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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

A NOVEL APPROACH TO THE PROBLEM OF CHARACTERIZING THE BINDING MEDIA IN EARLY ITALIAN PAINTINGS (13th / 16th CENTURY)

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This paper reports on the observations made on samples from five Italian paintings (13th/16th centuries) using Differential Scanning Calorimetry (DSC). Previous studies of paint samples using Differential Thermal Analysis (DTA) have demonstrated that the resulting curves are sensitive to the age of the sample [1], its chemical composition and the type of white pigment used [2]. Since DSC provides a direct measure of the heat evolved during an exothermic reaction, it can be used to quantify the effects previously observed using DTA.

Outline of the approach to the problem

The basic problem is characterizing binding media lies in the small amount of sample which is available and that the sample is often a complicated mixture of materials which have aged or changed in the process of various restoration treatments [3]. Then there is the additional problem of suitable reference materials and the influence of pigment mixtures.

The aim of this paper is to demonstrate that with careful sampling and small sample size it is possible to obtain DSC curves which reflect the type of medium used. Furthermore, measurements of the accompanying DSC parameters allows for quantification of the observed phenomena. The starting point of the investigation focussed on samples from a painting attributed to Coppo di Marcovaldo from the Chiesa del Carmine in Florence. As this is a painting from the second half of the 13th century it represents an example of an early tempera painting. Microchemical tests also confirmed the presence of proteinaceous medium [4]. Hence the DSC curves obtained

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from samples taken from this painting could be considered to represent standard curves for old proteinaceous material. These curves were then used to interpret results from the following paintings:

Tintoretto: The assumption of the Virgin Mary (ca. 1560), Bamberg Cathedral.
L'Ortonlano: Museo di San Martino Naples (1521).
Giovanni Bellini: The death of St.Peter Martyr.
Francesco Giorgio di Martini: Nativity of Christ (ca. 1500).

It is anticipated that the resulting DSC curves and measured parameters will assist in characterizing future samples from painting of this period. A comparison of the data obtained was also made with those resulting from standard samples containing lead white/egg yolk and lead white/egg yolk and oil mixtures which had been prepared in the laboratories at the Fortezza da Basso in Florence in 1978.

Brief review of thermal analysis studies on the binding media of paintings

Initially hot stage microscopy was used for the examination of samples from paintings to determine whether thermal analysis could provide a means of determining the age and hence the authenticity of a painting. Results indicated that differences were indeed observed for samples from paintings of different periods [5]. This work then led to the use of Differential Thermal Analysis where the observed age-related changes were measured and the results expressed in terms of the ratio of the two exothermic peaks observed. It was then maintained that this ratio varied in an exponential manner with age for paintings which were not more than 100 years old [1]. Subsequent studies on samples containing known pigment (basic lead carbonate) showed that the relationship between peak ratio and age could not be so precisely defined. The peak ratios seemed to provide only an indication of age induced changes rather than the basis of a dating test. The results demonstrated, however, DTA was of more direct value for characterising the binding media of paintings [2] and showed the inherent sensitivity of peak ratios to the presence of additives such as egg or resin in the mainly oil samples. It was also possible to readily distinguish between non-oil and oil-based paint media even in samples which were about 500 years old.

Experimental

(a) Sampling: Samples were taken from the upper layers of the paintings from areas where the varnish had been previously removed either mechanically or by cleaning with a solvent. A small amount was taken by scraping the surface with a scalpel blade and transferring the material to a glass slide.

(b) DSC measurements: Samples (0.1–0.4 mg) were heated in platinum crucibles in oxygen (flow rate 60 cm^3/min). The heating was carried out in a Perkin-Elmer DSC7, and the parameters were evaluated using the TAS-7 software.

Results and discussion

The white sample from the 13th century painting attributed to Coppo di Marcovaldo gave rise to a DSC curve as shown in Fig. 1*a*. The peaks represent the oxidation of the organic component together with the change of lead white pigment to red Pb_3O_4 and finally, if heated to 650°, to yellow PbO.

