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Investigation of the binding media of paintings by thermoanalytical and spectroscopic techniques ☆

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Abstract

Differential scanning calorimetry (DSC) has been used to study samples taken from three paintings during treatment in the Conservation Department of the Tate Gallery. The paintings include two from the 16th century: (1) "Queen Elizabeth 1" by Nicholas Hilliard (National Portrait Gallery, London NPG 190), (2) "An Allegory of Life" (unattributed ca. 1570 British School To 5729) and (3) 19th century, Turner's 'The Opening of the Walhalla, 1842' (Tate Gallery N00533). Knowledge of the type of paint media used is of interest both to the conservator who needs to select the appropriate materials for cleaning the painting and to the art historian for documentation of artists' techniques.

In the case of the Hilliard painting it was found that a mixed oil egg medium had been used. With regard to the unattributed 16th century British painting it was found that an oil-based medium had been used. The ground layer contained, as expected, a natural glue. Samples from the Turner painting showed that different regions of the painting had been executed with different materials; the region of the sky was painted predominantly with a drying oil, the lower regions of the painting contained mixtures of oil and resin and in some cases the samples were further complicated by the presence of proteinaceous material and wax. The recorded accompanying weight change gave information on the pigment volume concentration of the samples. In each case measurements were made of both the temperature and the heat evolved during the exothermic reactions. Thermomicroscopy and Fourier transform infrared spectroscopy (FTIR) confirmed the presence of complex mixtures, particularly in the case of the Turner samples.

Keywords: Binding media; DSC; FTIR; Painting conservation; Thermomicroscopy

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1. Introduction

1.1. Paint media; dried oil studies

Gas chromatography is usually applied to the characterisation of oil-based paint media. A method was developed almost thirty years ago based on the saponification of the dried oil samples. The fatty acid composition expressed in terms of the palmitic/stearic acid ratio is used to determine the oil type present [1]. This procedure provides information only on the fatty and dicarboxylic acids which are sufficiently volatile to be detected by gas chromatography. The problem remains in characterising the composition of the polymeric oil network which forms, and of polymerized fatty acids which are liberated when the dried oil is saponified.

The application of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) on dried pigmented oil-based samples have demonstrated that the ratios of the observed exothermic peaks can provide an indication of age-induced changes which are related to changes in the polymeric network of the oil-based samples [2, 3]. This has been further substantiated by (DSC) studies on naturally aged standard samples of paint films containing basic lead carbonate and the three main drying oils used in paintings; linseed, walnut and poppy oils. It was shown that it is possible to distinguish between the oils on the basis that a higher degree of polymerisation takes place in the linseed oil than in the other two oils [4]. The peak ratio can be considered as an indicator of age-induced changes and of the extent of cross-linked oil polymeric network which forms [3]. A two-peak exothermic pattern is observed; the first peak is in the region of 220 to 250°C, the second peak is in the region of 400 to 430°C. The values of the peak ratios vary significantly between the linseed and the other two oils.

1.2. Mixed media (oil–protein/oil–resin)

A difficult problem in the analysis of paint media has always been the ability to detect the presence of mixed media such as oil–protein and oil–resin mixtures [1]. Thermooxidative degradation curves obtained by differential scanning calorimetry are particularly sensitive to the presence of additives. In a previous paper it has been established that the presence of protein affects the nature of the exothermic peaks [5]. In a study of standard samples of a similar age it has been observed that in the presence of egg protein the recorded peak ratio is lower for the mixture than for oil-based samples of a similar age [3]. In the case of mixtures involving a drying oil and other proteins for example collagen-based animal glues, or casein, the first exothermic peak broadens to include in some cases an additional peak in the region of 300–340°C [5]. The magnitude of these effects can be small particularly in aged samples from paintings and for this reason additional measurements are made using infrared spectroscopy to identify the proteinaceous material through the presence of the amide absorption bands. Recently it has been demonstrated that it is possible to detect the presence of egg yolk in egg–oil media in a naturally aged sample (50 y) containing lead white through the presence of characteristic features at 3289, 3080, 1654, 1632, 1542, and 1515 cm^{-1}

[6]. Direct temperature-resolved pyrolysis mass spectrometry (DTMS) was also used on the same samples to confirm the presence of the protein [7].

In the case of oil–resin mixtures, preliminary DSC studies on prepared standard oil and oil-resin samples have demonstrated that the addition of resin to unaged oil paint introduces an exothermic peak at temperatures between 400–600°C [8]. Unaged paint alone does not have a peak in this region. Work is in progress to understand the nature of the oil–resin interaction [9]. In aged, unpigmented samples of oil–resin varnishes the author has observed that a two-peak exotherm is observed where the peak ratio has values which are considerably higher than those observed for oil-based samples of a similar age. Independent measurements on reference resin samples have shown that the temperatures of the second exothermic peak appear in the region of 470–500°C [10].

At this stage DSC studies on available reference materials indicate that the oxidative degradation temperatures vary in approximately the following order: beeswax $\leq$ drying oils $<$ proteinaceous material $<$ natural resins. This information has assisted in the characterisation of the complex mixture of materials found in the samples from Turner's painting 'The Opening of the Walhalla, 1842' which is discussed below.

The aim of this paper is to demonstrate how the combination of thermal and spectroscopic techniques has been used for the identification of the organic materials in samples from selected paintings.

2. Experimental

2.1. Samples

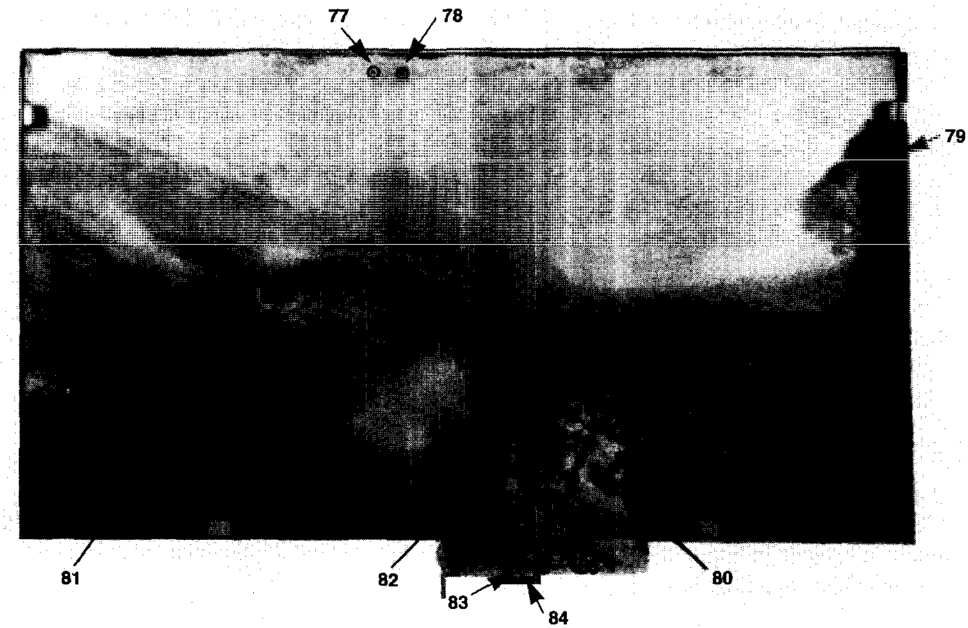
Samples were taken from different regions of the paintings. In the case of the Turner painting the sampling was carried out after the painting had been cleaned with xylene solvent gel. The various sampling positions are shown in Fig. 1. The surface was lightly scraped with a scalpel blade and the samples, removed as white powders, were stored between glass slides. Sampling was restricted to regions of white pigmented areas since background DSC information exists for naturally aged standard samples containing basic lead carbonate and drying oils [3]. Several samples were also taken from the regions of glaze. This procedure was also carried out in the case of the other two paintings prior to their cleaning.

2.2. Differential scanning calorimetry (DSC)

About 50 to 100 μg were placed in platinum micro-crucibles into a Perkin–Elmer DSC7 and heated in a stream of oxygen (60 $cm^3\,min^{-1}$) over the temperature range 40 to 600°C. The heating rate used was 40°C min^{-1}. The sample weight was recorded before and after heating by weighing on a Sartorius microbalance.

