

characteristic of a particular element - "X-ray fluorescence"; these can then be detected, measured and identified. A detector detects the various energies or wavelengths of X-ray being emitted, and the signals from the detection device are then converted into some readable form by the instrument. The precise form of the instrument (X-ray or electron source, detector type and so on) determines the range of elements that can be satisfactorily determined, so that it is important to select the most appropriate system for the circumstances. Detection is carried out in one of several ways, the most common perhaps being that known as energy dispersive X-ray spectrometry - EDX. This introduces limitations of its own, particularly with respect to the ability to resolve X-rays emitted by different elements, and therefore wavelength dispersive detectors are also employed. Clearly the application of SEM-EDX is complex in that there are many parameters that must be assessed for proper interpretation.

Identification of carbon alone (or with oxygen) in a sample usually implies analysis of an organic phase within the material. The presence of silicon and elements such as aluminium, potassium and manganese with iron often imply the use of a naturally occurring earth pigment; manganese specifically implies use of those pigments commonly referred to as Siennas and Umbers. Elements are listed as having **Major**, Minor or *Trace* levels based on relative peak heights. Listings (a), (b)... represent analyses in different areas or points of the sample.

Table 3. EDX Results

Sample	*Sample Colour*	*Elements*
1	Blue/green	a) **Pb** C O b) **C** *Cl*
2	Green	a) **C** *Cl Ca Cr* b) **C** Cr *Fe Cl Si*
3	Pale blue	a) **Pb** Al *Co* b) **S** Ca *Al*
4	Dark blue	a) **Al** Pb *Co* b) **C** *Cl Ca*
5	Pink	a) **Pb** *Zn Sb* b) **C** c) **C**
6	Dark pink	a) **Pb** *Al Fe* b) **Si** Al K Fe *Mn*
7	Pink	a) **Pb** Zn Al Si *K Ca*
8	Pink	a) **Pb** Si *Zn Sb* b) **C**
9	Brown	a) **Pb** Fe *Ca*
10	Brown	a) **Fe Pb** As *Al Cu* b) **C** Zn Cl *Si*

Gas chromatography-Mass spectrometry (GC-MS): GC-MS involves changing the oils and other components present in a sample into volatile compounds – 'derivatising' – and then passing them in the vapour phase through a fine capillary packed with an absorbent material. Competition for molecules of different forms between the gas and the static absorbent leads to separation of the components. Mass spectrometry is a method of determining the size of molecules and characteristic patterns of fragments formed when those molecules are broken up.

Whole fragments from the samples were used for this analysis and therefore the results may reflect the composition of any stratification still present. Methylation of the samples for analysis was conducted according to the slightly modified method of MacGee and Allen as published by White and Pilc[20], which gives improved results over the previous and widely used method involving diazomethane. In this method, derivatisation is conducted in a single-stage process with the reagent trimethyl(α,α,α-trifluoro-*m*-tolyl)ammonium hydroxide ('TMTFTH'; 5% in methanol). Samples were placed in a small glass vial with about 50µl of the TMTFTH reagent and placed in an oven at 50°C for 4 hours; on cooling, 1µl of this was injected with a 10:1 split into the GC-MS. The equipment used was a Varian CP3800 GC with Saturn 2200 MS-MS ion trap and a 30m capillary column with 'CPSil8' stationary phase. The oven temperature started at 100°C, held for 1 minute and then ramped up at 8°C.min^{-1} to 320°C. The injection port was at 300°C. Standard methyl ester mixes were injected as a 2µl aliquot split on at 1 minute.

[20] MacGee, J. & Allen, K.G. "Preparation of Methyl Esters from the Saponifiable Fatty Acids in Small Biological Specimens for Gas-Liquid Chromatographic Analysis" *Journal of Chromatography* **100** (1974) pp.35-42. White, R. & Pilc, J. "Analyses of Paint Media" *National Gallery Technical Bulletin* **17** (1996) pp.91-103.

Infrared reflectography/transmittography: Examination of objects in the infrared is commonly accomplished using an infrared vidicon system; such systems are sensitive to infrared of much longer wavelength than is the case with photographic emulsions and superior results can often be obtained as a result. An infrared vidicon is an electronic device which employs a tube with a photo-conductive material which allows an infrared image to be converted to an electronic (television) signal. The television signal can be viewed on a monitor and/or digitised into a computer - as in this case - from which a permanent record can then be made. A suitable source of infra-red light is also required for illumination.