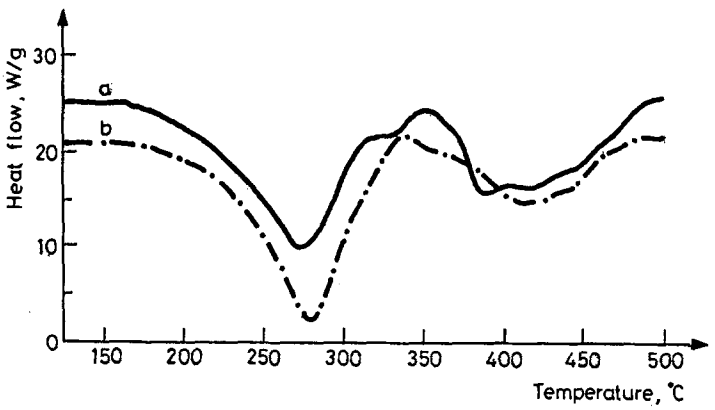

Fig. 1 DSC curves of 1 (*a*) Coppo di Marcovaldo, sample weight: 0.133 mg and 1 (*b*) F. di Giorgio Martini, sample weight: 0.145 mg. Heating rate: 40 deg/min

The similarity of the two curves (Fig. 1*ab*) indicates that the samples have similar chemical composition. If the curve from the Coppo di Marcovaldo sample (Fig. 1*a*) is considered as being representative of an early tempera painting then the sample from the Martini painting (Fig. 1*b*) must also be of that type. In both cases the dominant exothermic peak occurs over

the temperature range 170° to 350° with a peak maximum in the region of 270–280°.

The Martini sample was taken from the white of the architectural background. Another white sample from the same painting taken from the dog's paw in the foreground gave rise to quite a different DSC curve, Fig. 2*a*.

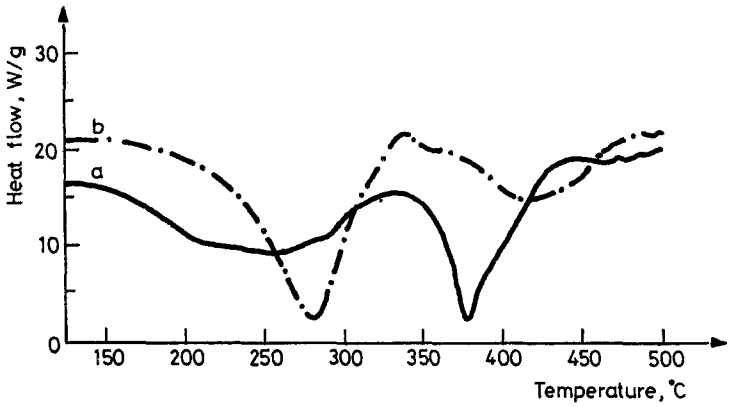

Fig. 2 DSC curves of 2 (*a*) F. di Giorgio Martini, sample weight: 0.191 mg and 2 (*b*) F. di Giorgino Martini, sample weight: 0.133 mg. Heating rate: 40 deg/min

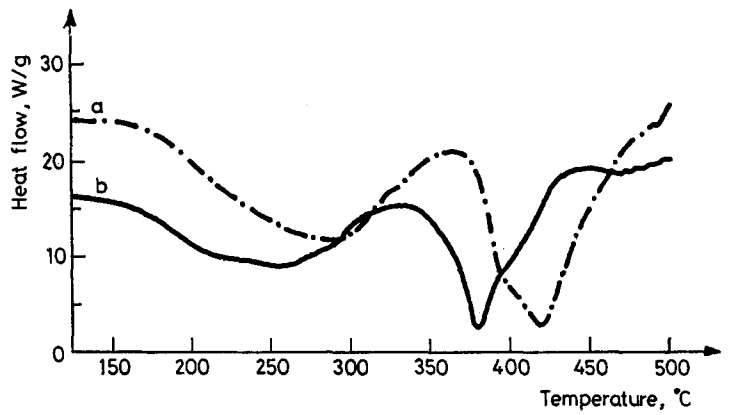

Fig. 3 DSC curves of 3 (*a*) Giovanni Bellini (shield), sample weight: 0.139 mg and 3 (*b*) F. di Martini (dog's paw), sample weight: 0.191 mg. Heating rate: 40 deg/min

Here the dominant exothermic peak appears in the temperature range 350–450° with a peak maximum in the region of 370°. There is another peak in the region 160–350° but this is broader and considerably smaller than the main exothermic peak of the first Martini sample, Figs. 1*b* and 2*b*. From pre-

vious work [6] this curve is identifiable as that which is obtained from an oil-based medium.

