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Thermal analysis for the characterisation of grounds used in works of art: preliminary results

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Abstract

Thermal analysis (thermogravimetry (TG) and derivative thermogravimetry (DTG)) has been applied to study the composition of commercially available base grounds. In several samples an additional XRD analysis was required for full characterisation purposes. Thermoanalytical curves of grounds, belonging to two works of art were also carried out. The results obtained by thermal analysis were related to the nature and composition of the ground layers providing useful information in further studies on grounds used in canvas, sculpture and altarpieces. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The present paper is part of a study of grounds used in sculpture and altarpieces from the Balearic Islands during the 15–18th centuries. The study of the basis of painting implies chemical characterisation of the samples. According to the literature, several studies on grounds have been carried out [1–4].

The application of thermoanalytical techniques in the investigation of ancient materials (wood, incense, weights and money) is illustrated with several examples by Wiedemann [5], who pointed out that thermal analysis especially in combination with other analytical techniques are powerful methods in archaeometry.

The aim of the present investigation is to show how thermoanalytical instrumental techniques can provide significant information on the component materials of base grounds and their purity. For this purpose, different commercially available grounds were analysed by thermogravimetry (TG) and derivative thermogravimetry (DTG) together with differential thermal analysis (DTA) and the results are reported in detail herein. In addition, the application to the analytical characterisation of grounds belonging to sculpture and altarpieces is presented allowing the determination of the nature and composition of the former ground layers.

2. Experimental

2.1. Materials, instrumentation and operating conditions

Commercially available calcite and gypsum-based grounds were employed as samples and obtained from

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conservator workshops. Thus, Scagliola (SCA), Anhydride Plaster (ANP), Terra Alba (TA) and Alabaster Plaster (ALP) supplied by Kremer were employed and chalk (CRE), chalk from Chamgagne (YCH), chalk from Bologna (YB) and Blanco de España (BFL) were purchased from Fluvia SL. Finally, Yeso mate (YM) was acquired from a local supplier. Dihydrate calcium sulphate (chemically precipitated from Panreac of 99% (w/w) of purity), calcium carbonate (Merck, 99% (w/w) of purity), hemihydrate calcium sulphate (Fluka, 97% (w/w) of purity) and dolomite (DO) from Bureau of Analysed Samples, containing $CaCO_3$ 55.2%; $MgCO_3$ 43.1%; SiO_2 0.88%; Fe_2O_3 0.21% (w/w) were used as standards.

For thermogravimetric analysis (TG–DTG), the samples were dried at room temperature (in dessecator with silica gel blue) for at least 1 week. The TG–DTG curves were obtained using a thermobalance from thermal analysis instrument (SDST 2960) with temperature and weight precision of 0.1 °C and 0.1 μg, respectively. The temperature calibration was performed using melting points of indium, lead and aluminium standards. The sample mass was varied between 10 and 15 mg and the samples were weighed on platinum pans. TG–DTG experiments were performed in flowing dry nitrogen atmosphere (100 ml min^{-1}) and at a heating rate of 10 °C min^{-1} within the temperature range 25–1000 °C and carried out in duplicate. Transmission IR spectra were recorded using a Bruker IFS 66 FTIR spectrophotometer. KBr pellets of powered samples were examined between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1}.

3. Results and discussion

TG–DTG curves for all the samples tested are shown in Figs. 1–3. The relevant thermogravimetric data, referring to the temperatures of the various steps and the loss of mass during the corresponding steps, were recapitulated in Table 1.

For the samples tested the main differences were obtained within the temperature ranges of 100–200 and 400–800 °C. The percentage experimental residue found at 900 °C is higher than 90% (w/w) in ALP, ANP, SCA samples; for TA, YB and YM is approximately 80% (w/w) and for BFL, CRE and YCH is about 60% (w/w).

To identify these steps dihydrate calcium sulphate, hemihydrate calcium sulphate, calcium carbonate and DO, in the same thermal conditions as the samples, were recorded and used as standards. The TG curve of $CaSO_4\cdot(1/2)H_2O$ shows a weight loss of about 5% (w/w) within the temperature range 70–130 °C (IGT_{max} = 111 °C for endothermic DTA peak). This value agrees with that calculated by stoichiometry for the formation of the anhydrous form of the salt. Under the experimental conditions used (heating rate of 10 °C min^{-1}), the weight loss due to the crystallisation water of $CaSO_4\cdot2H_2O$ takes place within the 110–180 °C range (IGT_{max} = IG139 °C for endothermic DTA peak) and occurs in a single (only) step. This apparent discrepancy with data reported in [6] has been previously mentioned by Dei et al. [7]. The experimental weight loss found (20.3% (w/w)) coincides with the calculated loss (20.9% (w/w)). The TG–DTG curves of calcium