Equipment used in this study for the infra-red reflectography/digital image processing (IRR/DIP) was a Peca 1010 camera fitted with an English Electric XQ1615 infra-red 2/3" Leddicon (sensitive to 2200nm, also with auto-gain circuitry that was employed), a Fujinon C6x17.5B zoom lens and a range of 'c' mount extension tubes (1mm-10mm) for producing the macro images. A 150W tungsten-halogen lamp was used as the infra-red source and a 1000nm cut-off filter (*not* Kodak Wratten) employed to remove visible light. The images were captured using a Hauppauge USB-Live with Sony Vaio computer. These were then transferred to a dual 733MHz Pentium III computer with Adobe Photoshop Ver. 7.0.1. There, images were contrast-stretched (most tended to have a bit-depth of about 7) and a combination of median and sharpening filters applied to remove noise and correct for the 'softness' of the original IR images. The images were retained as (loss-less) BMP files throughout the process.

It should also be noted that:

- Various filters and filter combinations are normally used for the IR reflectography, and that arrangement judged visually to give the optimum resolution was selected for obtaining the final images;
- The IR images will not *necessarily* differentiate between materials of different composition, so a degree of caution should be applied when reading the images;
- Infrared reflectographic images tend to be 'softer' in appearance than conventional photographs, due to the nature of the technique; some digital sharpening has been used to compensate for this.

X-radiography: In the conventional X-radiography of paintings on canvas an X-ray tube is directed toward the object and the radiographic image is recorded on a film that is placed on the other side of the painting. Better resolution is often achieved if the film is placed adjacent to the painted surface and irradiation is from the back. In any case, the resulting image depends on the fact that different areas of the painting transmit X-rays to a greater or lesser extent. Areas that do not, relatively speaking, transmit X-rays appear lighter on the X-radiograph. This will result from the combined effect of several factors including thickness, density, and the average atomic number of the chemical elements present. So, for example, lead white (which is a frequent component in paint) is often found in highlights that, because of its X-ray density, tends to block the exposure of the film, thus giving whiter areas. This pigment is also commonly used in grounds and tends to concentrate in the interstices between the canvas threads making the pattern of the canvas visible in the radiographs. On the other hand, organic materials such as the canvas itself, varnishes, or organic pigments and dyes are usually transparent to X-rays.

The radiograph was prepared using industrial X-ray film with an exposure at 50kV at 10mA for 30 seconds, the tube distance being *ca.* 1.5m from the painting. The individual plates produced were then digitised. Some changes to the contrast were also made so that images became as readable as possible.

UV fluorescence: The phenomenon of fluorescence - where a substance absorbs light of one wavelength (often in the ultra-violet, blue or green parts of the spectrum) and re-emits light of a longer wavelength - has a number of applications in the study of paintings. Most commonly the fluorescence of aged varnishes is used to show the presence of any disturbance to that varnish; discontinuities caused by cleaning (varnish removal) or the application of overpaint can show as dark regions within the lighter field of the fluorescing varnish. However, there are other fluorescences (such as those of pigments) which can be detected. Most importantly though it must be kept in mind that UV fluorescence is essentially a surface phenomenon in this context and varnish fluorescence can effectively mask features such as restoration overpaint residing beneath that layer. The painting was studied in this instance using UV/blue fluorescent tubes as excitation source.

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A3. Illustrations

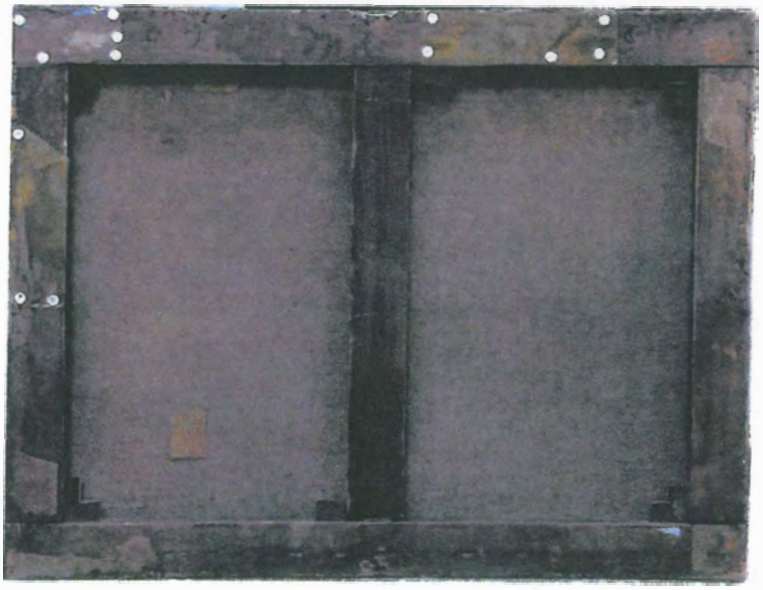

Plate 1a, b. The painting and the reverse.

