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Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (smalt tempera) by thermal analysis

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Abstract

One of the main concerns of conservators and curators is to find a method for evaluating the damage incurred by works of art in major galleries, historic houses, and castles with differing indoor environmental conditions. For this purpose, test tempera paintings were prepared and exposed at selected sites. The test paintings act as dosimeters and integrate the contributions from a range of factors which determine the overall environmental hazard to which paintings are exposed. Subsequent analysis of the test paintings involved an interdisciplinary approach using mass spectrometry (FOM Institute, the Netherlands), thermal analysis (Birkbeck College, UK) and non-invasive spectroscopic analysis (CNR–IROE, Italy). These techniques gave a measure of the physicochemical change and hence the resulting damage. In this paper, the thermoanalytical data will be presented, in particular of smalt tempera. Prior accelerated ageing of similar test paintings using controlled conditions was also performed to provide a comparison between artificial and natural ageing and a means for calibrating the test paintings.

Keywords: Indoor environments; Damage dosimeters; Cultural heritage; Paint tempera; DSC; DMTA

1. Introduction

The rationale for using test tempera paintings as dosimeters in art galleries has been described in the first paper in this section [1]. A brief description of the sites, the summary of their environmental conditions, and some of the earlier data resulting from their exposure at the selected sites have been recently reported [2]. In this paper, a more detailed description will be given together with more recent data obtained at a later stage in the project. The ERA project as mentioned in the Preface was an interdisciplinary project in collaboration with Prof. Jaap J. Boon of the FOM Institute (Amsterdam, the Netherlands) and Dr. Mauro Bacci, IROE (Florence, Italy). The results presented in this paper focus on the thermoanalytical data.

The thermal techniques used for the analysis of the test paintings were dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). The rationale for the application of these techniques is that they are known to be sensitive to changes in ageing of materials. In addition, there is some experience in their application to artists' materials. DMTA was first used in paintings conservation research to study the effect of solvent cleaning on paint films [3] and then to study the mechanical

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properties of a selection of artists' materials which include varnishes, oil-based paint, canvas and primed canvas samples [4]. In addition, the effects of artificial ageing on primed canvases and the effects of deacidification treatment have also been studied [4,5] as have the effects of ageing on leather samples [6]. In general, the technique is used extensively in materials testing [7].

DSC was used in the oxidative mode to obtain markers of thermal stability for the artificially and naturally aged samples. These are measured as onset temperatures of thermooxidative decomposition processes, peak heights and peak areas [7]. Previous work has been performed in this way and a methodology for small sample size developed for use on micro-samples from paintings [8]. This methodology was used on samples from the test paintings. On the basis of the earlier work, a database emerged of DSC curves from white pigmented samples (basic lead carbonate) from early Italian paintings to 19th century paintings, which was also useful for the present study [9].

2. Sample preparation

A set of differently pigmented temperas was prepared on a polymeric substrate (polyethylene terephthalate) as described in a previous paper [1]. In brief, the tempera medium was prepared according to traditional recipes by restorers at the Opificio delle Pietre Dure (Florence, Italy). The yolk was separated from the white of an egg. The foam from the egg white was then discarded and the liquid part was mixed with the yolk. A few drops of vinegar and a solution of mastic in white spirit were also added. The paint was then deposited (wet layer thickness 200 μm) on a sheet of Melinex using a film applicator. It was allowed to cure for a period of 3 months before it was subjected to artificial ageing.

2.1. Artificial ageing

The effect of controlled conditions of enhanced light levels, elevated temperature, and defined concentrations of pollutants on the paint strips were studied. In the case of light ageing, conservators refer to the object as receiving a light dosage, which is calculated from the product of light level and the time of exposure. In museums, the standard recommended light level is 200 lux. In this calculation, no account is taken of the spectral variation in the received light. However, the calculation provides conservators with a means for estimating dosage levels which can assist with making decisions concerning length of display time of objects [10].