2.3. Thermomicroscopy

A Mettler FP2 hot stage was used together with an optical microscope fitted with a Polaroid camera to record the changes on heating the samples. Since the microscope



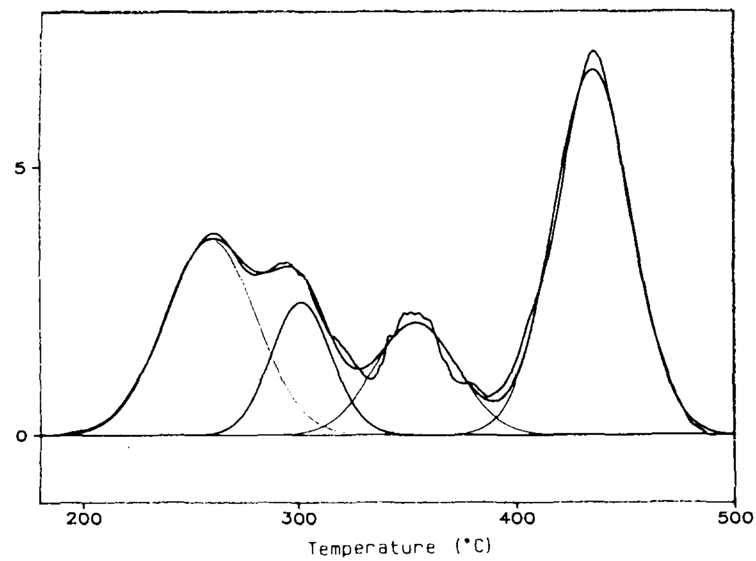


Fig. 1. "The Opening of the Walhalla, 1842" J.M.W. Turner (Tate Gallery N00533) showing the sampling positions for this study.

was set up for transmitted light, small samples from the glazes were investigated using polarised light, and then a quartz wedge at the $\lambda/2$ position, and a magnification of $400\times$. Samples were heated from 30 to 300°C at $5°C\,min^{-1}$.

2.4. *Fourier transform infrared spectroscopy (FTIR)*

A Perkin–Elmer FTIR 2000 spectrometer fitted with a beam condenser to give an effective spot size of 1.8 mm^2 and a diamond cell was used to record spectra (4 cm^{-1} resolution) in the 4000–600 cm^{-1} region. The diamond cell enables the analysis of minute samples. Since the sample is compressed it is possible to obtain spectral information in the transmittance mode. The spectrometer was equipped with aTGS detector.

3. Results and discussion

3.1. *Painting: portrait of Queen Elizabeth 1 by Nicholas Hilliard (16th cent. National Portrait Gallery, London, NPG190)*

A sample of greyish-white paint was examined from the region of the ostrich feather decoration of the dress worn by Queen Elizabeth 1 in the portrait by Nicholas Hilliard (National Portrait Gallery NPG 190). Initial FTIR analysis of the sample gave the following information. Peaks were found at (1) 2927(s), (2) 2857(m), (3) 1745(m), 1720–30 (w, shoulder peak) (4) 1655, (5) 1558 and (6) 689 cm^{-1} (Fig. 2). (Note s, m and w refer to the peak intensities: strong, medium and weak intensities of observed bands).

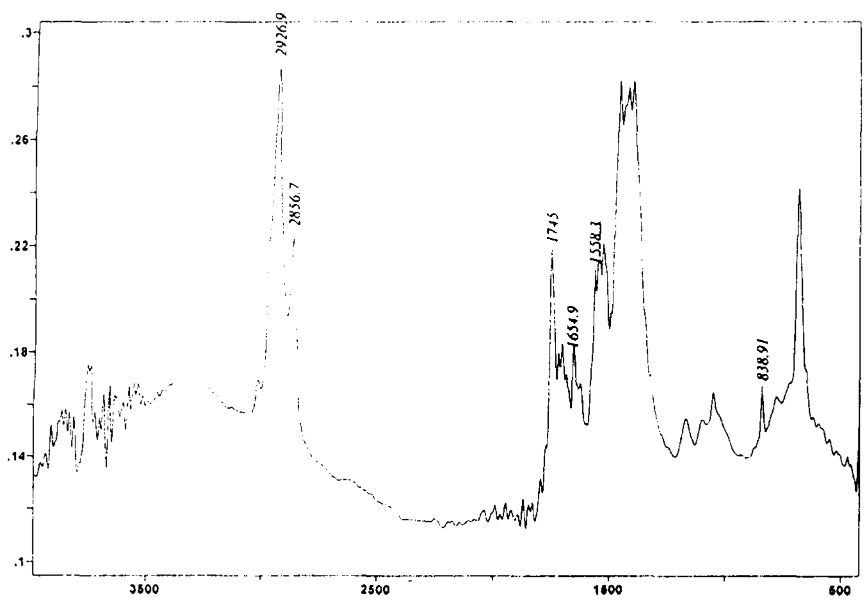


Fig. 2. FTIR spectrum of greyish-white paint from the 16th century portrait of Queen Elizabeth 1 by Nicholas Hilliard (National Portait Gallery NPG 190).

The presence of peaks (1), (2) and (3) indicate that wax is present (high hydrocarbon content and ester carbonyl); peaks (4) and (5) are characteristic of amide 1 C–O stretch and amide 11 absorbances associated with the protein of egg. Peak (6) is associated with the presence of the pigment basic lead carbonate. The small shoulder peak (4) may indicate that some drying oil is present (6). The presence of the latter was then confirmed by differential scanning calorimetry (DSC).

The resulting DSC curve (Fig. 3a) showed that the exothermic degradation occurred in two stages; a broad shallow peak over the temperature range 176–312°C followed by a stronger exothermic peak over the temperature range 366 to 483°C. The onset temperature of the second exothermic effect occurs at 370°C and it has a peak maximum in the region of 425°C. The presence of the strong second exothermic effect is indicative of the presence of a drying oil. Comparison of the DSC curve with one obtained from a sample (white) from Raphael's "Madonna del Baldacchino" (1506/8) showed a similar effect (Fig. 3b). Independent analysis of this sample by pyrolysis gas chromatography indicated that the medium was linseed oil [11]. It was also typical of the DSC curves obtained from prepared samples (1915) which contain basic lead carbonate and drying oil. From these observations it was concluded that the greyish-white sample from the ostrich feather contained a mixed oil egg medium with some wax.

A second sample from the same painting was analysed, this time of orange paint from an area of small damage at the lower edge of the painting. It was found to give the following peaks using FTIR (Fig. 4): 3535 (small, sharp), 3356 (broad, round) (w), 2927 (m), 2853 (m), 1745 (w), 1726 (w) 1633 (shoulder peak), 1545 (m), 1418 (s), 1173 (w), 1051 (m), 787 (w), 683 (s) cm^{-1}. The peaks at 3536 and 683 indicate that the pigment basic

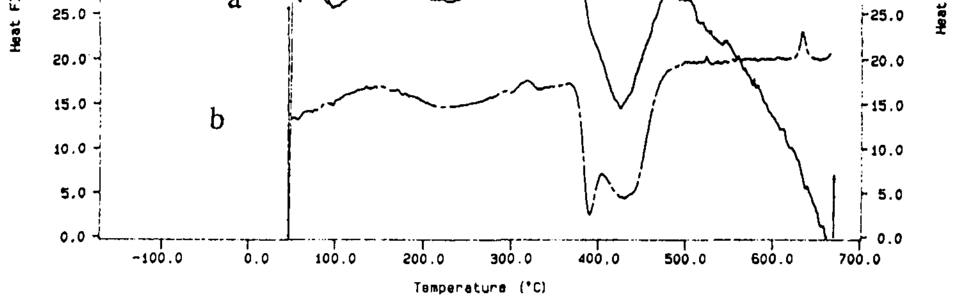


Fig. 3. DSC curve of (a) greyish-white paint from the portrait of Queen Elizabeth 1 by Nicholas Hilliard and (b) white paint from Raphael's "Madonna del Baldacchino" (1506/8).

lead carbonate is present. The orange colour was due to the presence of red lead [12]. The weak peaks at 1745 (unmarked), 1729, between 1633 and 1626, between 1545 and 1532, show similarity to the peaks observed for the greyish white sample. This indicates that the medium is similar and contains wax, protein and a drying oil. The peaks including those at 2927 and 2853 (which relate to the hydrocarbon content) are less intense than those for the previous sample. It implies that the medium content is less for the orange sample. This observation is confirmed by the fact that the orange sample was more brittle than the greyish-white one and that there was a smaller weight loss recorded after heating the sample to 650°C. The weight loss for the greyish-white sample was measured as 46.6% and that for the orange sample was measured as 34.4%. The weight change usually observed for samples containing basic lead carbonate and a drying oil only are in the range 20 to 30%. The higher values, particularly for the greyish-white sample from ostrich feather, also confirmed that components in addition to the drying oil are present. The DSC curve of the orange paint was similar to that observed from the greyish-white sample (Fig. 5). The second exothermic effect was stronger indicating that the sample contained more of the cross-linked polymeric oil network and a smaller proportion of the additional components (wax and protein).