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Plate 2. The Lochard photograph.

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Plate 3. Modified photograph of the painting as it currently is. A scanned image was digitally manipulated to emulate what might be expected of a blue-sensitive photographic process. While many of the features of the Lochard photograph are reproduced, other elements of this image are not found in the Lochard image. For example, the divan does not wholly disappear here, while the background has a different distribution. It should be noted though that differences, notably the illumination on the painting for the modern photograph, are brought out during the processing and distort the general balance (the centre background and the lower left for example).

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Plate 4. Overlay diagram showing how the Lochard photograph matches the painting.

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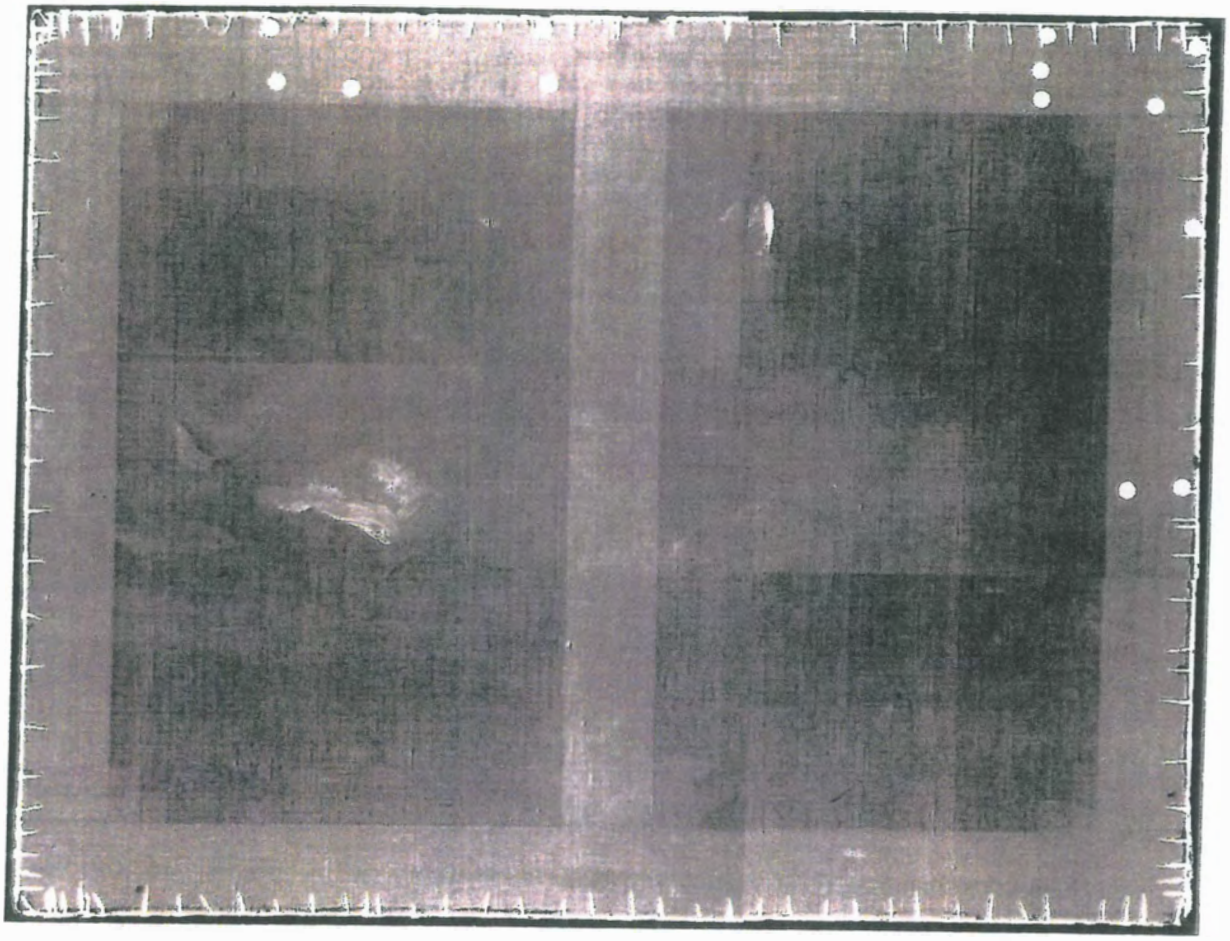

Plate 5. Composite X-radiograph

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Plate 6a. Infrared transmittography mosaic (left-hand side)

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Plate 6a. Infrared transmittography mosaic (right-hand side)

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Plate 7. Overlay of infrared transmittography results on the Lochard photograph (coloured red for contrast).

