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The 'enthalpic' value of paintings [1]

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Abstract

This paper reports on the potential of differential scanning calorimetry (DSC) for studying the binding media of samples from paintings. The DSC exothermic curves are complex and it was found that the overlapping effects, particularly in some samples from 19th century paintings, could be best resolved by fitting them to a normal distribution. The temperatures of the resolved peaks were recorded and interpreted in terms of values obtained for the oxidative degradation characteristics of standard materials. The results suggest that this approach may provide a means of characterising the complex mixtures which are frequently present in paintings.

INTRODUCTION

The rationale for using differential scanning calorimetry (DSC) is based on previous measurements made on samples from early Italian paintings [1]. The oxidative degradation characteristics of the samples were recorded and it was demonstrated that it was possible to distinguish between oil and non-oil samples, where the medium is referred to as tempera, on the basis of the observed exothermic effects. DSC provides a direct measure of the heat evolved during an exothermic reaction, and it can be used to quantify the effects previously observed using DTA. The basic assumption in treating DSC data is that the heat of reaction liberated at any time is proportional to the amount of reactants consumed.

Earlier studies using differential thermal analysis (DTA) included measurements which had been made on samples from accurately dated and signed paintings and included the following: German (early 19th–20th

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[1] Dedicated to Hans Georg Wiedemann.

century) and samples from Holman Hunt's palette ca. 1862 [2]. The main objective of this study was to collect data from a range of accurately dated samples to determine whether DTA could be used to date oil paintings. Measurements were made of the ratios of the two exothermic peaks as in the original publication [3] and on this basis it was concluded that the peak ratios did provide an indication of age-induced changes. Recent thermoanalytical studies on edible oils, which included linseed oil, support this claim and demonstrate that the peak area of a sample aged at a selected temperature and for a given half-life time appeared to be approximately half that of the unaged sample [4]. In the case of samples from paintings a certain degree of caution is required since it is known from various artists' recipes that additives, such as wax and natural resins, were used, and then there will always be contributions from previous restoration treatment and in some cases from pigments such as Prussian blue and copper-based pigments.

The basis for the interpretation of oxidative degradation curves is the fact that samples of similar chemical composition will give similar effects [5]. Therefore the resulting curves from oil-containing samples will be sensitive not only to the age of the samples but to the presence of additives, the type of pigments used and previous interventions. This has been demonstrated using DTA on samples from a Ruben's painting where it was necessary to determine whether part of the painting was a later addition [6]. In this case similarly pigmented areas were tested and DTA curves from the later addition were found to differ significantly from the original areas. More recently a study using DSC has been carried out on reference materials and their prepared mixtures and it was demonstrated that the technique could be used for characterisation of paint media in combination with other techniques [7]. In this paper although only DSC data are presented, additional methods such as FTIR spectroscopy, pyrolysis mass spectrometry, and thermomicroscopy have been used in most cases to further characterise the samples and this will be reported elsewhere [8]. The aim in this paper is to demonstrate the further possibilities in paint media characterisation using DSC together with curve resolution and then for the first time thermogravimetry on samples (about 500 μg) of prepared mixtures.

EXPERIMENTAL

The same experimental procedure was followed with respect to sampling from paintings and DSC measurements as described in previous publications [9]. The Perkin-Elmer DSC 7 and TGA 7 instruments were used. The thermogravimetry measurements were conducted using samples in the range of 500 μg and the heating was carried out in platinum crucibles at

2°C min^{-1} over the temperature range 35–660°C in N_2 gas with a flow rate of 50 cm^3 min^{-1}.

RESULTS

Previous DTA measurements on samples from paintings of the period 1890–1909 and form Holman Hunt's palette (ca. 1862) have been expressed in terms of the peak ratio of the two exothermic effects observed. The samples from the paintings gave a ratio in the region of 4–5 and then in the region of 2 [10]. These values were compared with those obtained from standard samples containing basic lead carbonate and linseed oil which had been prepared at the Doerner Institute in the early to mid part of this century. In some cases the peak ratio was higher than that observed for standard samples (1915) and in other cases the peak ratio was closer to that observed for standard samples (1941). This variation in similarly aged and pigmented samples is evidence for the heterogeneous nature of the samples examined where not only ageing effects but also additives influence the DTA curves.