Figure 3*a* shows the DSC curve of a white sample from the Bellini painting (white area of shield). This is similar to the Martini sample (Figs 2*a* and 3*b*), in oil-based medium, except that both peaks have been shifted to higher temperatures. GC/MS work [7] has indicated that the medium contains a

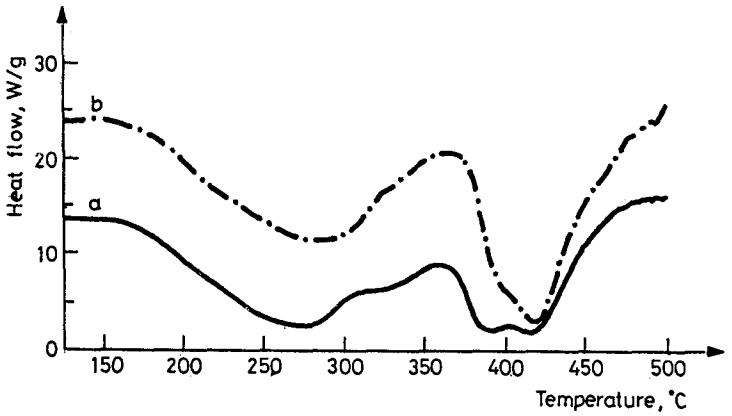

Fig. 4 DSC curves of 4 (*a*) Giovanni Bellini (robe), sample weight: 0.129 mg and 4 (*b*) Giovanno Bellini (shield), sample weight: 0.139 mg. Heating rate: 40 deg/min

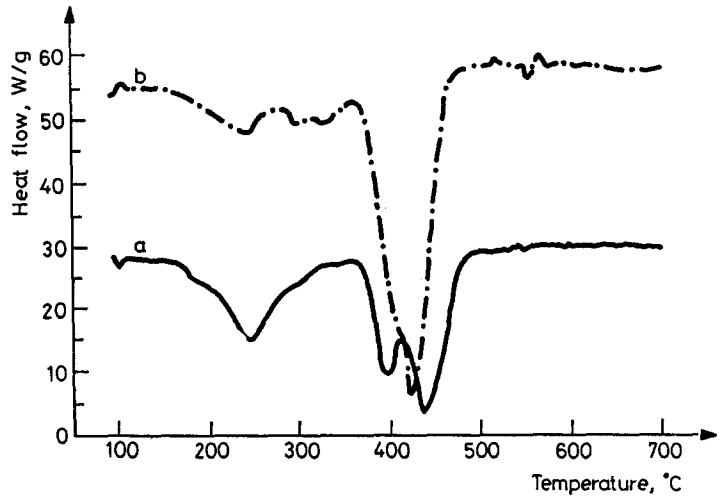

Fig. 5 Standards: DSC curves of 5 (*a*) Linseed oil/egg yolk, sample weight: 0.210 mg and 5 (*b*) Linseed oil, sample weight: 0.378 mg. Heating rate: 40 deg/min

drying oil which has been heat-bodied. The latter may well introduce a greater degree of cross-linking in the oil and this would result in the oxidative degradation processes occuring at higher temperatures. Further samples need to be studied to confirm this observation.

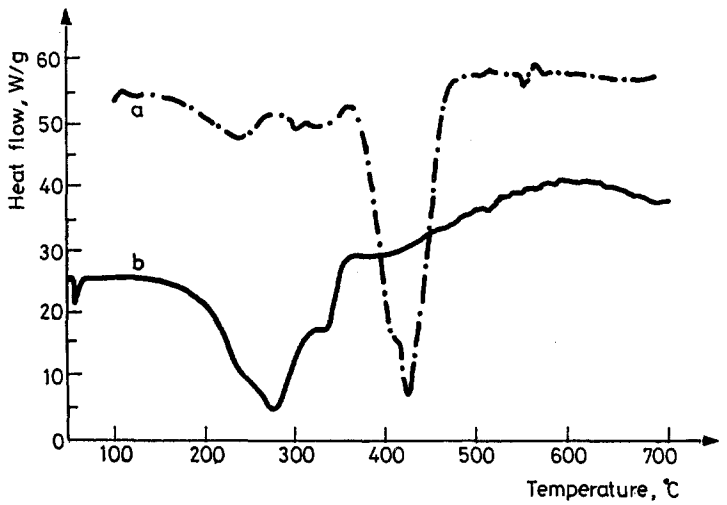

Fig. 6 Standards: DSC curves of 6(*a*) Linseed oil, sample weight: 0.224 mg and 6 (*b*) egg yolk, sample weight: 0.210 mg. Heating rate: 40 deg/min

A sample from a different area in the Bellini painting, the white of the Dominican robe, gave rise to a DSC curve, Fig. 4*a*, where the total exothermic effect is less than the value for the previous sample (heat-bodied oil) but greater than that obtained for the egg tempera sample, Fig. 1*a*.