The paint films were cut into strips and exposed in a light ageing cabinet at the Tate Gallery (London) for 4, 8, 16, 32 and 64 days at an intensity of 18 000 lux as described in the first paper. The effect of pollutants was also studied. Samples were exposed for a period of 4 days only (in the dark) to SO_2 (10 ppm) and NO_x (NO: 11.4 ppm and NO_2: 5.2 ppm) in a chamber maintained at a temperature of 23°C and relative humidity (RH) at 55% in the TNO Laboratories, the Netherlands. Thermal ageing of samples was carried out in an oven at the Tate Gallery at a temperature of 60°C and 55% RH. No light was admitted to the oven. Samples were exposed for 7, 14 and 21 days.

2.2. Natural ageing at selected sites

Similar samples, after their period of curing, were exposed in selected major art galleries and historic houses. A range of pigmented and unpigmented samples (strip size: 35 mm × 10 mm) were selected and mounted on a dark card supported in a frame (14 cm × 19 cm) (schematic diagram of dosimeter is shown in Fig. 1 of [1]) to create a test tempera painting which was then exposed at the chosen sites.

Sites were chosen to provide a range of indoor environmental conditions for the test tempera paintings (Tables 1 and 2). Each site is labelled with a three letter code: Tate Gallery, London (TAT), Rijksmuseum, Amsterdam (RNW) and Rijksmuseum store room "Depot Oost" (RDO), Galleria degli Uffizi, Florence (UFF), Sandham Memorial Chapel, Burghclere, UK (SAC), and El Alcázar, Segovia (ALC) Spain.

Two sensors were placed in the Rijksmuseum. One was exposed in the Nightwatch room (RNW), diagonally opposite the famous "Nightwatch" painting by Rembrandt (the full title of which is "The Company of Captain Frans Banning Cocq and Lieutenant Willem van Ruytenburgh"). The second sensor was placed in the depot "Oost" storage area (RDO), which is located in the attic of the Rijksmuseum. This room

Table 1
Summary of site environmental data

Site	RH (%)	T (°C)	Light intensity (lux)	UV intensity (μW/m^2)	No. of visitors
ALC	20–84	6.5–28	80–1000	7500 (UV-A)	417 461
RDO	28–64	16–29	2–12	0	Negligible
RNW	42–71	17–24.5	<100	0	848 791
SAC	54–68	8.8–21	30–600[a]	30 (UV)	8200
TAT	40–60	19–22	<200	0	190 000[b]
UFF	30–60	13–30	120–150	500–700 (UV-A)	1 044 350

[a] Occasional direct sunlight gives illuminance of up to 30 000 lux.
[b] Number of visitors to the Clore Gallery specifically, rather than to the entire Tate Gallery.

Table 2
Summary of data on pollutant gases (ppb) at selected sites[a]

Site	NO_2	SO_2
ALC	0–42 (O)[b]	0
RDO/RNW	35 (O)	2 (O)
SAC	10–15 (O)	2–4 (O)
TAT (Clore)	<2 ppb (all gases)	
UFF	16–27 (I)[c]	0.4–2.1 (I)
	20–50 (O)	<6 (O)

[a] NO_2 levels highest in winter, O_3 levels highest in summer.
[b] Indoor value.
[c] Outdoor value.

is not connected to the central air-conditioning system, and relative humidity is controlled by three mobile RH units, although these units are not always employed. It also has very low light levels.

At the Uffizi Gallery, the ERA sensor, as described in the second paper, was located in Leonardo's room next to ''The Baptism of Christ'' by Andrea Verrocchio and Leonardo da Vinci (1472–1475). This room was selected since spectroscopic measurements have been previously made on the predella by Luca Signorelli (opposite to the painting) [11]. Monitoring of air quality at regular intervals is also performed in the Uffizi Gallery. In the Botticelli room, e.g. levels of nitrous and nitric acid (formed from the reaction of NO_2 and H_2O in heterogeneous phase) of up to 12 μg/m^3 have been detected [12].