DSC measurements have indicated that the effect of additives can be measured in terms of the enthalpy values of the total exothermic effect observed [11] where ΔH linseed oil $>\Delta H$ mixture containing linseed oil and egg tempera $>\Delta H$ egg tempera. This trend was observed in samples from early Italian paintings and also in prepared standards containing the same white pigment, basic lead carbonate.

Measurements in addition to those reported above have been made on samples from paintings from similar and differing periods. During the conservation treatment of Raphael's painting "La Madonna del baldacchino" samples from white pigmented areas were taken and analysed using pyrolysis–gas chromatography (PY–GC) and DSC. Results obtained by PY–GC showed that the pyrogram of the sample was similar to that obtained for a reference sample of siccative linseed oil and differed from that of egg yolk and linseed oil [12]. Results from DSC showed a typical two peak exothermic curve for lead white and linseed oil where the exothermic peak in the region of 400°C is dominant. The enthalpy value for the complete exothermic effect was similar to that for reference material containing a drying oil and differed from values for reference materials containing oil and egg yolk. These values together with further values from reference samples and more paintings are listed in Table 1. Both relatively fresh and standard materials and "old" standards, the two Bellini samples, define the medium in the Raphael painting as a drying oil. The Bellini samples can be considered as "old" standards since they have previously been characterised by independent GC–MS [13] and temperature resolved PY–mS [14]. Measurements showed that in the case of (1) the medium was

TABLE 1

Overall enthalpy change and mass loss for paintings and reference samples measured by DSC

Sample[a]	ΔH/J g^{-1}	Mass loss/%
Raphael	2230	20.1
Linseed oil (1933)	2223	27.8
Linseed oil/egg yolk (1978)	3986	38.0
Bellini (1) (16th cent.)	3706	–
Bellini (2) (16th cent.)	4498	25.9
"Oxidised" linseed oil (1915)	5818	29.6
Raw linseed oil (1941)	2471	24.2
Martini (1) (16th cent.)	2623	33.8
Martini (2) (16th cent.)	2515	39.8
Memling (ca. 1490)	3366	–
Tiepolo	4056	–
Sassoferratto (16th cent.)	3364	38.6
Studio of Pedro Berruguete (16th cent.)	2000	36.4
Landseer (1862)	2356	25.5
Bennozzo Gozzoli	405.1	56.8
casein	321.4	26
Mummy portrait (Petrie Museum)	11284	45.6
Turner (1) (1842)	2128	26.7
Turner (2) (1842)	2884	21.2
Turner (3) (1842)	2252	32.9
Turner (4) (1842)	4043	30.7

[a] Numbers indicate that sampling occurred on the same painting but in differing regions.

a drying oil (probably walnut) with some tempera, and in the case of (2) the medium was a drying oil which had been heat-bodied. The value for Bellini (2) lies closer to that found for the reference sample of "oxidised" linseed oil (1915) [15]. No explanation in this case is given to the term "oxidised" and it can be assumed, on the basis of the Bellini (2) result, to refer to a more polymerised oil which would have a higher enthalpy value for oxidative degradation. The last two values from Francesco di Giorgio Martini's painting of the Nativity of Christ (ca. 1500) have been included to demonstrate that the enthalpy values need to be interpreted together with the overall shape of the DSC curves and the peak ratios. Martini (1) has been previously characterised as containing a non-oil based or tempera medium where the dominant exothermic peak appears in the region 270–280°C [16], and Martini (2) contains a drying oil as the major component.

At this stage there is an indication from the enthalpy values that where paint media are clearly different, as in the case of the wax encaustic Mummy portrait (UC 14692) and the casein based paint, enthalpy values differ from those which are oil-based or contain a mixture of oil and egg.

Although the values for a sample from the wall paintings of Bennozzo Gozzoli in the Palazzo Medici Riccardi lie in the region of casein lead white paint further tests are required to confirm this result since residues from previous cleaning are known to exist [17]. In the case of Turner [4] GC–MS data indicated that the medium corresponds to a pre-polymerised drying oil [18], and the corresponding enthalpy value does lie in the region of Bellini [2]. Though enthalpy values alone are insufficient to provide characterisation of paint media they can be considered as an additional marker, together with other parameters such as peak ratios, to further assist in media characterisation.