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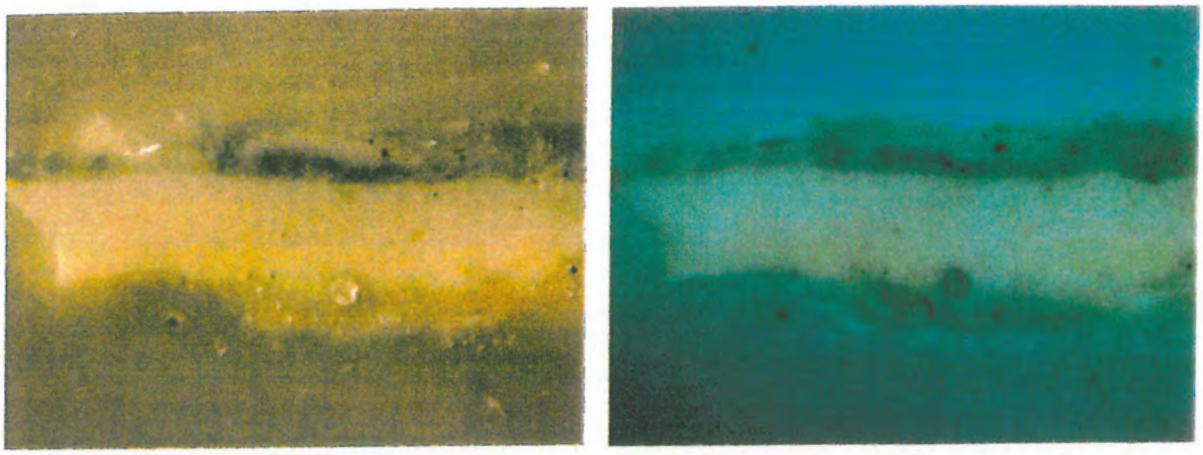

Plate 8a. Sample 11 as a cross-section, in ordinary light (left) and UV fluorescence (right)

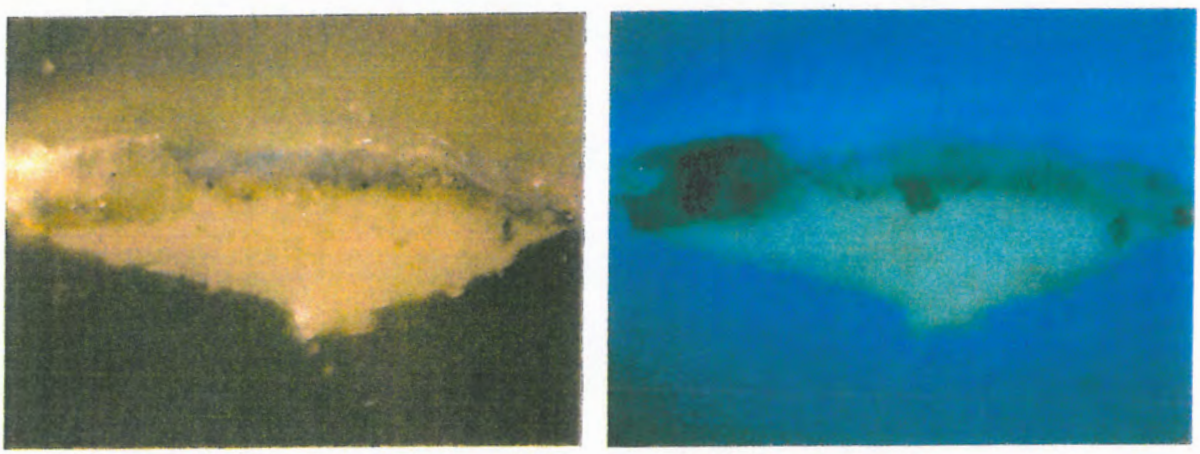

Plate 8b. Sample 12 as a cross-section, in ordinary light (left) and UV fluorescence (right)