El Alcázar in Segovia is Spain's third most important monument and as such is a much visited site. It contains a mixed collection of tapestries, paintings and armoury. The dosimeter was exposed in the Cord room (Fig. 1). This room was selected for its high levels of

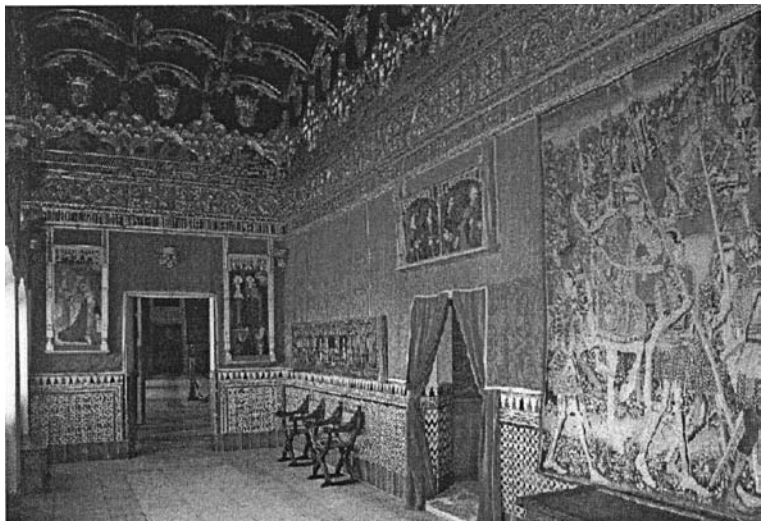

Fig. 1. The Cord room of El Alcázar.

light. The high light levels (unfiltered daylight) are due to the presence of large windows, a later modification to the structure which was made in the 1950s. The name "Cord room" arises from the cord that surrounds it. According to Segovian legend, Alphonse X ordered this Franciscan cord to be placed there as a sign of penance for his excessive pride. The walls are decorated with a tapestry showing the Battle of Arcila, a 15th century panel of The Annunciation, another of St Barbara and St Lucia and a triptych altar made of carved and gilded wood showing different saints and martyrs.

In this paper, data from the smalt pigmented temperas only will be discussed. The following papers in this issue will discuss the results from the basic lead carbonate and basic copper carbonate pigmented temperas. In the case of these pigmented temperas additional spectroscopic techniques (FTIR and XPS) were used in their evaluation.

Smalt tempera has been selected for discussion since it gave the optimum response for both DSC and DMTA techniques. Traditionally, smalt pigment was prepared from the cobalt ore which was roasted. The resulting cobalt oxide was then melted together with quartz and potash or added to molten glass [13,14]. EDX quantitative microanalysis (spot size 2 μm) of the smalt pigment used in this project [obtained from artists' suppliers, Kremer, Aichstetter (O)] recorded values in terms of wt.% as follows: SiO_2 (75%), K_2O (12%) and CoO (11%).

Results smalt tempera are presented from the artificial ageing experiments and compared with the natural ageing of samples exposed at the sites for a 9 month period.

3. Experimental

3.1. DMTA

Samples were examined on the polymeric substrate using a Rheometric Scientific Analyser (Mk3) in bending mode. The measurement parameters are given in Table 3. The artificially aged samples were already cut to a suitable size for the measurements. In the case of the site exposed sensors, a piece, approximately 15 mm long, was cut from the paint strip. In order to conserve as much sample as possible for other experimental work (DSC), the area that would have been directly under the DMTA clamps was scraped off the Melinex substrate. Only the area that was situated between the clamps remained (Fig. 2).