Recently work has focussed on 19th century paintings and standards have been prepared at the Tate Gallery according to the recipes used at the time. It is known, for example, that in the 19th century artists made their own additions to the commercially available materials. These were known as "megilp" formulations [19] and mastic megilps were made from mastic varnish and linseed oil prepared with driers such as lead acetate or litharge. The standards prepared to assist in the analysis of samples from 19th century paintings were based on Cremnitz white and Vandyck brown tube paint. To the paint which contains the respective pigments in safflower oil (Winsor and Newton, manufacturer's information) known proportions of oil and resin mastic were added and some of the samples were thermally aged [20].

The measured enthalpy value for Cremnitz white tube paint, was found to be lower than that for Vandyck brown tube paint (Table 2). This corresponds to the pigment's capacity for absorbing medium; brown, iron oxide containing pigments have a higher proportion of medium (about 70%) than those containing Cremnitz white (about 30%) a form of basic lead carbonate which was produced in Germany in the late 18th century [21]. The difference can be measured in terms of the difference in the mass loss which occurs on heating the samples to 650°C. The values for percentage mass loss as listed in Table 2 have been derived from DSC

TABLE 2

Effect of additions to commercial artist's tube paint on overall enthalpy change and mass loss measured by DSC

Sample	ΔH/J g^{-1}	Mass loss/%
Vandyck Brown DR (tube paint alone)	5765.9	66.7
Vandyck Brown AM5DR (tube paint, linseed oil and lead acetate 3:1 mastic varnish)	10193	64.7
Cremnitz white Cr (tube paint alone)	2577	27.7
Cremnitz white tube paint and some varnish (1915)	5840	38.6
Raw linseed oil (1941)	2471	24.2

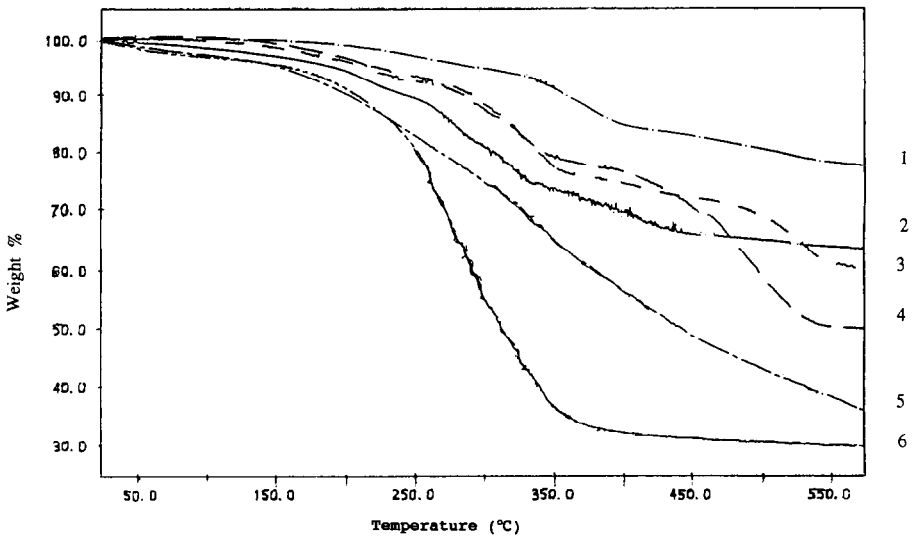


Fig. 1. TG curves of (1) the Landseer sample; (2) CR, Cremnitz white tube paint; (3) AM1CS2, aged Cremnitz white tube paint and additive (oil:resin mastic 1:1); (4) AM1C, unaged Cremnitz white tube paint and additive (oil:resin mastic 1:1); (5) AM1DR, unaged Vandyck tube paint and additive (oil:resin mastic 1:1); (6) DR, Vandyck tube paint alone.

measurements, and thermogravimetric measurements confirm this difference (Fig. 1: CR Cremnitz white, DR Vandyck brown tube paint alone, AM1DR contains the tube paint together with 1: oil, resin mastic). Figure 2 shows the DSC curves for the Vandyck tube paint (DR) and the sample containing additive (AM5DR). Parameters measured by DSC and TG of the effect of additions to commercial artist's tube paint, in this case drier, and oil appear in Tables 2 and 3 respectively. The value for Cremnitz white tube paint is of the same order of magnitude as standards prepared in 1941. The addition of some resin increases the enthalpy value as in the case of the Vandyck brown samples.