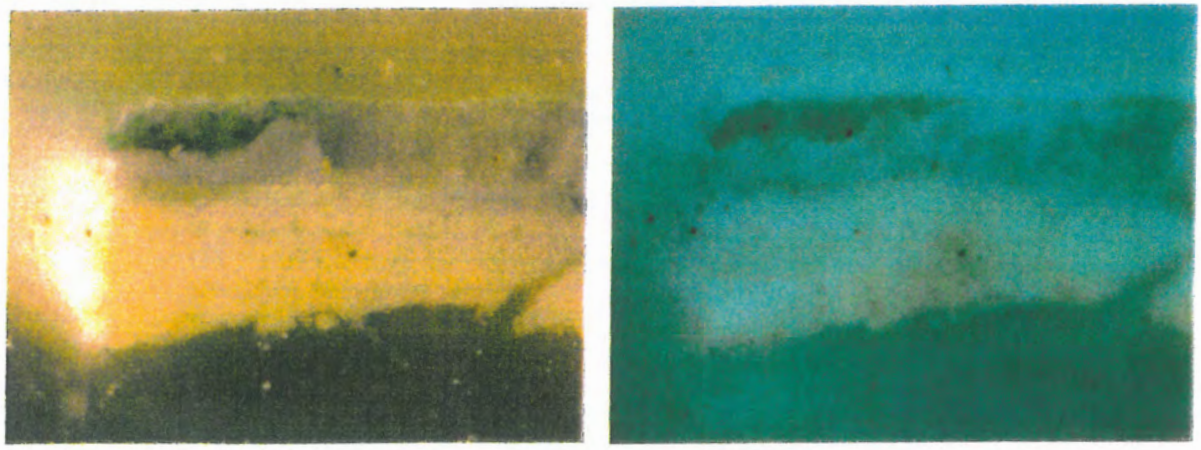

Plate 8c. Sample 13 as a cross-section, in ordinary light (left) and UV fluorescence (right)

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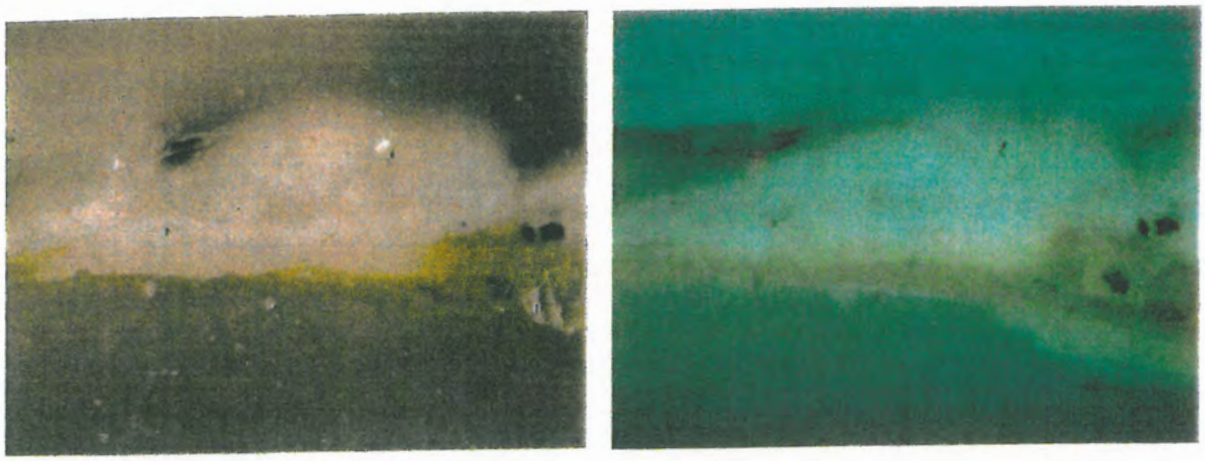

Plate 8d. Sample 14 as a cross-section, in ordinary light (left) and UV fluorescence (right)