Table 3
Experimental parameters for DMTA measurement

Mode	Single cantilever bending
Frequency	1 Hz
Strain	4 (approximately 64 μm peak to peak displacement)
Frame	Small
Clamping	Flat face spreader
Averaging	None
Temperature range	−130 to 150°C
Heating rate	3°C/min

3.2. DSC

Samples were taken from the dosimeters by scraping with a sharp scalpel blade. They were then transferred to non-standard micro-Al crucibles (prepared in house) and weighed (1–2 mg) using a Sartorius electronic micro-balance. A more generous amount of sample was used from the test paintings than in the case of real paintings where only 50 μg is generally used. DSC analysis was performed using a Shimadzu DSC-50 analyser in O_2 (60 cm^3/min) and a heating rate of 10°C/min. Measurements were made in triplicate. Analysis of the resulting curves was performed using the Shimadzu (TA50) software (includes partial area calculations).

4. Results

4.1. DMTA

The control smalt tempera sample showed an intense broad peak in tan delta (starting at −40°C

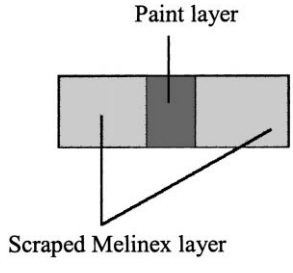

Fig. 2. Test strip after preparation for DMTA measurement.

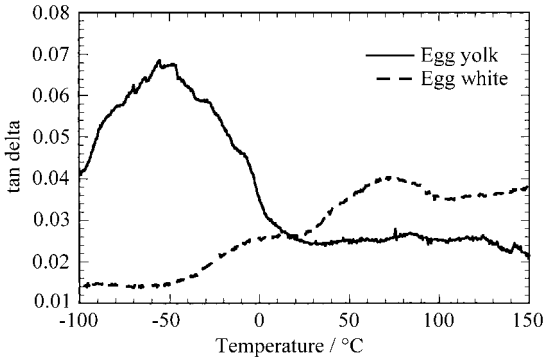

Fig. 3. Tan δ peaks in egg yolk and egg white.

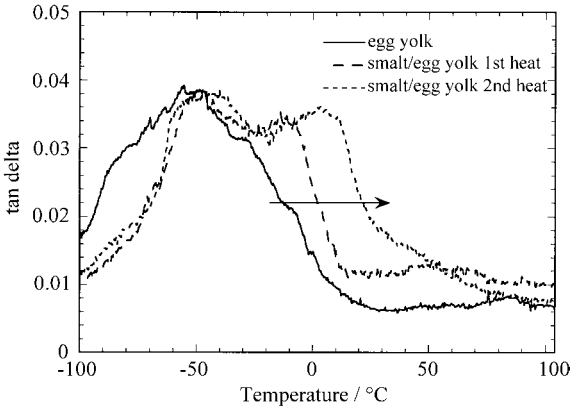

Fig. 4. Tan δ peaks in egg yolk and smalt/egg yolk mixtures.

and continuing to 50°C) with a peak maximum at room temperature (24°C). Fortunately, this lies between the two transitions of the PET substrate at −70 and 120°C.

Although previous studies using DMTA included oil-based paint, there had been no measurements performed on egg tempera-based paint. Additional studies were therefore made on the egg itself in order to understand the observed transition in smalt tempera.

The DMTA curve for naturally aged (ca. 12 months) egg yolk and egg white is given in Fig. 3. The measurements were made on steel substrates. The transition in egg yolk is broad and its maximum is in the region of −50°C. The transition is broad since it probably results from a number of overlapping processes which include phase changes from the various lipid components of egg, e.g. tri- and di-glycerides, cholesterol and the free long-chain fatty acids, and the additional alteration products which form, and which have been discussed in the first paper [1].

The proteinaceous component (from egg white alone) has a transition at higher temperatures (region of 60–70°C), which has also been observed in measurements on cheese [15] and known polypeptides [16]. The effect of the addition of smalt to egg yolk (Fig. 4) is to shift the observed transition to higher temperatures and cause splitting of the peak. This is based on the effect of both physical processes (reinforcing effect of the pigment) which makes the sample harder and chemical processes, e.g. the cobalt ion has been shown to form network structures with lecithins composed of cross-linked aggregates [17]. A repeated scan of this smalt/egg yolk sample produces a shift to high temperatures.