Resolution of the thermogravimetric curves by fitting to a normal distribution provides peaks at temperatures consistent with the temperatures of the mass losses and their intensities correspond to the magnitude of the mass losses (Fig. 3). The resolved curves show four peaks in all cases. The enhanced sensitivity enables the detection and separation of effects which are not clearly defined on the original curves. This procedure for curve fitting has recently been applied to thermogravimetric curves of silica [22].

The effect of adding further oil and resin is to shift the temperature of maximum mass loss and observed thermal effect to higher temperatures. The effect of ageing is to introduce a peak at even higher temperatures which reflects the increased polymerisation of the medium. The overall mass loss is reduced with heat ageing (compare AM1C and AM1CS2) and

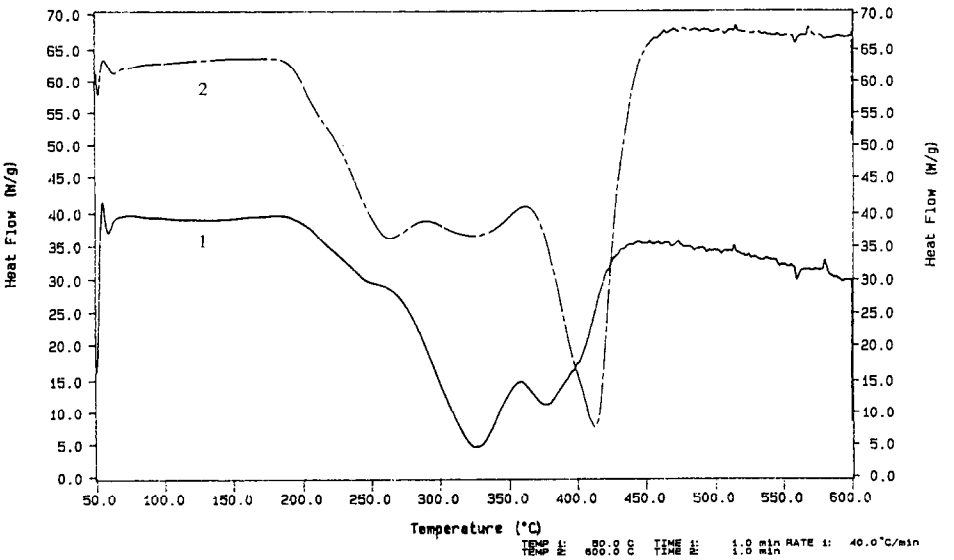


Fig. 2. DSC curves of (1) DR, Vandyck tube paint and (2) AM5DR, Vandyck tube paint and additive (oil:resin mastic 3:1).

is similar to the value obtained for a sample in Table 2 (1915) which can be taken as being representative of an oxidised linseed oil and resin containing sample.

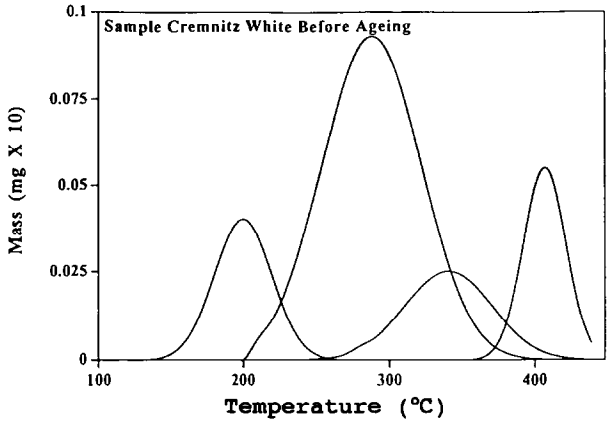
The rationale for collecting information on standard materials is, on the one hand, to understand the behaviour of simple mixtures of materials used as binding media, and their interaction with the pigments and to evaluate the possibilities and limitations of the techniques used, and on the other hand, to assist in the characterisation of samples from paintings.