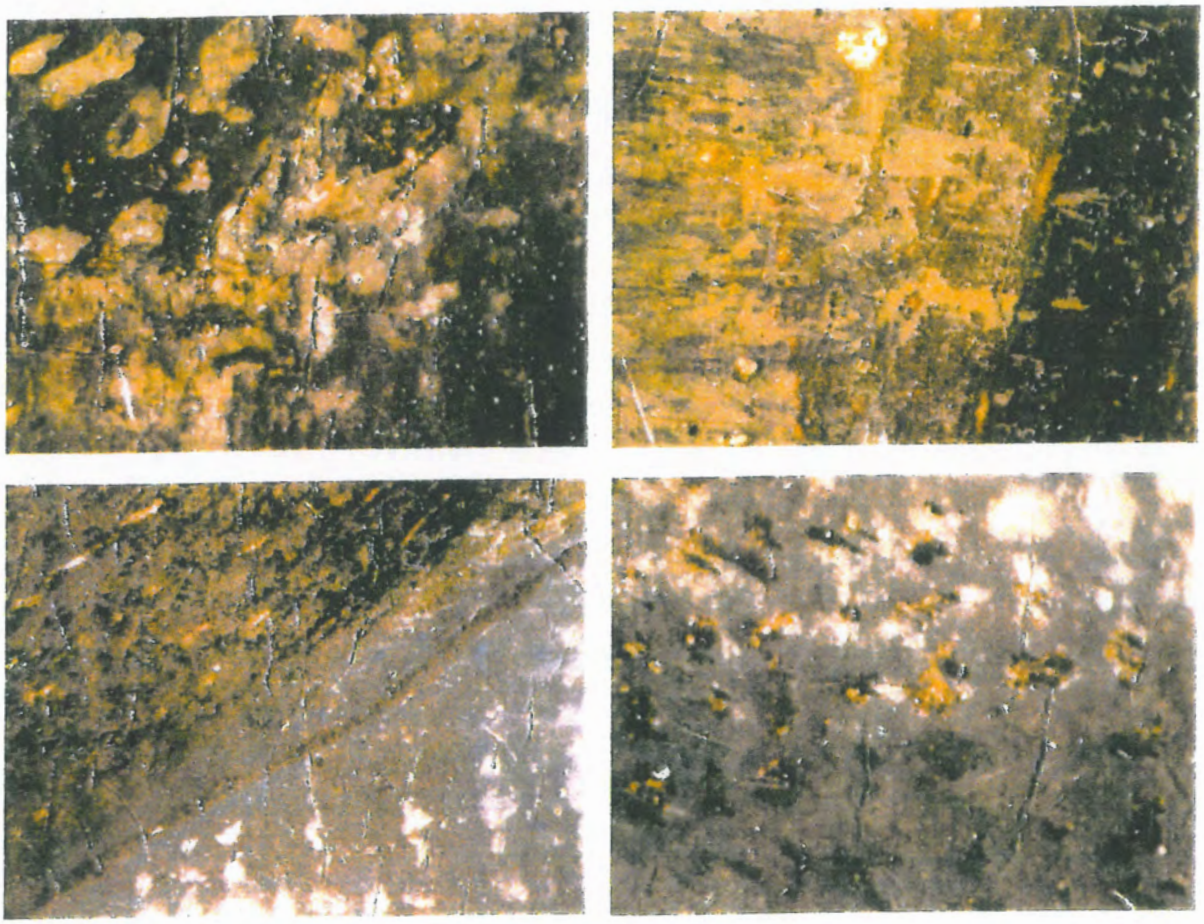

Plate 9a-d. Micro-photographs of the painting's surface