3.2. *Painting: "An Allegory of Life" (ca. 1570 unattributed British School To 5729)*

A pale blue sample from the surface of the painting was analysed using FTIR (Fig. 6). The sample showed peaks at (1) 3542 (sharp medium), (2) 2926(m), (3) 2853(m), (4)

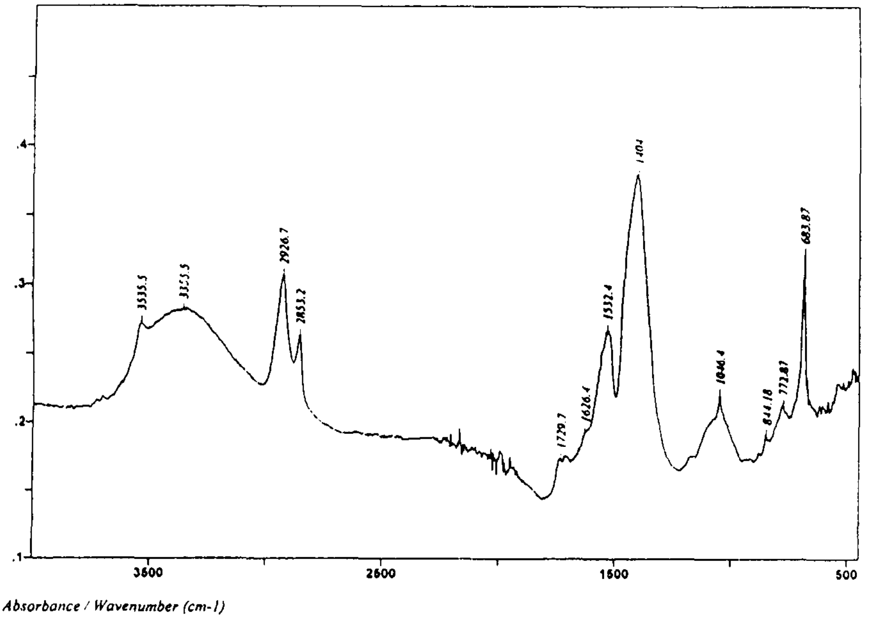


Fig. 4. FTIR spectrum of orange paint from the portrait of Queen Elizabeth 1 by Nicholas Hilliard.

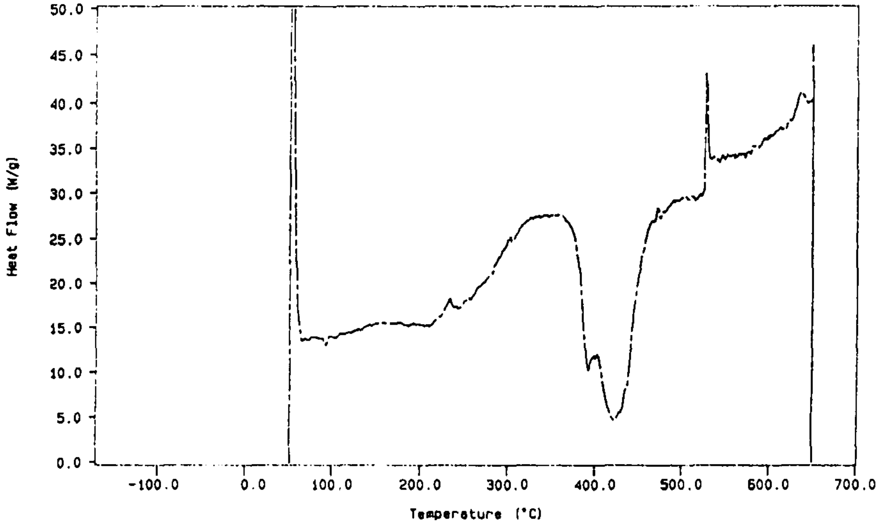


Fig. 5. DSC curve of orange paint from the portrait of Queen Elizabeth 1 by Nicholas Hilliard.

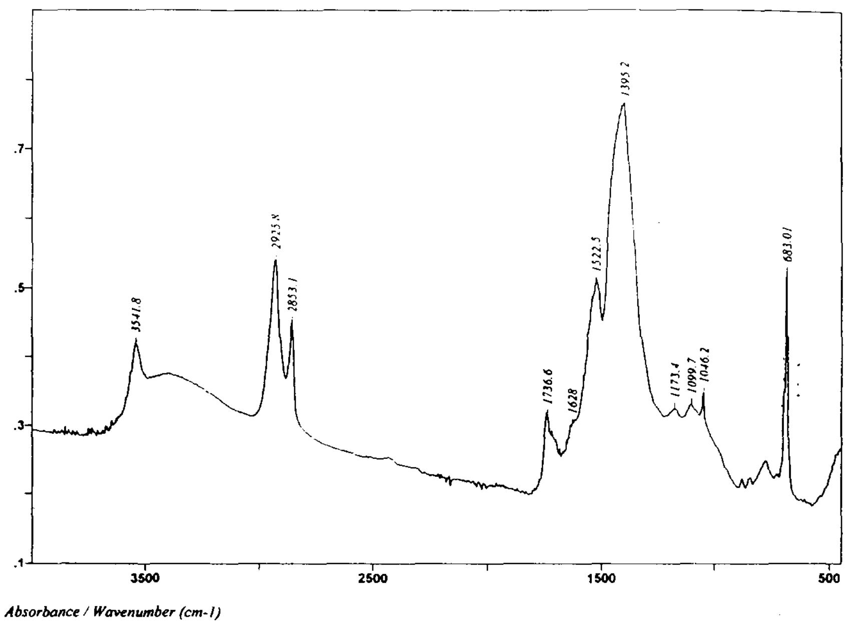


Fig. 6. FTIR spectrum of pale blue paint from the 16th century painting "An Allegory of Life" (ca. 1570 unattributed British School To 5729).

1737 (m), (5) 1628 (w) (6) 1523 (m) (7) 1395 (s) (8) 1173 (w) (9) 1099 (w) (10) 1046 and (11) 683 (s) cm^{-1}. The presence of peaks (1) and (10) indicate that basic lead carbonate is present. Peaks (1) and (11) are associated with the presence of the pigment basic lead carbonate. Peak (4) indicates that a drying oil is present. The presence of the latter was then confirmed by DSC.

The resulting DSC curve (Fig. 7b) of the pale blue sample (71 μg) showed that the exothermic degradation occurred in two stages; a broad shallow peak over the temperature range 152–317°C followed by a stronger exothermic peak over the temperature range 368 to 468°C. The onset temperature of the second exothermic effect occurs at 378°C and it has a peak maximum in the region of 430°C. The presence of the strong second exothermic effect is indicative of the presence of a drying oil. It was similar to the DSC curve obtained from a naturally aged sample (1915) of basic lead carbonate and drying oil (Fig. 7a). It was concluded that the plae blue sample contains as a medium a drying oil (probably linseed oil) together with basic lead carbonate. The percentage weight loss was recorded as 32.5% which is the value expected for standard basic lead carbonate and oil films heated over this temperature range. The residue was a deep orange yellow in colour, lead (II) oxide (PbO).

A white sample of priming or ground layer was analysed using (FTIR) (Fig. 8). The sample showed peaks at (1) 3412 (m), (2) 2922 (m) (3) 2855 (m), (4) 2515 (m) (5) 1798 (6) 1653 (m) (7) 1403 (s) (8) 1091 (w) (9) 876 (s) (10) 714 (s) cm^{-1}. The presence of peaks (5) and (9) indicate the presence of carbonate. Peaks (2) and (3) indicate the presence of hydrocarbon content and peaks (1) and (6) indicate the presence of proteinaceous materials. DSC measurements confirm this and characterise this further as a natural glue.

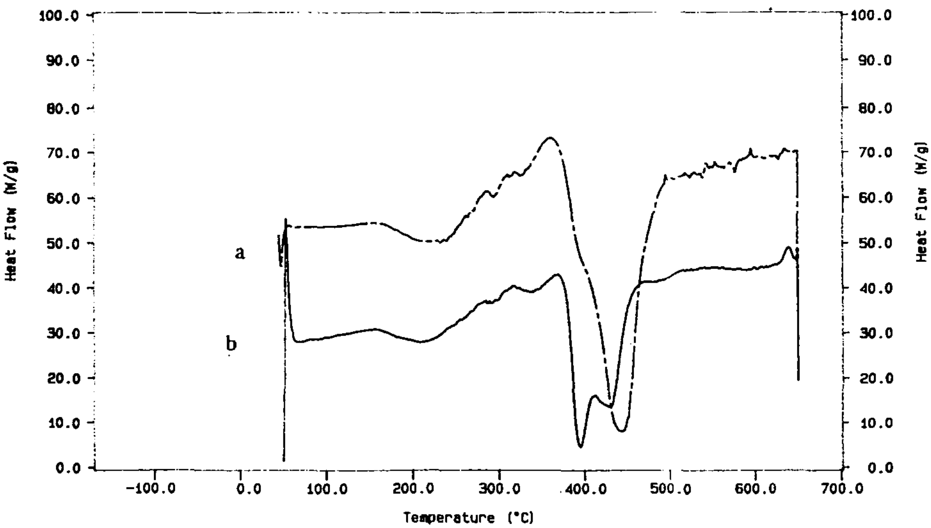


Fig. 7. DSC curves of (a) naturally aged (1915) lead white and linseed oil (b) pale blue paint from "An Allegory of Life" (ca. 1570 unattributed British School To 5729).