Table 1 Measured enthalpy value (ΔH) for total observed exothermic effect

Figure No.	ΔH	Medium-type
3a	4498.6	heat-bodied oil
4a	3705.9	oil/egg tempera
1a	3193.2	egg tempera
6a/5b	5709.4	linseed oil
5a	3986.1	linseed oil/egg yolk
6b	3383.0	egg yolk

$\Delta H = \mathrm{Jg}^{-1}$

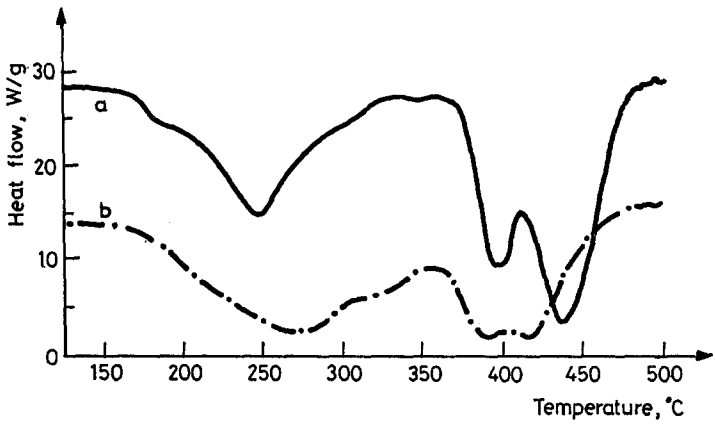

Fig. 7 DSC curves of 7 (*a*) Giovanni Bellini (robe), sample weight: 0.378 mg and 7 (*b*) Linseed oil/egg yolk (standard), sample weight: 0.129 mg. Heating rate: 40 deg/min

In case of standard samples, Figs 5 and 6, prepared in 1978 the total measured exothermic effect was found to be greater for linseed oil/lead white than for a mixture of linseed oil/egg yolk/lead white, and this in turn was greater than that measured in a sample of egg yolk/lead white (Table 1). Hence it appears likely that the sample from the white of the Dominican robe contains a mixture of oil and egg tempera, Fig. 7. GC/MS measurements confirmed that the medium contained a drying oil with some egg tempera.

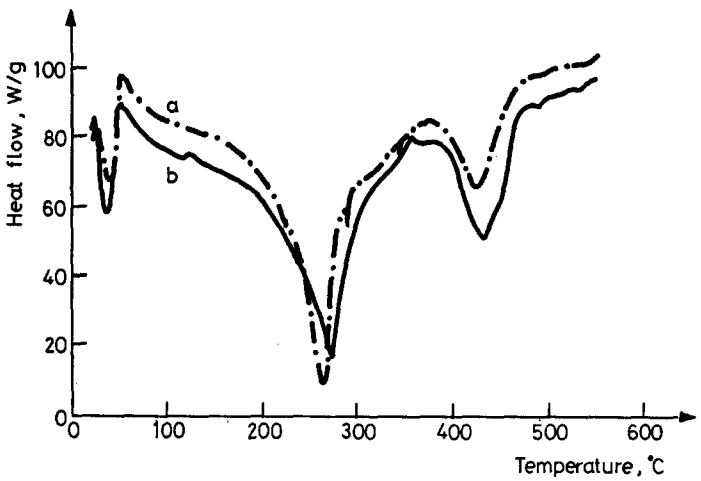

Fig. 8 DSC curves of 8 (*a*) Tintoretto, sample weight: 0.113 mg and 8 (*b*) Coppo di Marcovaldo, sample weight: 0.098 mg. Heating rate: 40 deg/min