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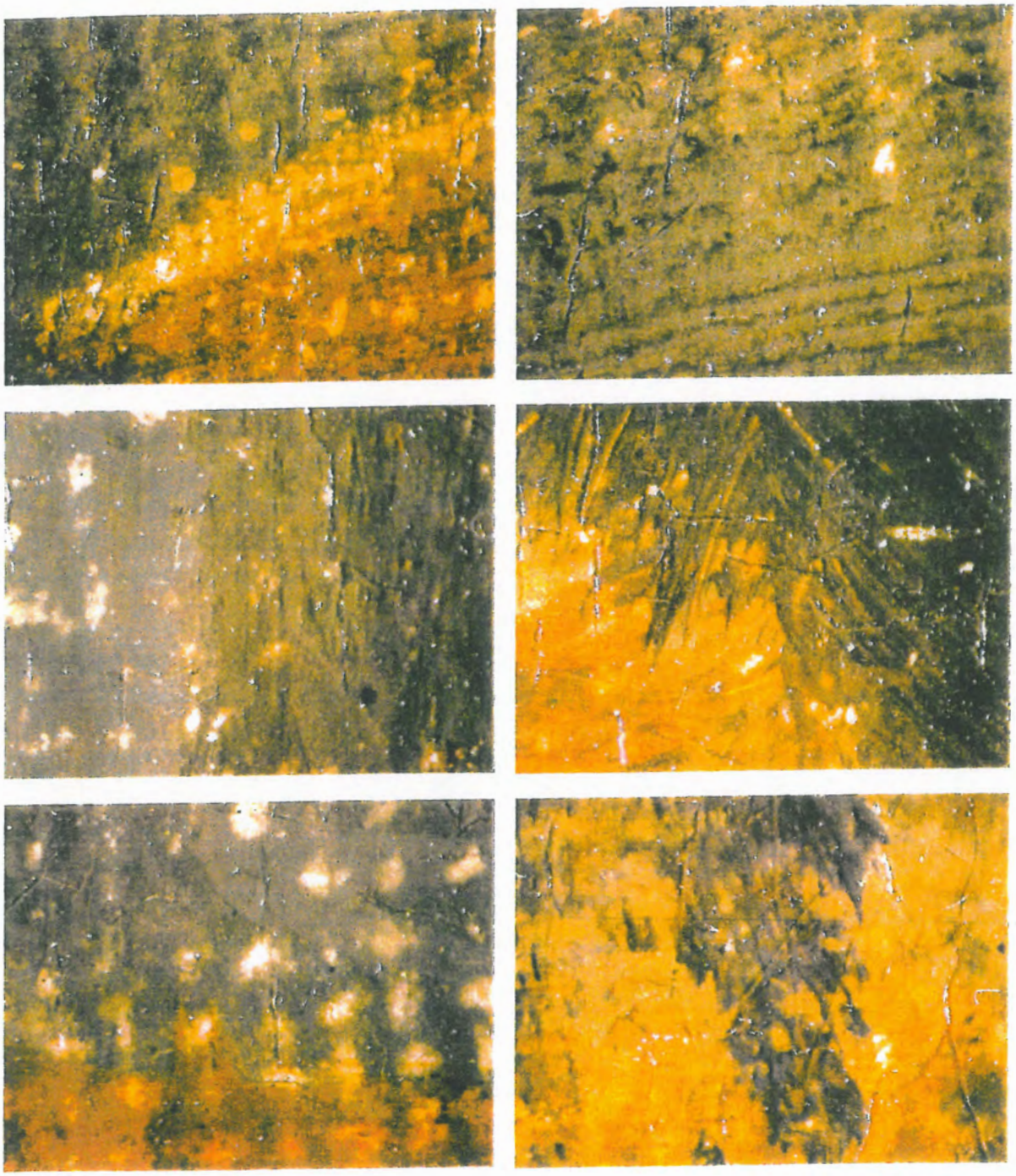