Table 1
Data from TG–DTG curves

Sample	Weight loss (%)						
	30–100 °C	PT[a] (°C)	100–300 °C	PT[a] (°C)	400–800 °C	PT[a] (°C)	
ALP	1.08	35	5.1	114	1.45	556	654
ANP	–	–	1.2	112	0.25	605	–
BFL	–	–	–	–	42.7	–	757
CRE	–	–	–	–	36.8	722	752
SCA	0.99	33	5.2	112	1.68	575	663
TA	–	–	11.9	122	2.33	–	646
YB	–	–	19.3	132	2.05	–	655
YCH	–	–	–	–	44.0	–	755
YM	–	–	20.1	121, 135	–	–	–

[a] PT: peak temperature of the DTG curve and represents the temperature at which the rate of mass-change is at a maximum.

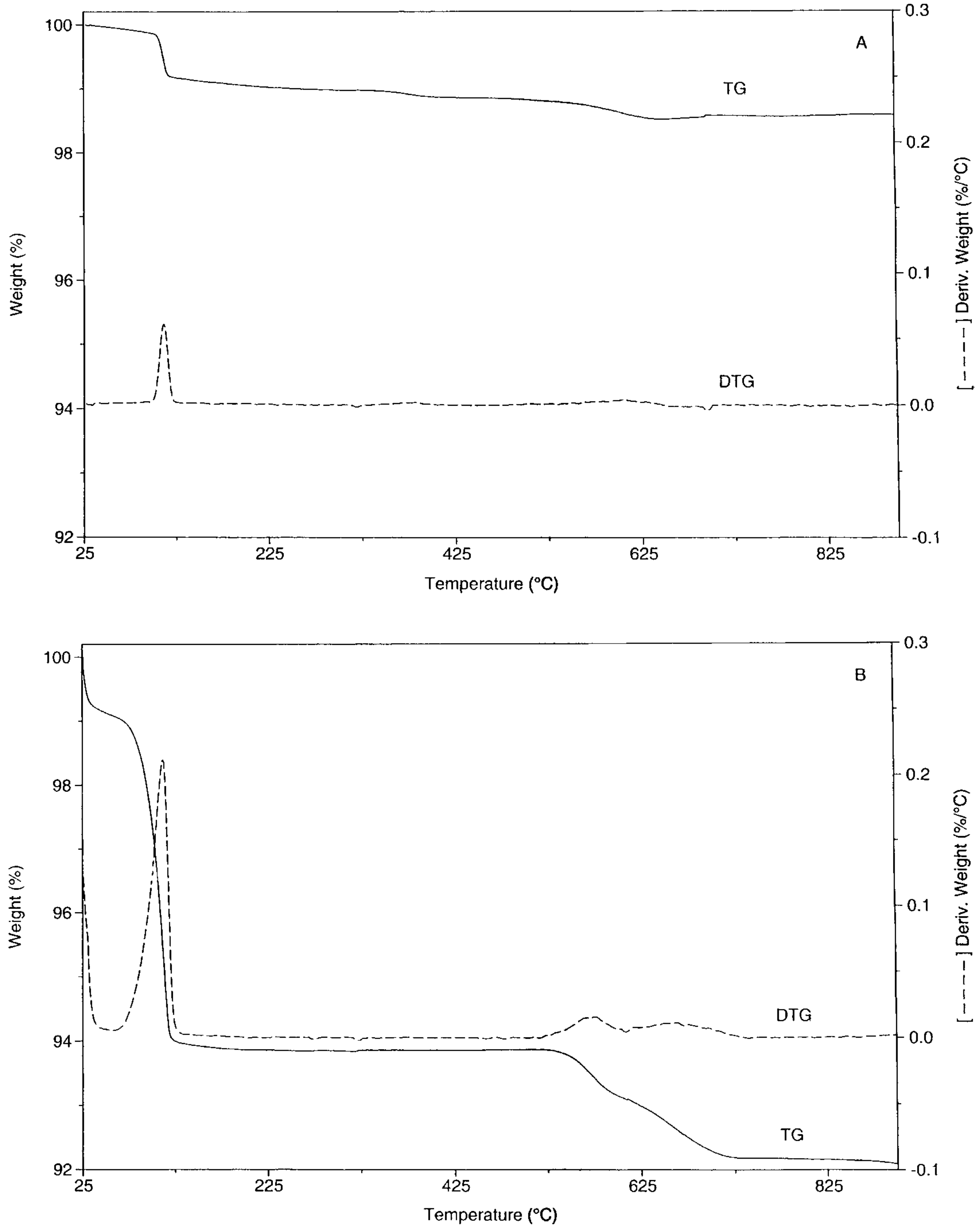


Fig. 1. TG and DTG curves of the grounds studied: (A) ANP; (B) SCA.