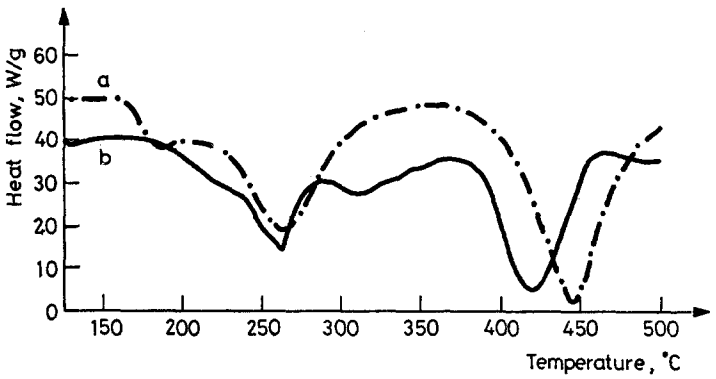

Fig. 9 DSC curves of 9 (*a*) Giovanni Bellini, sample weight: 0.059 mg and 9(*b*) L'Ortonlano, sample weight: 0.156 mg. Heating rate: 40 deg/min

Table 2 DSC parameters for white samples

	1st exotherm			2nd exotherm		
Figure No.	$T_{o,1}$	H_1	A_1	$T_{o,2}$	H_2	A_2
1a	171.8	14.9	1650	366.0	9.0	1173
1b	174.3	19.1	1854	367.0	6.9	775
2a	163.5	6.8	1068	360.6	14.8	848
3a	176.4	10.4	1709	378.3	18.8	1523
4a	175.9	8.9	1345	368.3	10.5	963
5a	167.7	12.9	1317	375.2	24.9	2289

Note: T_O = ^oC; H = Wg^{-1}; A = Wg^{-1} min

Figures 8 and 9 show additional results obtained from samples taken from green areas from four of the paintings. The DSC curves in Fig. 8 are similar to the tempera-type of Fig. 1. The stronger exothermic nature of the first peak can be attributed to pigment interaction which would occur to a larger extent with Cu based pigments and proteinaceous medium than with lead white. The green sample from the Tintoretto painting was analysed by emission spectroscopy and was found to contain Cu-type pigments [8]. Microchemical tests also indicated the presence of protein. Figure 9 shows curves which are similar to Figs 3*a* and *b*, oil-type.

GC/MS confirmed that the medium of the sample from the green of the plants in the Bellini painting does contain a heat-bodied oil. This again could be the reason for the noticeable shift of the high temperature exotherm of the Bellini sample to higher temperatures. The calculated DSC

parameters for the white samples are given in Table 2; those for the green samples are given in Table 3.

Table 3 DSC parameters for green samples

	1st exotherm			2nd exotherm		
Figure No.	$T_{o,1}$	H_1	A_1	$T_{o,2}$	H_2	A_2
8a*	261.7	70.5	5947	386.2	24.2	1660
8b*	193.9	56.3	5272	395.4	33.9	2346
9a*	187.3	24.1	2386	387.8	32.3	1939
9b	168.8	30.5	3332	399.7	44.8	3677

* Samples were heated in aluminium crucibles

Conclusion

DSC curves and calculated parameters indicate that it is possible to quantify the observed differences and then to use such information for pattern recognition of future samples. The small sample size and no sample pre-treatment offers an attractive method which together with GC/MS or pyrolysis/MS should provide a powerful means for characterizing binding media.

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6 See ref.2, p.1051.
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8 Die Bamberger "Himmelfahrt Mariae" von Jacopo Tintoretto. Internationales Kolloqium in München. 27-28th January 1986 und Restaurierungsbericht Arbeitsheft, 42 Bayerisches Landesamt für Denkmalpflege, p. 135.

Zusammenfassung — Diese Arbeit berichtet über DSC-Beobachtungen an Proben von fünf italienischen Gemälden (13./16.Jahrhundert). Vorangehende Untersuchungen von Farbenproben mittels DTA zeigten, daß die sich ergebenden Kurven vom Alter der Probe [1], ihrer chemischen Zusammensetzung und von der Art des verwendeten weißen Pigmentes abhängen [2]. Da DSC eine Möglichkeit bietet, die bei einer exothermen Reaktion freigesetzte Wärme direkt zu messen, kann sie benutzt werden, um die mittels DTA gefundenen Ergebnisse zu quantifizieren.