Plate 9e-j. Micro-photographs of the painting's surface

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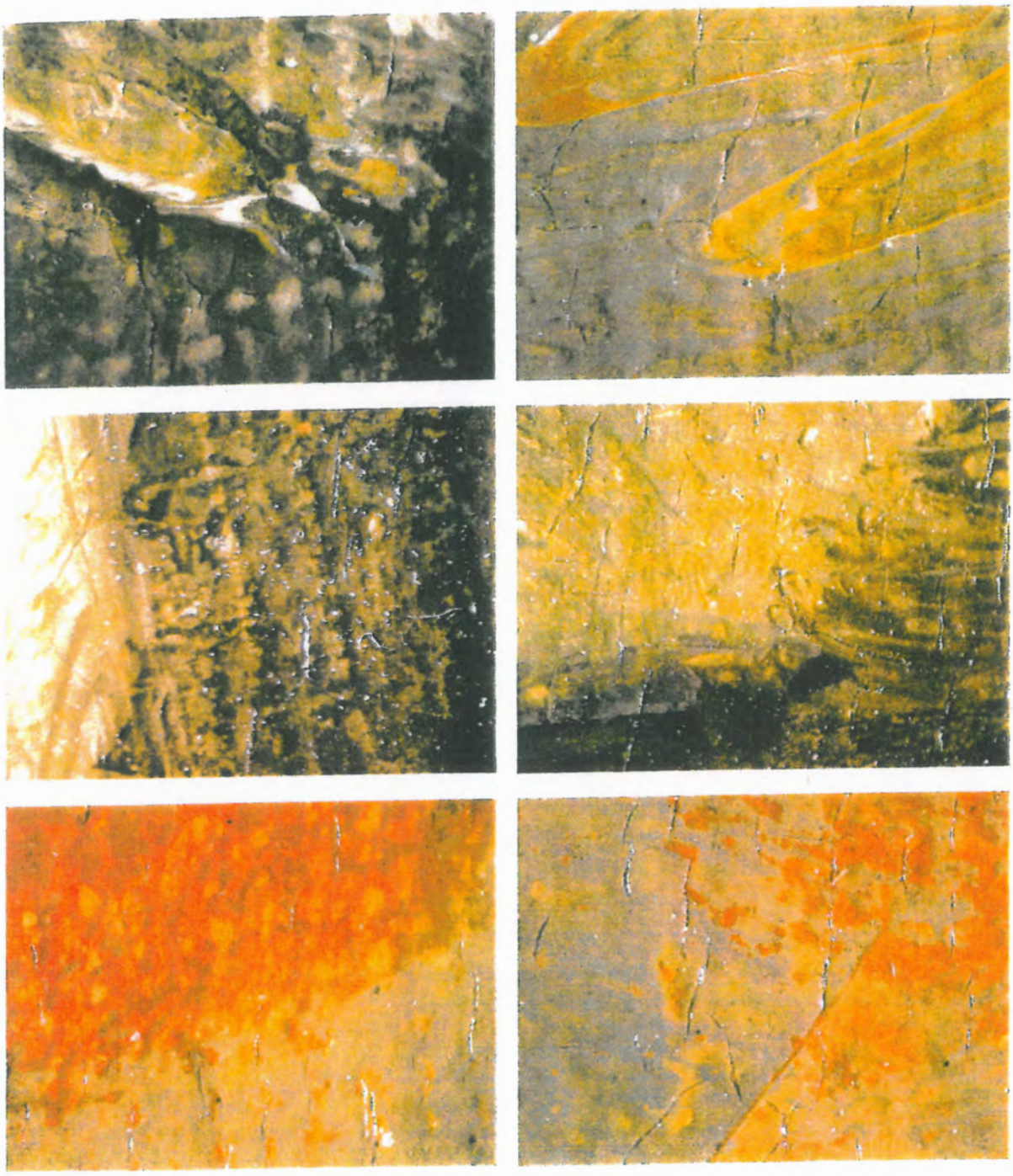

Plate 9k-p. Micro-photographs of the painting's surface

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Dr. Nicholas Eastaugh holds a B.Sc. in physics from the University of Durham (1978) and a Postgraduate Diploma in Conservation of Easel Paintings from the Courtauld Institute of Art, University of London (1981). His doctoral studies, on the history and analysis of artists' pigments, were also conducted at the Courtauld Institute of Art, this being awarded in 1988.

He has held posts at the Courtauld Institute of Art, University of London (1981-83) and the Textile Conservation Centre, Hampton Court Palace (Lecturer/Scientific Advisor, 1983-87), also taking a Fellowship at the Canadian Conservation Institute, Ottawa, Canada (1987-88). Nicholas Eastaugh is currently an Academic Visitor at the Research Laboratory for Archaeology and the History of Art, University of Oxford.

Since March 1988 Nicholas Eastaugh has been a consultant in the scientific study of paint and paintings, preparing specialist technical reports for clients examining the materials and techniques used in pictures and other artefacts. Clients from the UK and world-wide include numerous national museums, galleries and other organisations, all major auction houses as well as many leading dealers, numerous private collectors and conservation studios. Nicholas Eastaugh regularly teaches a range of conservation science and technical art history topics on various conservation and forensic science courses in the UK, and has held a number of part-time or visiting lectureships at several graduate and post-graduate institutions. He also runs regular courses in microscopy as well as frequently lecturing about his work. He has wide research interests, including developing new imaging techniques, setting up image-based databases (including establishing metadata and protocol standards) and pigment characterisation methods.

Nicholas Eastaugh is currently involved in establishing and leading the *Pigmentum Project*, an inter-disciplinarary programme aimed at developing comprehensive high-quality analytical data on historical pigments (and associated analytical protocols) in a format that can be shared within the conservation and allied fields such as technical art history and archaeological or forensic sciences[21].

In addition to numerous published papers, Nicholas Eastaugh has recently published two volumes and a combined CD-ROM (as lead author, with Valentine Walsh, Ruth Siddall and Tracey Chaplin) under the general title *The Pigment Compendium: A Dictionary of Historical Pigments* and *Polarised Light Microscopy of Historical Pigments* (Elsevier, 2004).

[21] See: www.pigmentum.org.