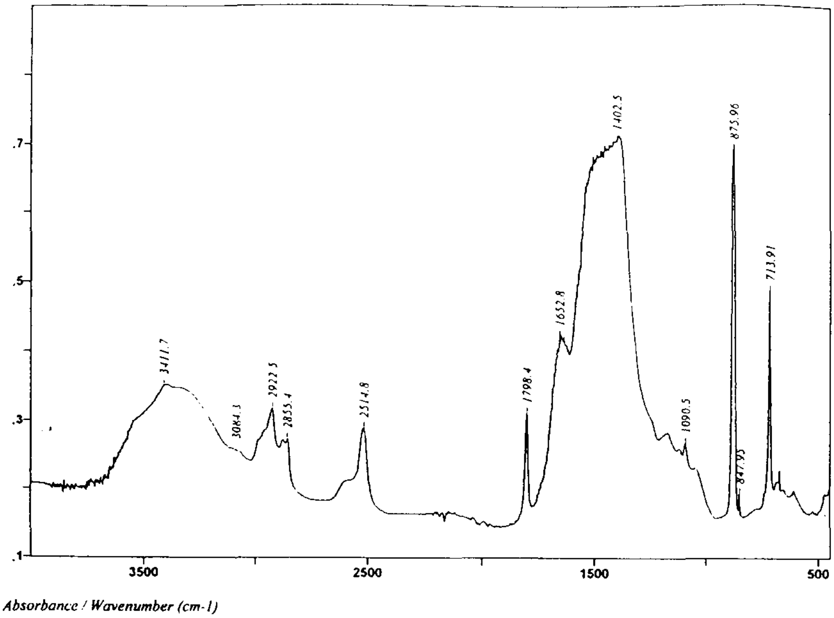


Fig. 8. FTIR spectrum of the priming or ground layer of "An Allegory of Life" (ca. 1570 unattributed British School To 5729).

The resulting DSC curve (Fig. 9a) of a small sample of the priming (86 μg) showed that the exothermic degradation occurred in two stages; a well-defined exothermic peak over the temperature range 286–410°C followed by a weaker exothermic peak over the temperature range 419 to 492°C. The onset temperature of the first exothermic effect occurred at 296°C and it has a peak maximum in the region of 347°C. The presence of the first exothermic effect at this temperature is indicative of the presence of animal glue. Comparison of the DSC curve with those obtained from samples of rabbit skin glue (Fig. 9b) cast as thin films showed that the first exothermic peak was in a similar temperature range. The residue on heating was white in colour. This observation together with the infrared data confirm that a carbonate is present in the priming. The percentage weight loss was calculated as 38.4%. If only the carbonate is present (as calcium carbonate) in the sample then its decomposition begins in the region of 650°C and so the weight loss can be attributed solely to the organic component present in the sample. It was concluded that the white sample from the lower portion of the priming contains natural animal glue togetherwith calcium carbonate as major components. Work is in progress using thermogravimetry on prepared samples containing calcium carbonate together with known organic materials such as egg yolk, casein, animal glue and their mixtures. The aim of this project is to develop the use of thermogravimetry for determining values of pigment volume concentration of samples from both easel and wall pantings [13].

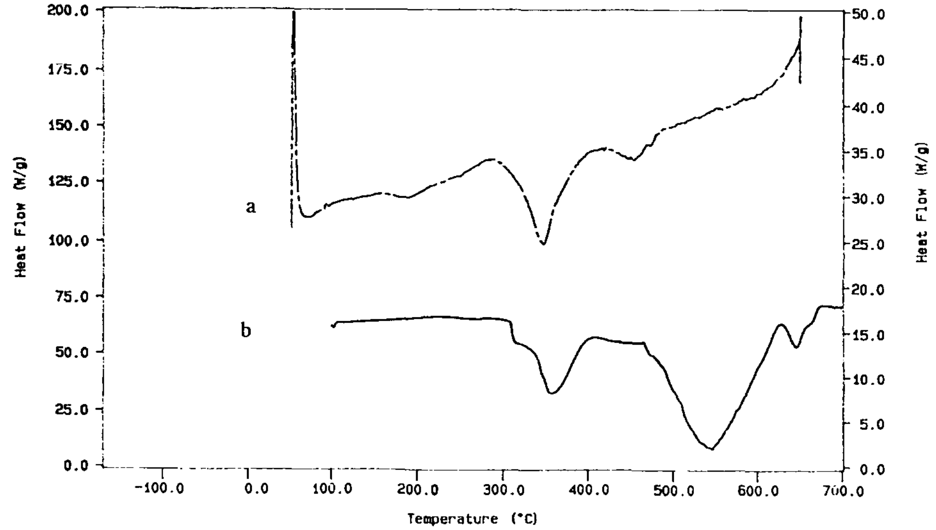


Fig. 9. DSC curves of (a) priming layer from "An Allegory of Life" (ca. 1570 unattributed British School To 5729) and (b) sample of rabbit skin glue cast as a thin film.

The sample of priming from the upper portion of the painting showed a similar infrared spectrum to that of the lower portion. The DSC curve of the sample, however, was more complex and indicated that a number of components were present. Four exothermic peaks were observed with peak maxima in the region of 200, 270, 365, and 460°C. Interpretation is in progress. Further examination of the infrared spectrum is required to assist in the interpretation. Unfortunately the sample as indicated by the weight loss is low in medium content and there is not much evidence of organic material in the infrared spectrum. At this stage it is only possible to say that it differs in composition from the priming of the lower portion. The percentage weight loss was 28.9% which is less than the sample from the lower portion of the priming. The residue was again white (calcium carbonate).

A brownish sample from the painting was also analysed. Infrared spectroscopy showed peaks at the following positions: 3544(m), 3412 (sharp), 2938(w), 2860(w), 1726(w), 1643 (shoulder), 1620(s, sharp) 1560 (shoulder), 1402(w), 1121(s), 670(m, sharp), 604(m, sharp) cm^{-1} (Fig. 10). From the spectrum it is not possible to characterise the medium of the sample. The intense peak at 1620 cm^{-1} could be ascribed to the presence of ionized carboxyl groups such as would be present in salts formed from resinous acids. In this case copper has been detected and so it is likely that copper salts of resin acids could be present. However, as Kühn points out, verdigris as a copper salt of acetic acid also produces a peak in the region of 1615–1560 cm^{-1} and this should not be overlooked [14]. The loss in weight for the sample was 77.8%. This is comparable to weight losses measured in copper-containing samples of paint media as distinct from paint media containing basic lead carbonate where the weight loss is of

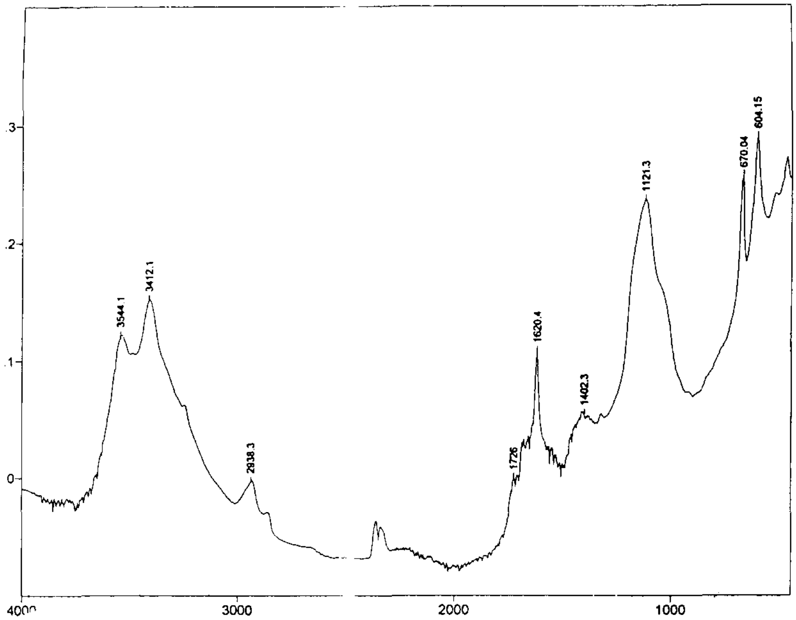


Fig. 10. FTIR spectrum of brownish copper-containing sample from "An Allegory of Life" (ca. 1570 unattributed British School To 5729).

the order of 30%. Most of the residue contained black specks indicating the presence of black copper oxide.