The response that was observed in the smalt tempera dosimeter must therefore be due to changes in the lipid component of the egg. This corresponds with the mass spectrometry studies in the first paper which also focussed on the lipid component. In Fig. 4, the shift on addition of smalt brings the response into the range of room temperature. The weaker peak in Fig. 4 between 50 and 70°C, and coming from the proteinaceous component will not be observed as it coincides with the transition of PET.

The reason for the good response obtained from the smalt tempera can be explained as follows: (1) in physical terms, a stronger response indicates good mechanical integrity of the coating which includes factors such as pigment reinforcement and adherence to the substrate; (2) in chemical terms, a stronger response indicates that processes are occurring in the medium to promote formation of a polymer. For lecithins, the cobalt ion as mentioned previously has been shown to form network structures composed of cross-linked aggregates [17] and this is also known to occur in drying oils in the presence of lead, cobalt and copper ions [18]. This tendency will increase the mechanical integrity of the film as it promotes the formation of the lipid polymer network.

The high pigment volume concentration in the smalt tempera sample is another factor that affects its mechanical properties. The pigmented tempera samples used in this study contained, on an average, approximately 90 wt.% pigment as determined by thermogravimetry (TGA). Sienna tempera, which had been prepared with a higher medium content

(33 wt.%), gave a very weak transition and was not suitable for DMTA measurement. With the higher medium content, the matrix then dominated the mechanical properties [19]. It was also found that additional smalt tempera samples that were prepared with higher medium content (ca. 40 wt.%) did not show the equivalent and expected strong transitions. The smalt pigment particles appear to have a reinforcing effect which assists in promoting the intensity of the transition and hence contribute to the mechanical strength of the coating.

Detailed investigations of the mechanical properties of filled polymers have been reported [20], as has the influence of pigmentation on the mechanical properties of paint films [21]. Particulate fillers, especially inorganics, can significantly affect the structure of the matrix polymer and hence the properties of the final composite. Molecules of the matrix polymer can be adsorbed onto the surface of the particulate phase, and the strength of this attachment determines the composite properties [19].

4.2. Changes with artificial and natural ageing (DMTA)

The characteristic changes for the light aged samples can be described in terms of an overall broadening of the main peak together with its observed splitting. Fig. 5 shows the control and light aged sample (64 days). On the high temperature side of the peak this corresponded to a shift away from the control peak of

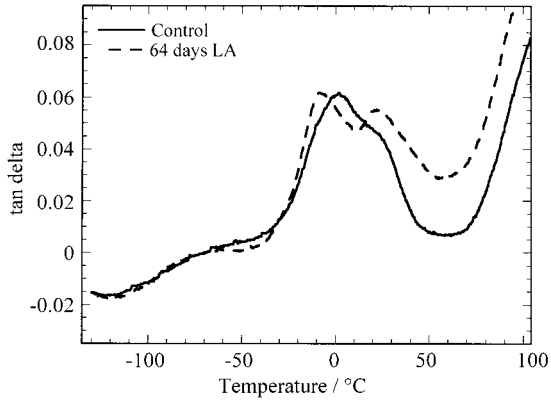

Fig. 5. Tan δ peaks for smalt tempera control and 64 days light aged sample.

over 10°C. This is seen to an even greater extent in the case of the dosimeter exposed in the Cord room in El Alcázar. These curves have been previously reported [2]. However, additional measurements and quantification of the change are reported in this paper. The change was quantified by calculating a peak ratio (i.e. the intensity of the peak at higher temperature to that of the peak at lower temperature).