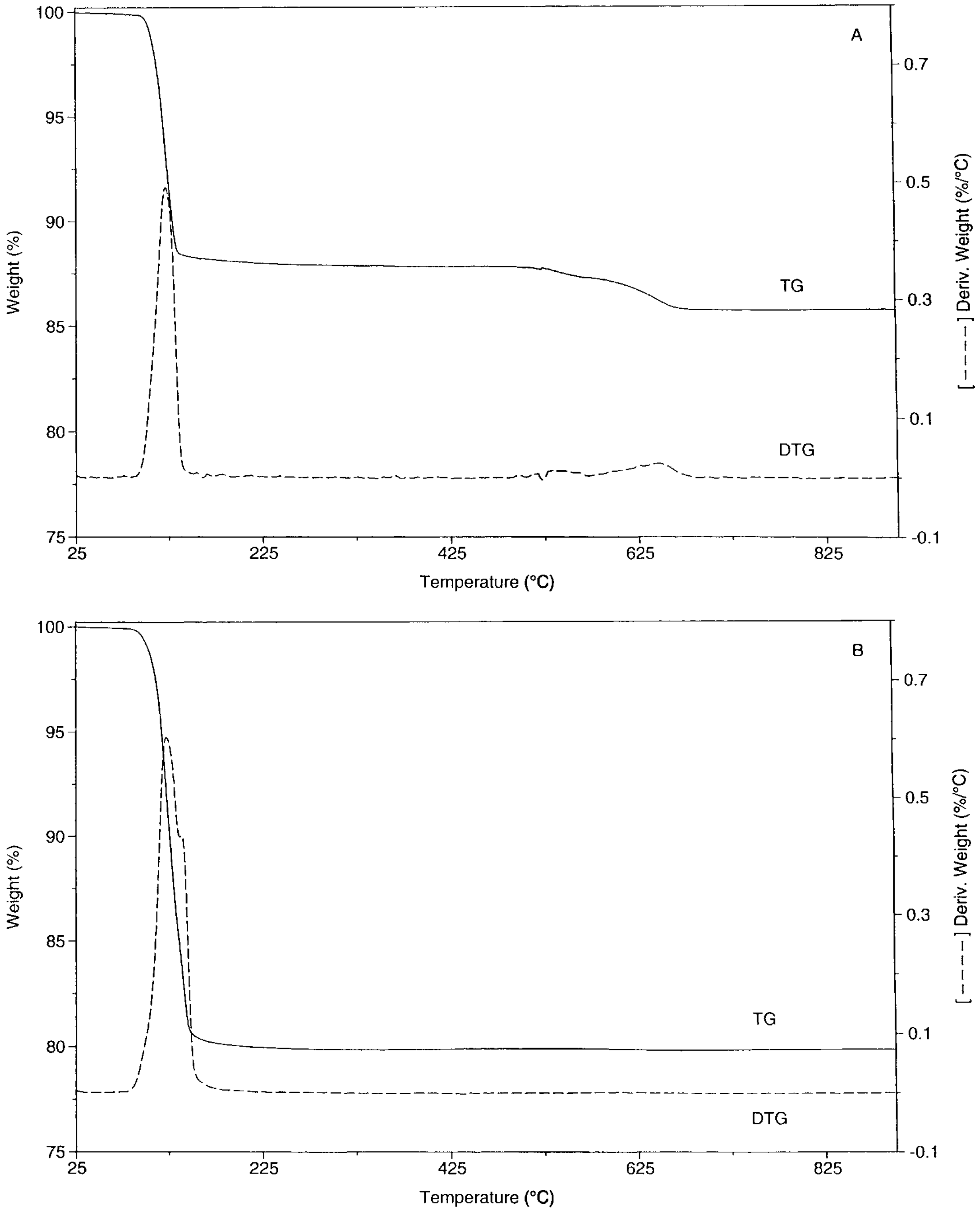


Fig. 2. TG and DTG curves of the grounds studied: (A) TA; (B) YM; (C) YB.