The DSC curve of the sample showed two exothermic peaks. The first peak is in the region of 200°C and the second in the region of 340–350°C. The peaks are not well defined due to the small sample size (18 μg). However, from the infrared it appears that salts of resin acids could be present. The information available at the present time from DSC measurements does not have stored data on samples containing copper salts of resinous acids. The only available comparison is the DSC curve of dehydroabietic acid where the major exothermic peak is in the region of 330 to 350°C. The latter was used to assist in the determination of resin in paint media since it is known that pine resin contains or gives rise to the relatively stable diterpenoid dehydroabietic acid [1]. Work is in progress to characterise the medium in this sample.

3.3. Painting: J.M.W Turner's painting 'The Opening of the Walhalla, 1842'

During the treatment of the Turner painting nine samples were removed for analysis. Fig. 1 shows the sampling positions on the painting. DSC curves were recorded of the nine samples. Of immediate interest were the significant differences in values of overall weight loss and the heat evolved in the exothermic degradation of the samples. The values are given in Table 1 and can be compared with those obtained from naturally aged reference samples (containing basic lead carbonate and drying oil) and which are

Table 1
List of the samples together with the weight loss incurred during heating between 30–600°C and the heat which is evolved. The naturally aged samples (1915, 1941) are from the collection of prepared reference materials, Doerner Institute, Munich

Sample		Wt. loss/%	ΔH (Enthalpy)/(J g^{-1})
77	Sky uncracked	26.7	2128
78	Sky cracked	21.2	2884
80	Sleeve	29.2	3179
81	Tower	30.7	4043
84	Near centre—bottom white	43.3	9511
85	Near centre—bottom brown glaze	98.3	17069
82	Thick yellow glaze above 84	100.0	11857
83	Yellow glaze below 82	98.0	16708
79	Ground layer	32.9	2153
	Landseer priming	25.5	2356
	"Oxidised" linseed oil 1915	29.6	5818
	Raw linseed oil (1941)	24.2	2471

also included in this table. The weight loss recorded in this case over the temperature range 30–600°C includes the oxidative degradation of the medium, the pigment, and any alteration products which have formed. To determine the medium content measurements have been made using thermogravimetry on naturally aged 19th century samples from the priming (which contains basic lead carbonate, calcium carbonates and linseed oil) of a lining canvas attached to Landseer's painting 'Study of a Lion' Tate Gallery (N01350) to determine the medium content [15]. It was found that the difference in weight loss recorded in the two TGA curves, the one for the priming and the other for the basic lead carbonate, was of the order of 10%, and this could be attributed to the medium. In Table 1, the values of weight loss of the two reference samples (and this includes pigment contribution) are similar to that of the sample of Landseer's priming, and samples 77 to 81 of Turner's painting. On this basis it can be said that these samples are lean in medium content.

In contrast to the samples lean in medium content are the samples from regions of glaze (82, 83 and 85), which show almost complete weight loss over the same temperature range and have corresponding higher enthalpy values. The value for the weight loss of sample 84 lies between the two groups mentioned before of low and high medium content. Sample 84 was taken from the white pigmented area near the region of glaze (sample 85).

Fig. 11 shows DSC curves from five of the samples (77 to 80). Those from the ground layer (79) and regions of sky (77, 78) have two shallow and broad exothermic peaks between temperatures of about 179 to 320°C and then 340 to 500°C. The presence of the two peaks, the measured weight loss, and enthalpy values, indicate that the binding medium is similar to that of the reference samples, and consists essentially of a drying oil. The lower intensity of the second exothermic peak indicates that either an

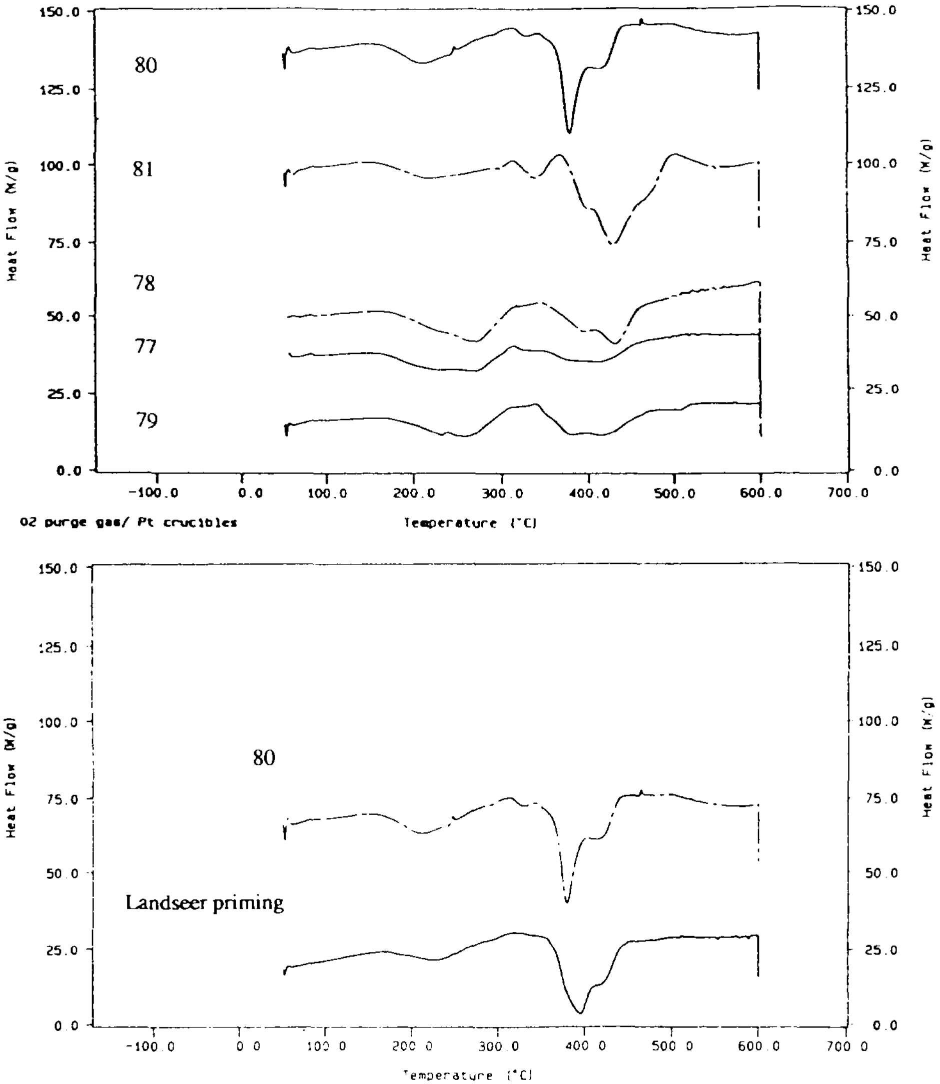


Fig. 11. DSC curves for samples 77 to 81 from "The Opening of the Walhalla, 1842", and sample from the priming of a lining canvas attached to Landseer's 'Study of a Lion' (c. 1862) (Tate Gallery N01350).

additional component is present (particularly in the case of sample 77) or that the oil medium is relatively unaged which could be possible in the case of the ground layer (79). The DSC curves for samples 80 (from sleeve of figure) and 81 (from church with tower) differ from those of 77, 78 and 79 in that they have a more intense second exothermic peak. The DSC curve for sample 80 is very similar to that obtained from the sample of