Using this calculation, for the light aged samples there is a clear positive correlation of peak ratio with received light dosage (Fig. 6). With the thermally aged samples there is no apparent trend. This calculation also shows that the effect of pollutants is less than that of light and works in the opposite manner. In terms of the shape of the DMTA curve, the peak for the NO_x

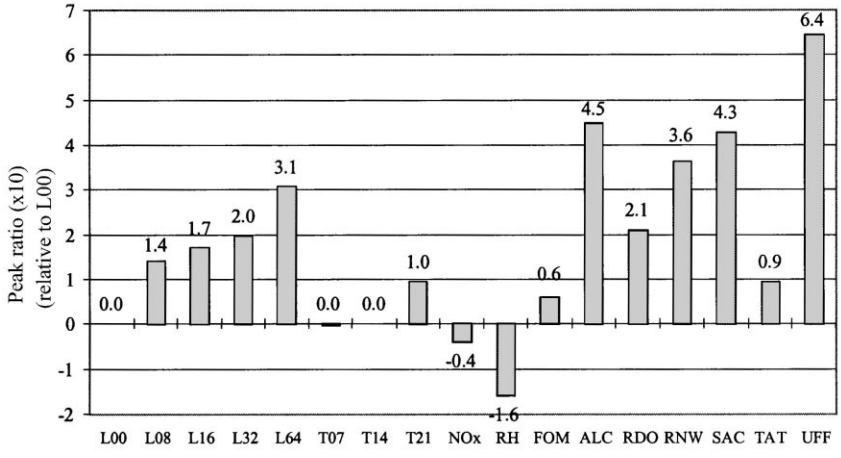

Fig. 6. Change in viscoelastic properties of smalt tempera dosimeters, measured as peak ratio of observed tan δ peaks.

sample is much reduced indicating that cross-linking had occurred in the sample rather than the evolution of the new peak at higher temperature. This indicates that the calculation is biased to the effect of light ageing. (The 4 days light aged sample is not shown as results were anomalous, an observation that is supported by the DSC data, shown later in this paper).

The field site dosimeters are also shown in Fig. 6. Sites where light levels are controlled (e.g. TAT) show a lower response than those where levels are not controlled (e.g. ALC). In the case of UFF, the preceding paper [22] also found that the role of light in the Uffizi Gallery was manifest. However, the role of pollutants remains uncertain. In the DSC evaluation described in Section 4.3, it will be shown that pollutant effects cannot be excluded from the factors contributing to the high value registered for the UFF dosimeter.

It is important to note that the results from the two control samples (L00 and FOM) are similar. The FOM control was stored separately from the L00 control, in an anti-corrosive bag sealed from atmospheric oxygen, whereas the L00 and the other artificially aged samples were placed in cryo-vials. The similarity in data from the separate control samples therefore indicates that the measurements performed are reliable, and that the changes seen in the other samples are real.

4.3. Differential scanning calorimetry (DSC)

A typical DSC curve for the exothermic degradation of smalt tempera control is shown in Fig. 7. DSC curves for the other pigmented temperas have been reported previously [2]. The exothermic degradation occurs over a wide temperature range and the resulting curve is complex. The smalt pigment is thermally stable over the measured temperature range, and the observed curve results purely from the thermooxidative degradation of the binding medium. Fig. 7 also shows that the complex curve can be fitted to give four Gaussian peaks. These have been marked in terms of the components of egg tempera and their corresponding thermal stabilities, i.e. long-chain fatty acids, di- and tri-glycerides are less thermally stable than proteins and resins. The assignment according to thermal stability is based on previous DSC studies of paint media [9].