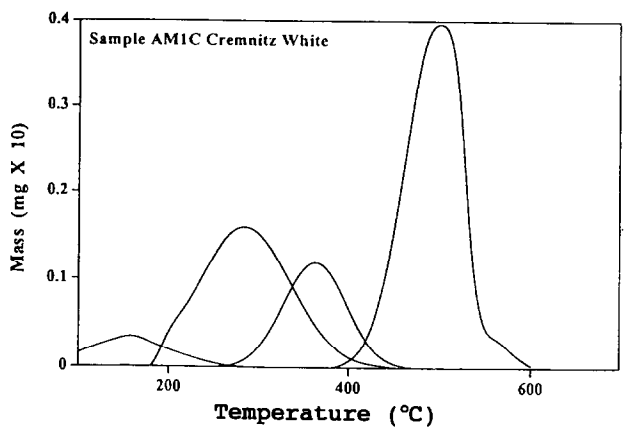
TABLE 3

Effect of additions and ageing on commercial artist's tube paint measured by TG

Sample	Stage 1		Stage 2		Stage 3		Stage 4		Total Δm/%
	Δm/ %	Temp./ °C	Δm/ %	Temp./ °C	Δm/ %	Temp./ °C	Δm/ %	Temp./ °C	
Cremnitz white (tube paint alone)	6.6	186–257	15.6	252–347	7.0	348–462	–	–	29.2
AM1C [a]	8.9	118–272	13.7	261–254	26.7	395–554	–	–	49.3
AM1CS2 [b]	6.5	118–258	15.9	269–358	4.1	357–438	11.8	453–573	38.3

[a] AM1C refers to a mixture of Cremnitz white tube paint and added linseed oil and resin mastic in equal proportions. [b] AM1CS2 refers to the AM1C mixture after thermal ageing at 70°C for 34 days.





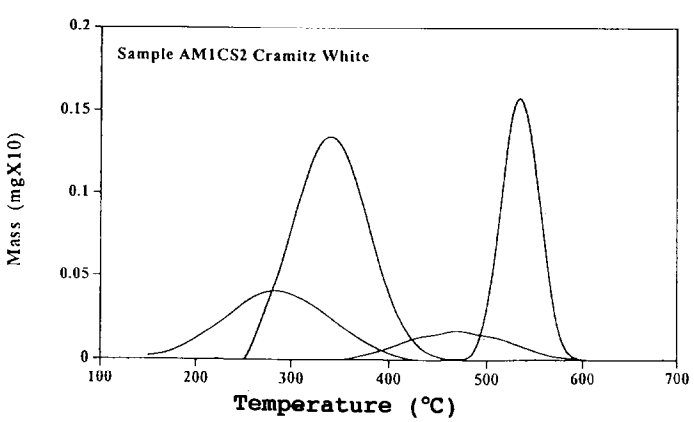


Fig. 3. Resolved curves for, CR Cremnitz white tube paint, AM1C Cremnitz white tube paint and additive (oil:resin mastic 1:1), and AM1CS2 which corresponds to mixture AM1C thermally aged for 34 days at 70°C.

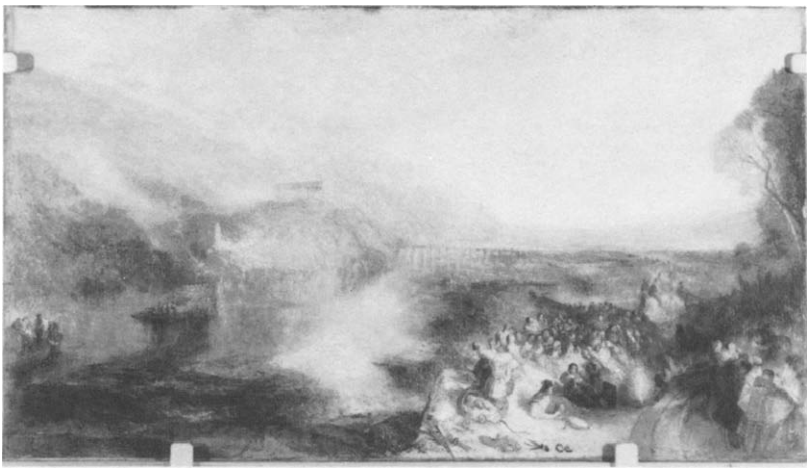


Fig. 4. Turner's painting "Opening of Valhalla" (N00533) by courtesy of the Tate Gallery, London.