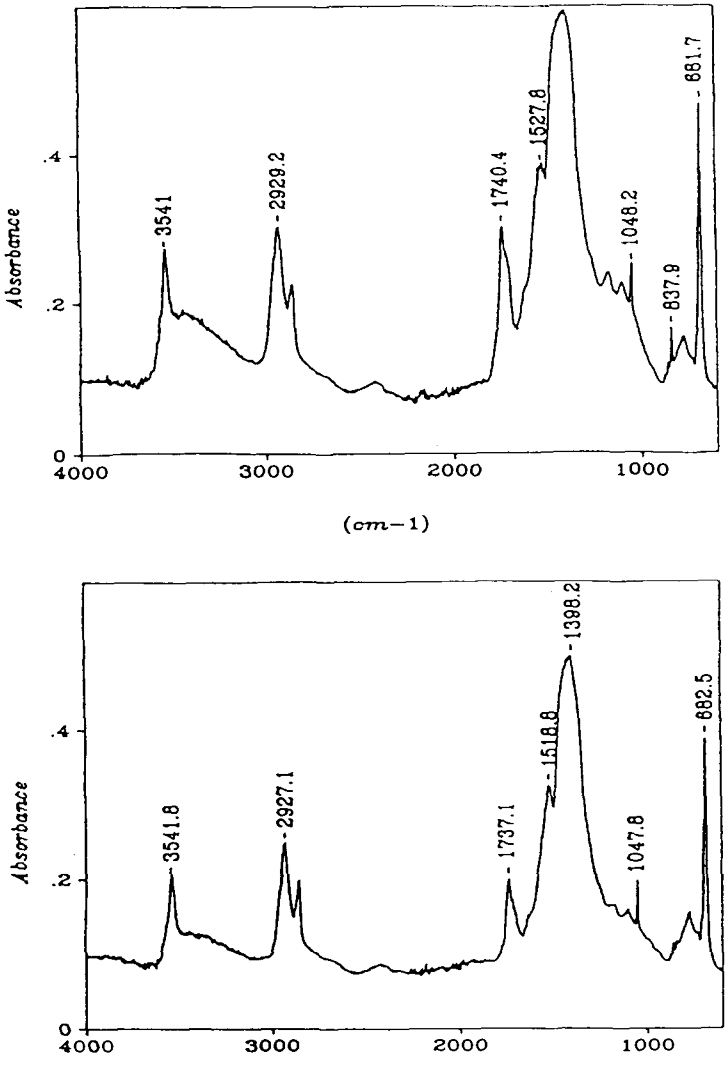


Fig. 12. FTIR spectra of samples 80 (a) and 81 (b) from 'The Opening of the Walhalla, 1842' J.M.W. Turner (Tate Gallery N00533).

Landseer's priming (Fig. 11) which is known to contain linseed oil [16]; the DSC curve for sample 81 shows a much broader second exothermic peak and evidence of an additional peak in the region of 320–350°C. The FTIR spectra (Figs. 12a and 12b) show an overall similarity.

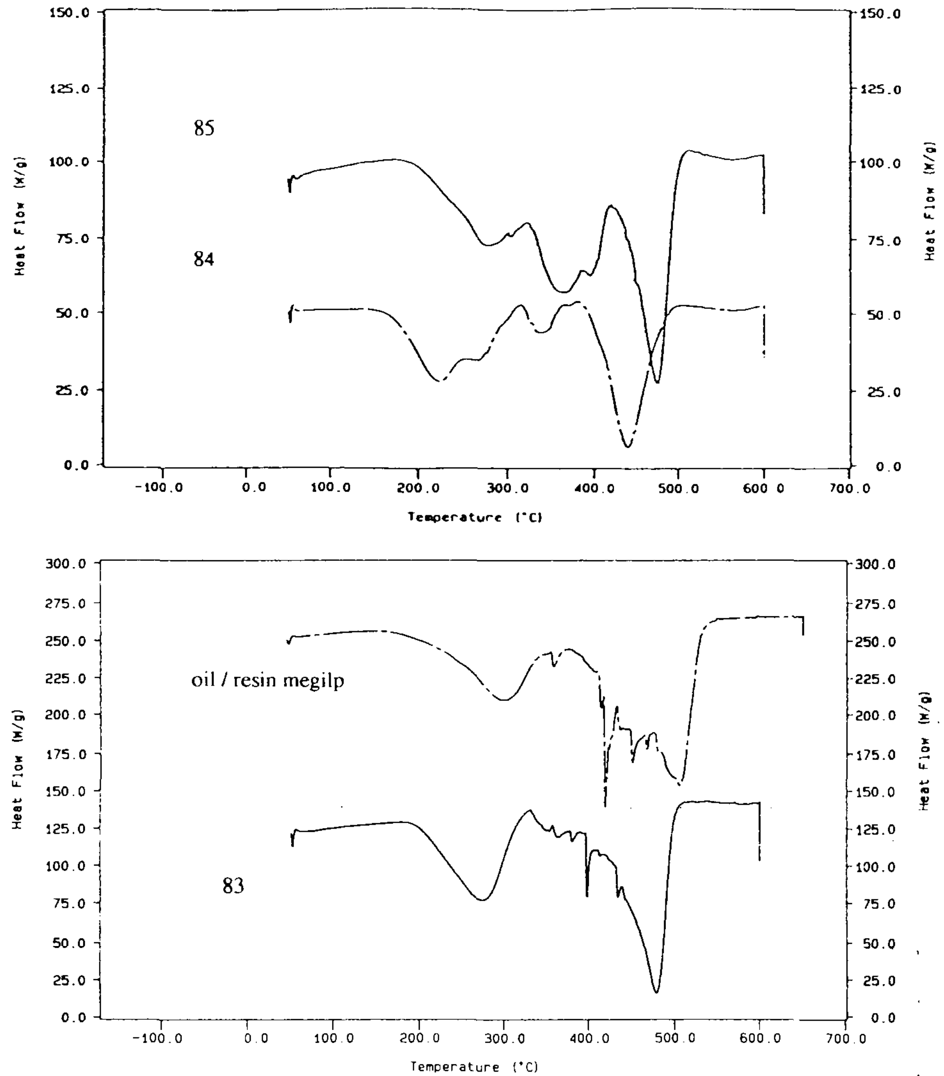


Fig. 13. DSC curves of (a) samples 82 (thick yellow glaze) and 83 (brown glaze) from "The Opening of the Walhalla, 1842" by J.M.W. Turner (Tate Gallery N00533), and (b) from the oil/resin megilp (1:2).

Fig. 13a shows the DSC curves for samples 82 and 83, and Fig. 13b shows the DSC curves for the following samples: naturally aged oil/resin megilp [17] containing one part oil to two parts resin mastic in oil of turpentine with lead acetate drier, and sample 83. There is a close similarity between the curves for the reference material and sample 83, which indicates that a high proportion of resin is present in the sample. The

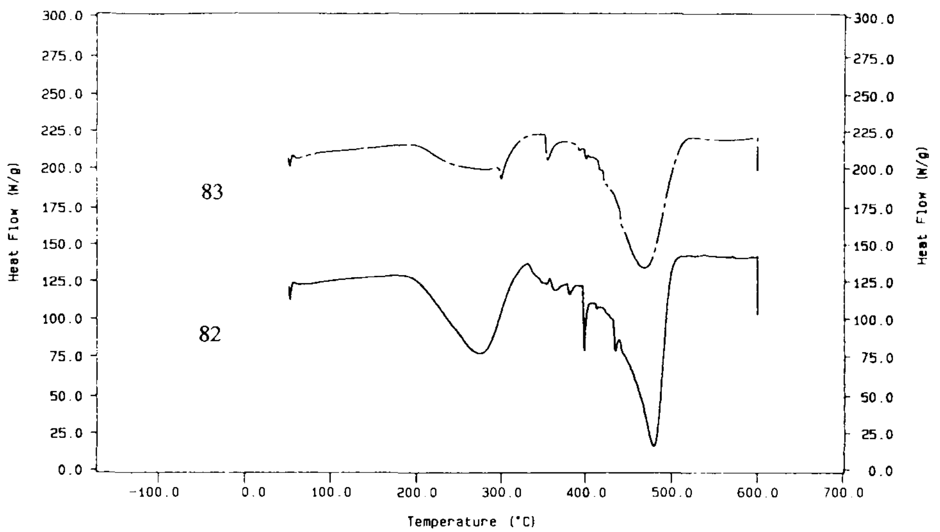


Fig. 14. DSC curves for samples 84 and 85 from "The Opening of the Walhalla, 1842" by J.M.W. Turner (Tate Gallery N00533).

second exothermic peak also occurs at higher temperatures than in the previous samples and confirms recent reported observations on reference resin samples where the temperatures of the second exothermic peak appear in the region of 470–500°C [10].

Sample 84, as mentioned previously, differs both in the weight loss and enthalpy values from the set of samples described above. In Fig. 14 the DSC curve of 84 clearly shows that the first peak is not due to a single component and there is an additional effect at about 320–340°C. The DSC curve is shown together with that from the sample in the neighbouring region of glaze (85). The accompanying FTIR spectra are shown below the DSC curves (Fig. 15). In the spectrum of sample 84 there is, in addition to the carbonyl peak at 1739 cm^{-1}, a shoulder peak at about 1716 cm^{-1} which is indicative of the presence of resin. The latter is seen as the dominant peak in the sample from the region of glaze (85).