After artificial ageing, with light, temperature or pollutants, changes can be seen in the overall shape of the DSC curve (Fig. 8). Light ageing causes changes at the low temperature end of the DSC curve. Informa-

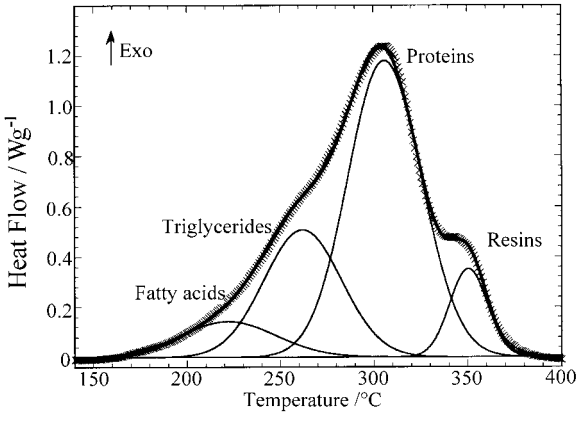

Fig. 7. Fitted DSC curve for the smalt tempera control sample.

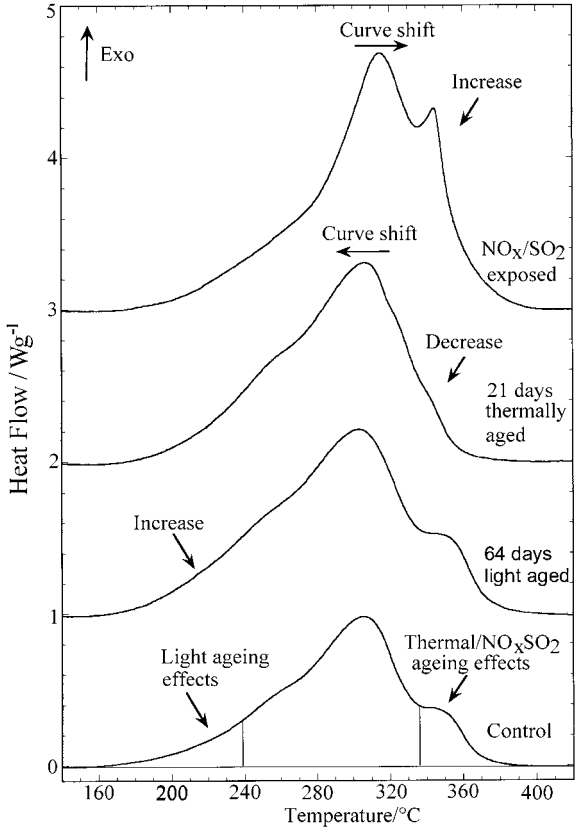

Fig. 8. Selected smalt tempera DSC curves.

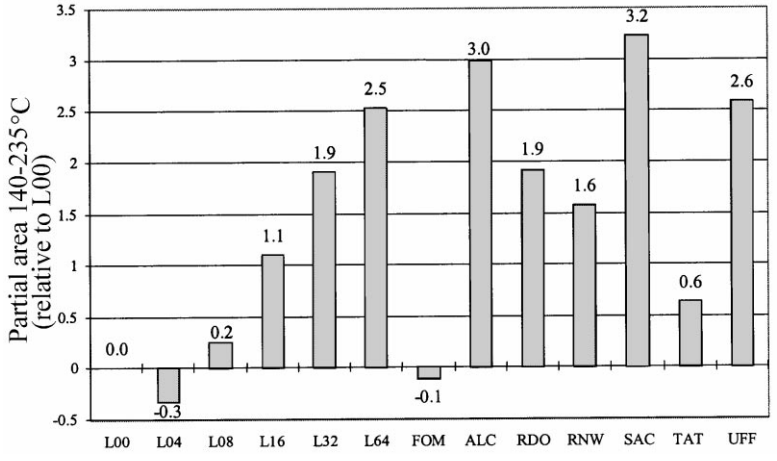

Fig. 9. Thermal stability of smalt tempera based on percentage converted at 235°C.

tion on the chemical nature of the structures which evolve in this region was obtained from mass spectrometry [1]. Increased levels of saturated fatty acids (palmitic, stearic) were identified as cholesterol levels were depleted and its oxidation products were formed. The formation of these products with changes in the chemical composition are then responsible for the changes in the shape of the initial part of the DSC curves.