In this study the enthalpy values of samples from several paintings have been measured and these are reported in Table 1. Of particular interest are the results from samples taken from Turner's painting "Opening of Valhalla" (Fig. 4) (Tate Gallery N00533). This is a large panel painting executed towards the latter part of Turner's life and it represents one of the few examples of his work on panel. In terms of sampling this means that there will be no contamination from materials used to reline canvas paintings which would be the case for the majority of Turner's paintings and so this provides an opportunity to obtain samples which are representative of the actual materials used. The results from four samples taken from white pigmented regions of the painting are listed in Table 1. Values for additional samples taken from regions of glazes and of high medium content are listed in Table 4. The nature of the DSC curves particularly in the case of samples Turner (5) and (6) (Fig. 5) with a number of overlapping peaks suggested that further information could be obtained using a deconvolution procedure mentioned above which attempts to fit the overlapping peaks to a normal distribution. Resolution of the DSC

TABLE 4

Overall enthalpy change and mass loss for samples from regions of glazes and high medium content of Turner's painting "Opening of Valhalla" measured by DSC

Sample no.	$\Delta H/J\,g^{-1}$	Mass loss/%
Turner (5) (1842)	9511	43.3
Turner [6] (1842)	17069	98

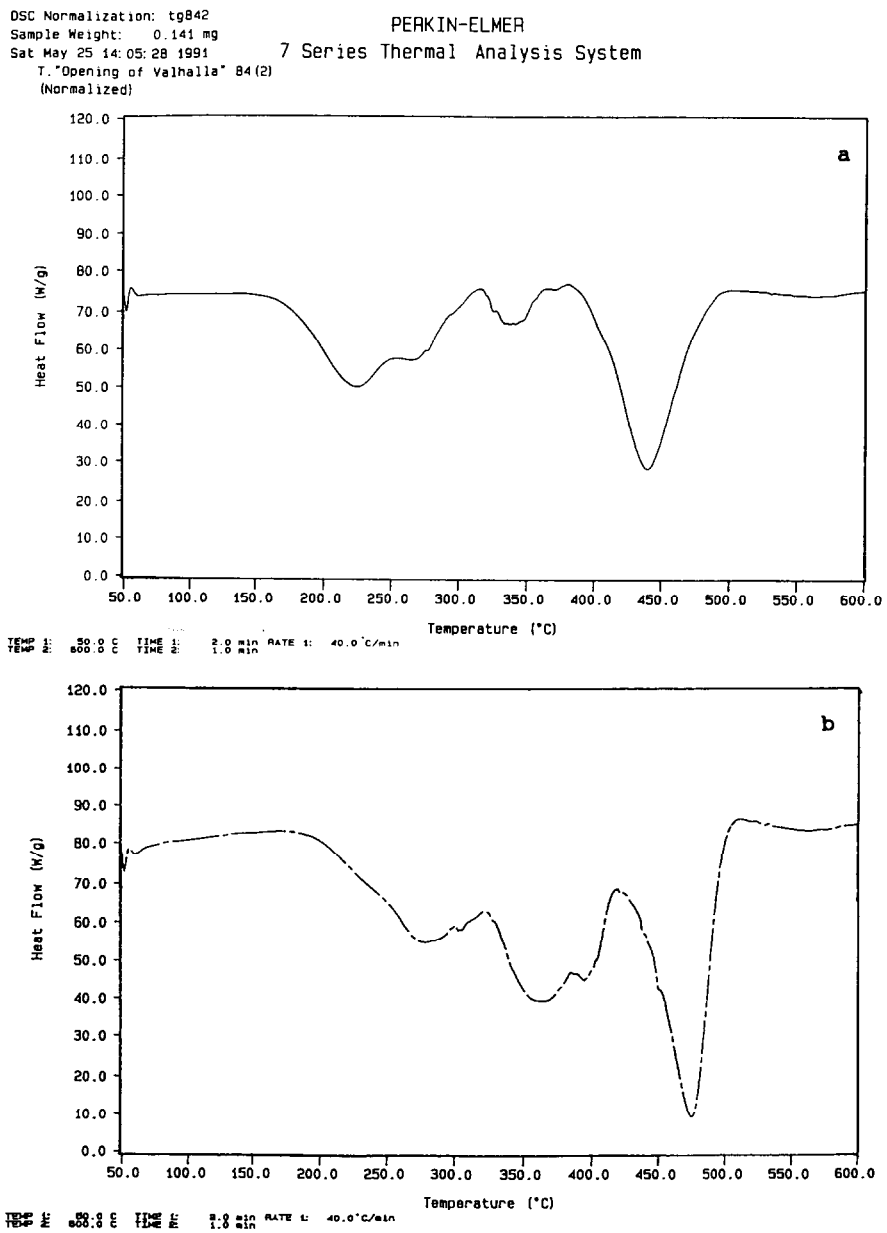


Fig. 5. DSC curves of (a) sample Turner (5) and (b) Turner (6) from the centre of the lower edge of the "Opening of valhalla".