The DSC curve of sample 84 was further evaluated by curve-fitting procedures to give four peaks. The results have been reported previously [8]. The curve resolution of the peaks and the accompanying table are shown in Fig. 16 and Table 2, respectively. In this case the peaks correspond to progressive oxidative degradation of the components in the sample. The first peak in the region of 220°C indicates that beeswax may be present since studies on samples of beeswax have shown that it degrades in this region. There are also indications that some natural glue may be present since samples of rabbit skin glue have been shown to degrade in the region of 320–340°C. The remaining peaks can be attributed to the presence of resin in the oil-based medium. The occurrence of resin in the sample is confirmed spectroscopically by the shoulder peak at 1716 cm^{-1} as mentioned above. Direct temperature pyrolysis mass spec-

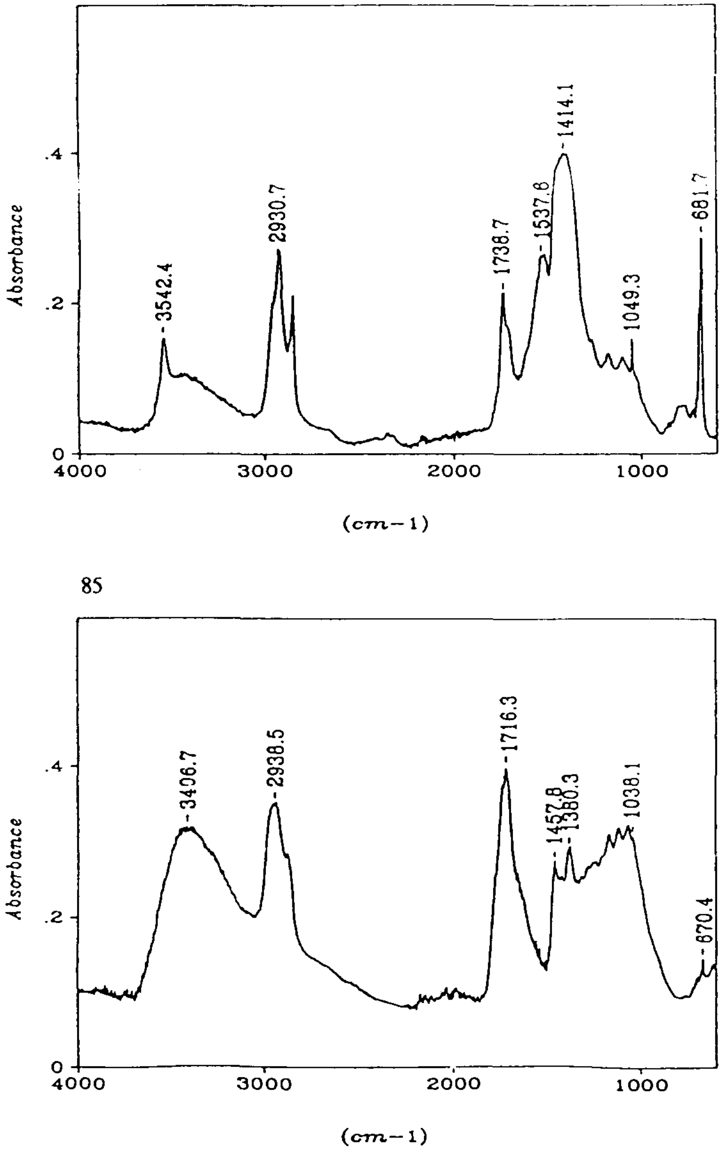


Fig. 15. FTIR spectra of samples 84 andf 85 from "The Opening of the Walhalla, 1842" by J.M.W. Turner (Tate Gallery N00533).

trometry (DTMS) has shown that the sample is basically a lead white oil paint with spermaceti, beeswax and resins as additives. A small amount of protein appears to be present in the sample. However, it is not clear whether this is genuine or introduced later [7].

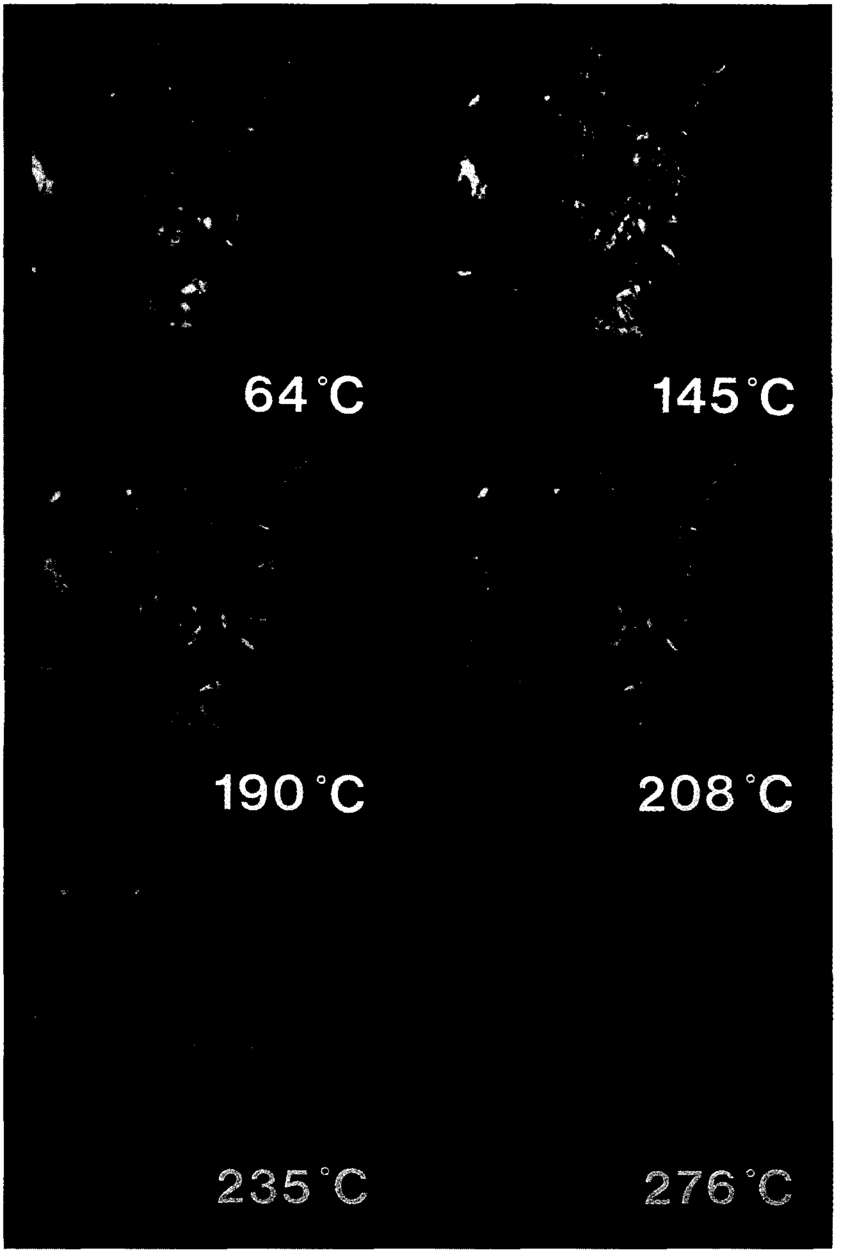


Fig. 16. Resolved DSC curve for sample 84 (white paint).

Table 2
The parameters obtained from the resolved DSC curves for samples 84 and 85

Sample no.	No. of peaks	Temperature (peak maxima)/°C	Intensity	Ratio
84	4	223	37.0	1.0
		273	26.0	0.7
		341	23.0	1.6
		439	75.0	2.0
85	5	270	11.9	1.0
		310	33.9	2.8
		370	43.0	3.6
		400	25.0	2.1
		470	106.0	8.9

Thermomicroscopy also showed that several components were present in samples 84 and 85; this was observed as a softening of the low temperature components at early stages in the heating and the subsequent progressive charring of the rest of the components present in the sample. Thermomicroscopy is not a new technique and it has been used to study the changes during heating of oil, oil varnish and tempera films [18] and more recently on samples from paintings [19]. The instrumental operation and procedure for recording the changes, however, have greatly improved.

Plate 1a is a photomicrograph of sample 85. With illumination using a quartz wedge (pink background) there is a subtle change in the sample between 30 and 55°C which was observed as partial melting indicating the presence of a low melting point component (e.g. wax). There are further changes between 55 and 131°C which could correspond to a softening of resin (e.g. mastic powder softens at about 90°C). Between 131 and 181°C there is onset of charring which increases with temperature to 238°C and finally to 291°C. It is known that oils will char before proteinaceous materials [18] and where charring is observed at different temperatures it could indicate that mixtures of these materials are present as was observed in this case. In Plate 1b (polarised light) it is clear that at 276°C some uncharred specks are still visible. These can be attributed to the presence of resins where incomplete charring has been observed at these temperatures. The presence of several components in sample 85 is further verified by the DSC curve (Fig. 14) and where it has been resolved to give five peaks (Table 2) which correspond to temperatures where oils (about 250–300°C), proteins (animal glue 300–340°C) and resins (470°C) degrade. Further work is required on individual naturally aged resins, natural and synthetic, and on resin films, to provide information for characterising resin type. Mass spectral data showed the presence of oil, protein, beeswax and the presence of paraloid B72 [7] which was undetected by DSC.