Quantification of the changes described above was achieved by calculation of the partial area of the low temperature region of the curve (140–235°C). This is plotted against received light dosage in terms of days of exposure (Fig. 9). There is a positive correlation of response (damage/chemical change as measured by partial area calculations) with received light dosage. The graph can then be used to evaluate the amount of damage dominantly from the received light dosage of the test paintings exposed in the museum and galleries.

Once again values for samples from sites such as SAC (Sandham Memorial Chapel) and ALC (El Alcázar, Segovia) which have uncontrolled light levels, can be seen to be the most affected. The TAT dosimeter shows the least alteration and therefore damage. This is somewhat surprising, given that the RDO dosimeter was located in a dimly lit storeroom and should therefore have had the lowest exposure to light. It is therefore likely that the low temperature features of

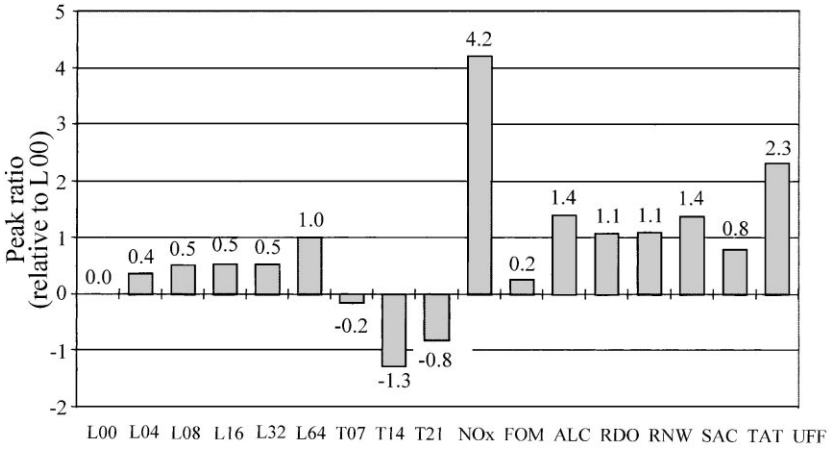

Fig. 10. Thermal stability of smalt tempera sensors based on peak ratio changes.

the DSC curve on which the calibration is based may be affected by other factors such as NO_x/SO_2, as well as light, and these enhance the RDO dosimeter response.

The effect of NO_x on the shape of the DSC smalt tempera curve is strong and can be mainly seen in the evolution of a new high temperature peak (Fig. 8). If another calculation is performed on the ratio of the new HT peak to the original peak, then the resulting calculation favours the effect of NO_x on the samples (Fig. 10). In terms of this calculation, there is a noticeable difference between TAT and UFF. At the TAT location, filters are in place and pollutant levels are negligible; at the UFF location, as mentioned earlier in this paper, there are no filters and values for NO_x have been measured. The effect of pollutants at UFF location is further confirmed by the results from the sienna dosimeter as obtained by mass spectrometry and reported in another paper in this issue [1].

5. Conclusions

The principle of dosimetry has been shown to work in that a systematic change in the DSC curve (related to change in chemical composition) occured with received and known dosages of light. Since light exposure provides a good calibration, the naturally aged sites can be interpreted in terms of this data. The background information on the environmental parameters at each of the sites then serves as a check on the calibration. The smalt dosimeter was able to discriminate between sites which were environmentally controlled (e.g. TAT and RNW) and those which were uncontrolled (e.g. ALC and SAC). One aspect which has not as yet been explained is that the results of the naturally aged samples far exceed those of the artificially aged samples, despite the fact that in the artificial ageing enhanced light levels were used which would produce an equivalent museum exposure of 50 years (for 64 days artificial ageing), compared to the 9 months of actual museum exposure. This may be explained in terms of the synergistic action of the museum environmental parameters e.g. relative humidity, temperature, light and pollutant levels, the effects of which exceed those generated by artificial light ageing alone.

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