curve for sample Turner (5) has produced the results given in Table 5 and Fig. 6.

Sample Turner (5) exhibits a complex DSC curve (Fig. 5(a)). From previous work mentioned above it is known that a material containing a drying oil and basic lead carbonate pigment exhibits a simple two peak

TABLE 5

Resolution of DSC curve for Turner [5] sample

No. of peaks	Temp. of peak maxima/°C	Intensity	Ratio
4	223	37	1.0
	273	26	0.7
	341	23	1.6
	439	75	2.0

exotherm. This indicates that sample Turner (5) contains components in addition to the mainly oil-based medium. These may be characterised from the temperatures at which resolved peak maxima occur and then identified from values of temperatures previously recorded for the oxidative degradation of known materials. Presently data exists on relatively unaged material. From this it is known that the oxidative degradation temperatures vary approximately in the following order: beeswax $\leq$ drying oils $<$ proteinaceous material $<$ natural resins. On this basis the above sample should contain a mixture of wax, proteinaceous material, resin and a drying oil. The presence of wax has been independently confirmed by thermomicroscopy. Temperature resolved pyrolysis mass spectrometry has identified wax, resins and oil [23].

A sample from a similar period, Landseer (ca. 1862) which is known to contain a drying oil with basic lead carbonate and some calcium carbonate has on resolution given three peaks in the region of 230, 390 and 430°C (Table 6). Peaks in the region of 230–250°C and 390°C are expected for oil-based media alone. The additional peak at 430°C appears in the DSC

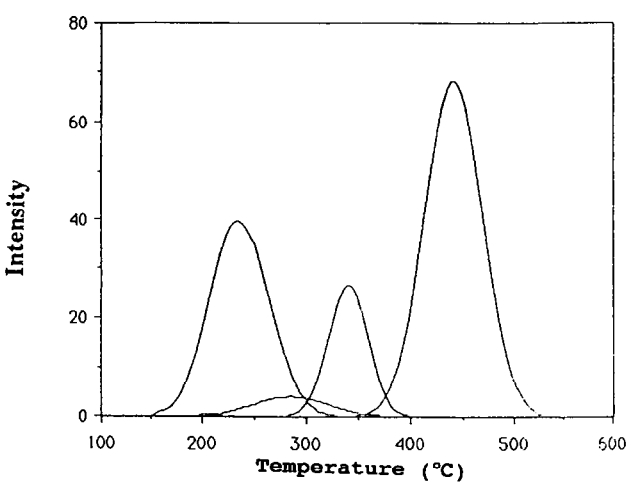


Fig. 6. Resolved curve for sample Turner (5).