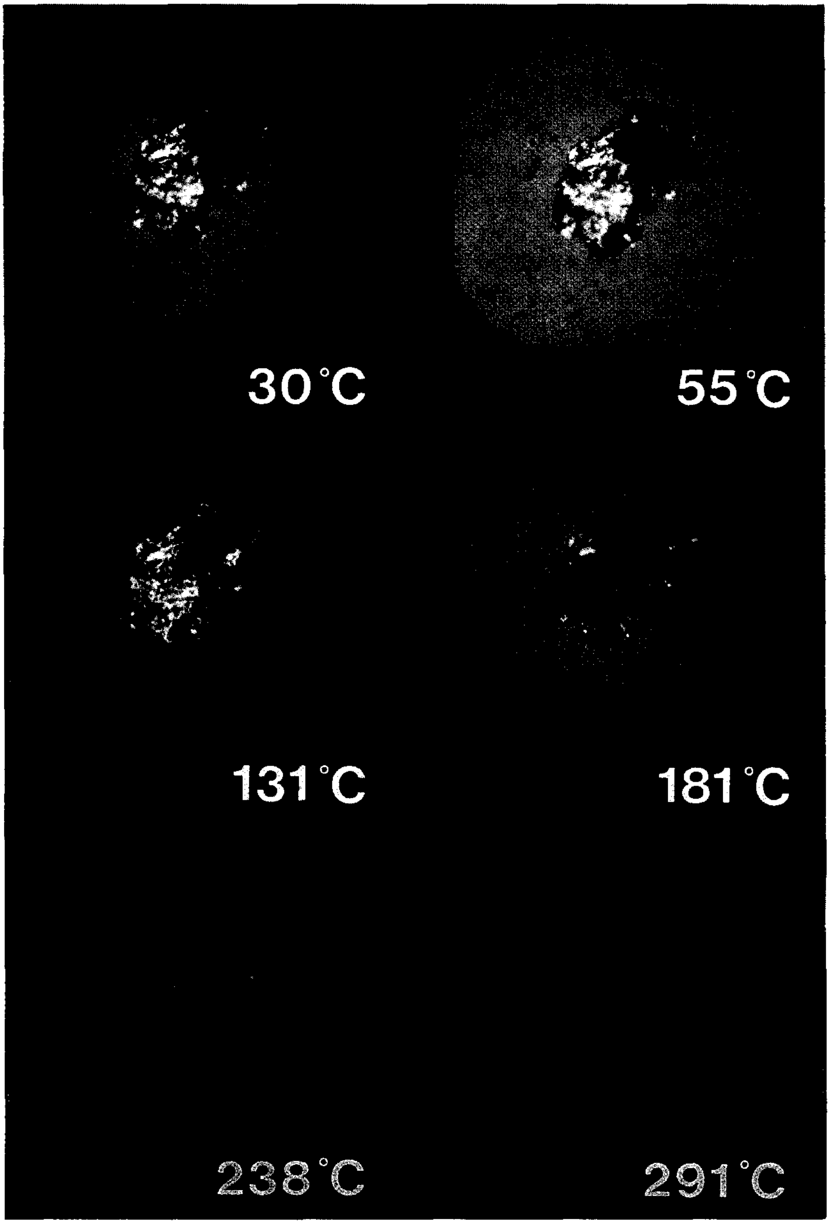


Plate 1 Sample 85 heated from 30 to 300°C at 5°C min^{-1} under magnification (× 400): (a) quartz wedge (b) polarised light.

4. Conclusions

DSC provides a means for characterisation of paint media at the macroscopic level; FTIR spectroscopy and thermomicroscopy can be used to confirm the assignation. The recorded weight change on heating the samples can be used to provide information on the pigment volume concentration of the samples. The DTMS results on the same samples then give the detailed characterisation of the samples at the molecular level and so allow the particular wax or resin type to be characterised.

The main problem in interpreting thermoanalytical data is the lack of information on standard mixtures containing known pigment, oil, and resin content, and this reflects the existing problem of a lack in standard samples which have been aged under controlled conditions. Some standard materials have been prepared at the Doerner Institute and include naturally aged paint films prepared in 1915 and 1941.

In more recent times (1976) samples have also been prepared at the Opificio de Pietre Dure e Laboratori di Restauro (Florence). The Tate Gallery's Conservation Department maintains an archive of naturally aged artists' materials, and is actively employed in the preparation and artificial ageing of modern paints, and nineteenth century paint formulations such as megilps [20]. DSC, TGA, FTIR and thermomechanical (TMA) measurements are in progress on these prepared samples. Results of the investigations on these samples will be reported elsewhere and it will be demonstrated how these samples have assisted in characterising samples from further 19th century paintings including those of J.A.M. C. Whistler.

However, despite the lack of appropriate standards, the combination of thermal, spectroscopic and weight loss measurements has provided an indication of the complex mixtures present in some of the samples studied. Information at the molecular level can then be obtained using direct temperature-resolved pyrolysis mass spectrometry (DTMS); such detailed studies made it possible, for example, to characterise the wax observed in sample 84 not only as beeswax but also as spermaceti wax, a material which was available to artists of Turner's time [21].

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References

[1] Mills and R. White, Organic Mass Spectrometry of Art Materials: Work in National Gallery Tech. Bull. 6 (1982) 3–19.
[2] F. Preusser, J. Therm. Anal., 24 (1979) 277–283.
[3] M. Odlyha and A. Burmester, J. Therm. Anal., 33 (1988) 1041–1052.
[4] M. Odlyha, Thermochim. Acta, 85 (1988) 134.
[5] M. Odlyha, C.D. Flint and C.F. Simpson, Anal. Proc., 26 (1989) 52–56.
[6] R.J. Meilunas, J.G. Bentsen and A. Steinberg, Studies in Conservation, 35 (1990) 33–51.
[7] J.J. Boon, J. Pureveen, D. Rainford and J.H. Townsend "The Opening of Walhalla: studies on the Molecular Signature of J.M.W. Turner's Paint by Direct Temperature resolved Mass Spectrometry (DTMS) in "Turner's Painting Technique in Context" UKIC publication, London (1995).
[8] M. Odlyha and R.P.W. Scott, "The enthalpic value of paintings" Thermochim. Acta, 234 (1994) 165–178.
[9] O. Pages, A. Lamure, C. Lacabanne, Y. Dove and M. Odlyha, "Percolation Phenomena on oil-resin mixtures", Poster prepared and presented at ESTAC 6 (Grado 1994).
[10] A. Burmester, "Investigation of Paint Media by Differential Scanning Calorimetry. Stud. Conserv., 37 (1992) 73–82.
[11] M. Matteini, A. Moles, G. Lanterna and M.R. Nepoti, "Raffaello a Pitti, La Madonna del Baldacchino" (1991) 55–64; Firenze, Palazzo Pitti, Sala Bianca, 23 giugno–15 settembre.
[12] J.H. Townsend, Conservation Department, Tate Gallery, personal communication.
[13] Progetto Strategico CNR "Beni Culturali" 1994 Coordinamento Gruppo" Diagnostica dei Materiali Pittorci".
[14] H. Kühn, "Verdigris and copper resinate", Stud. Conserv., 15 (1970) 12–37.
[15] M. Odlyha, D.Q.M. Craig and R.M. Hill, "Dielectric Analysis of Relative humidity Variations in Canvas Paintings", J. Therm. Analy., 39 (1993) 1181–1192.
[16] D. Rainford (personal communication) and N. Melissinou, M.Sc Dissertation (1994/5).
[17] J.H. Townsend, "Turner's use of Materials, and Implications for Conservation" in "Turner's Painting Techniques in Context" United Kingdom Institute for Conservation UKIC (1995).
[18] F. Ewald, "Studien zur Alterbestimmung von Ölgemälde durch Schmelzversuche an Farbschichtproben", Fette, Seifen, Anstrichm., 65 (1963) 358–368.
[19] J.H. Townsend., "The materials and Techniques of J.M.W. Turner RA 1775–1851, Doctoral thesis, Courtauld Institute of Art, University of London (1991).
[20] Megilp samples were prepared by Katherine Ara.
[21] L.A. Carlyle, "A Critical Analysis of Artists' Handbooks, Manuals, and Treatises on Oil Painting, Published in Britain from 1800 to 1900: with Reference to Selected Eighteenth Century Sources, Doctoral thesis, Courtauld Institute of Art, University of London (1991).