TABLE 6

Comparison of resolved DSC curves for two nineteenth century paintings

Sample no.	No. of peaks	Temp. of peak maxima/°C	Intensity	Ratio
Landseer (ca. 1862)	3	230	6.7	1
		390	33.9	5
		430	20.0	3
Turner [6] (1842)	5	270	11.9	1
		310	33.9	2.8
		370	43.0	3.6
		400	25.0	2.1
		470	106	8.9

curve as a shoulder and may be related to changes on ageing. Work is in progress on standard basic lead carbonate and linseed oil samples to understand the effect of ageing of lead white and oil mixtures. At this stage the Landseer sample can be considered to be representative of an aged oxidised and cross-linked oil sample. The resolved peaks may also correspond to contributions from components of the drying oils such as fatty acids and the lead salts which are known to form.

Sample Turner (6) can be characterised as containing oil and some protein (see Table 6 and Fig. 7). GC–MS analysis confirmed the presence of casein, and linseed oil [24]. From DSC curves casein in a standard mixture of lead white casein gives peaks at 285, 320 and 354°C which are the regions in which peaks occur. Beeswax also occurs and this was confirmed by thermomicroscopy. The oxidative degradation temperature of beeswax overlaps with the value for oil and so additional confirmatory tests with thermomicroscopy are required. The higher value for mass loss compared to the previous sample can be explained by the almost complete absence of

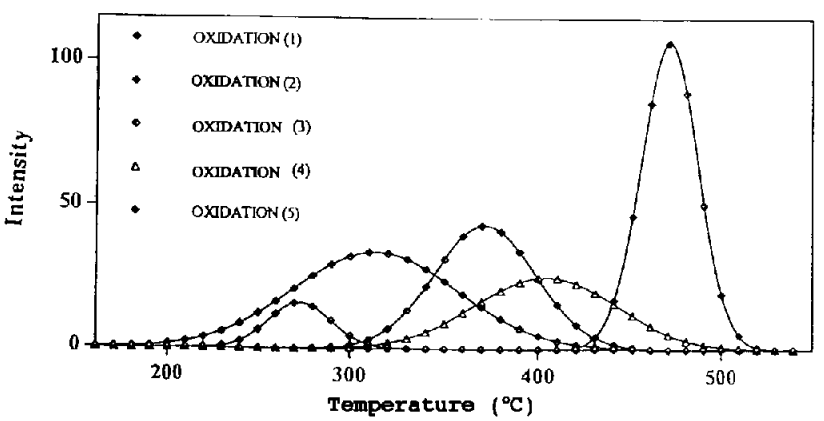


Fig. 7. Resolved curve for sample Turner (6).

pigments in this region of the painting. This is a region containing higher proportion of glazes and possibly traces of residual oil varnishes. The latter would be too difficult to remove during previous cleaning and so such contamination is inevitable. The higher proportion of resin and possibly wax present in sample Turner (6) compared to Turner (5) is reflected in the higher proportions of components present at 310, 370 and 470°C. TG measurements, as described above, have indicated that the presence of resin does shift the degradation temperatures of oil–resin mixtures to higher values. Standard materials containing simple mixtures in known proportions are also being evaluated; for example a recent mixture of beeswax and dammar resin (60:40) has given peaks at 290°C (large) and 490°C (small) which is in the region of temperatures observed for sample Turner [7]. PY–MS has also confirmed the presence of wax and resin.

In the case of sample Turner [5] the type of wax, namely spermacetic wax, has also been defined by PY–MS [25] and this coincides with the materials available at the time [26].

CONCLUSIONS

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. The standards investigated from the Doerner Institute did provide a starting point for the study of materials prepared in 1915 and allowed to age naturally. Then samples obtained from the Opificio de Pietre Dure e Laboratori di Restauro (Florence) provided a source for both fresh and oil standards (i.e. samples from several early tempera paintings) and recent work at the Tate Gallery has included the preparation of a further set of standards which reflect the nature of materials used in the 19th century. DSC, TG, FTIR and TMA measurements are in progress on these prepared samples. However, despite the lack of appropriate standards some interpretation of the DSC results from the media in Turner's samples, particularly with the assistance of the resolved peaks, can still be made which are consistent with results from parallel temperature resolved PY–MS.

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