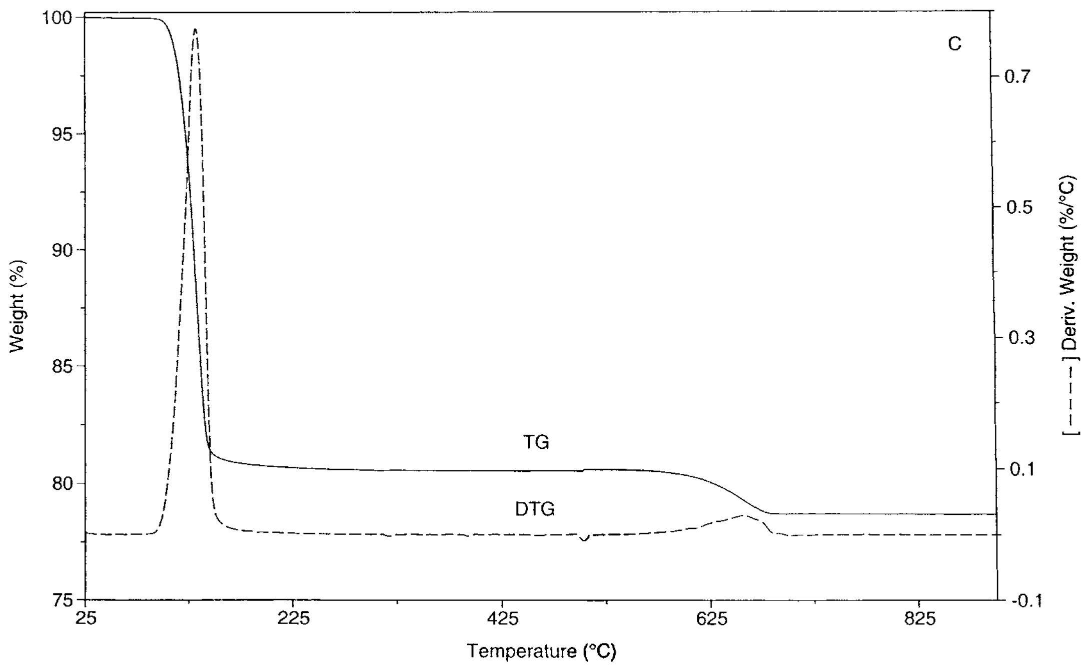


Fig. 2. (*Continued*).

carbonate and DO were also recorded. Weight losses of 43.6 and 46.7%, respectively were obtained (theoretical values: 44 and 46.8% (w/w)). Calcium carbonate and DO exhibited endothermic DTA peaks at 690 and 748 °C, respectively.

The thermal effects related to the weight loss of ANP and SCA samples can be observed in Fig. 1A and B. TG–DTG curves of ALP and SCA samples being very similar. Endothermal effects on the DTA curves with T_{max} at 115, 118 and 119 °C, respectively are closely related to the DTA peak for hemihydrate calcium sulphate. The loss of about 5% (w/w) for both SCA and ALP samples are similar to that of hemihydrate calcium sulphate (theoretical value 6.2% (w/w)). Nevertheless, if total weight loss of water was considered (steps 1 and 2) theoretical and experimental results are in good agreement for hemihydrate calcium sulphate. From the residue it may be deduced that in the ANP sample the major compound happened to be anhydrous calcium sulphate, impurified with calcium carbonate and hydrated calcium sulphate.

The TG–DTG curves corresponding to samples YM, TA and YB are represented in Fig. 2. The weight loss between 100 and 300 °C for YB and YM samples (about 20% (w/w), see Table 1), can be attributed to bound water and clearly reveals that practically only calcium sulphate, as dihydrate form, is present. Samples TA and YB showed a second step, between 550 and 650 °C, which can be assigned to the presence of calcium carbonate impurities. The DTA curves show endothermic peaks at $\mathrm{IG}T_{max} = 128$ °C for TA sample and $\mathrm{IG}T_{max} = 139$ °C for YB sample, whereas an endothermic peak, which slightly splits into two T_{max} at 122 and 139 °C, was observed for YM sample. Endothermal effects on the DTA curves of CRE, YCH and BFL samples with T_{max} at 755, 756, 758 °C, respectively, were observed (Fig. 3). No weight losses are detected in the step comprising between 100 and 300 °C. Within the 400–800 °C range a significant weight loss was found in the former samples, which represents about 40% of their weight. DTA curves for calcite ($\mathrm{IG}T_{max} = 750$ °C) and DO ($\mathrm{IG}T_{max} = 748$ °C) are closely related to those of the samples above mentioned. These results clearly reveal that only carbonates are present in these samples. Experimental and theoretical residues, assuming calcium carbonate, at 900 °C are in good agreement for BFL and YCH samples.

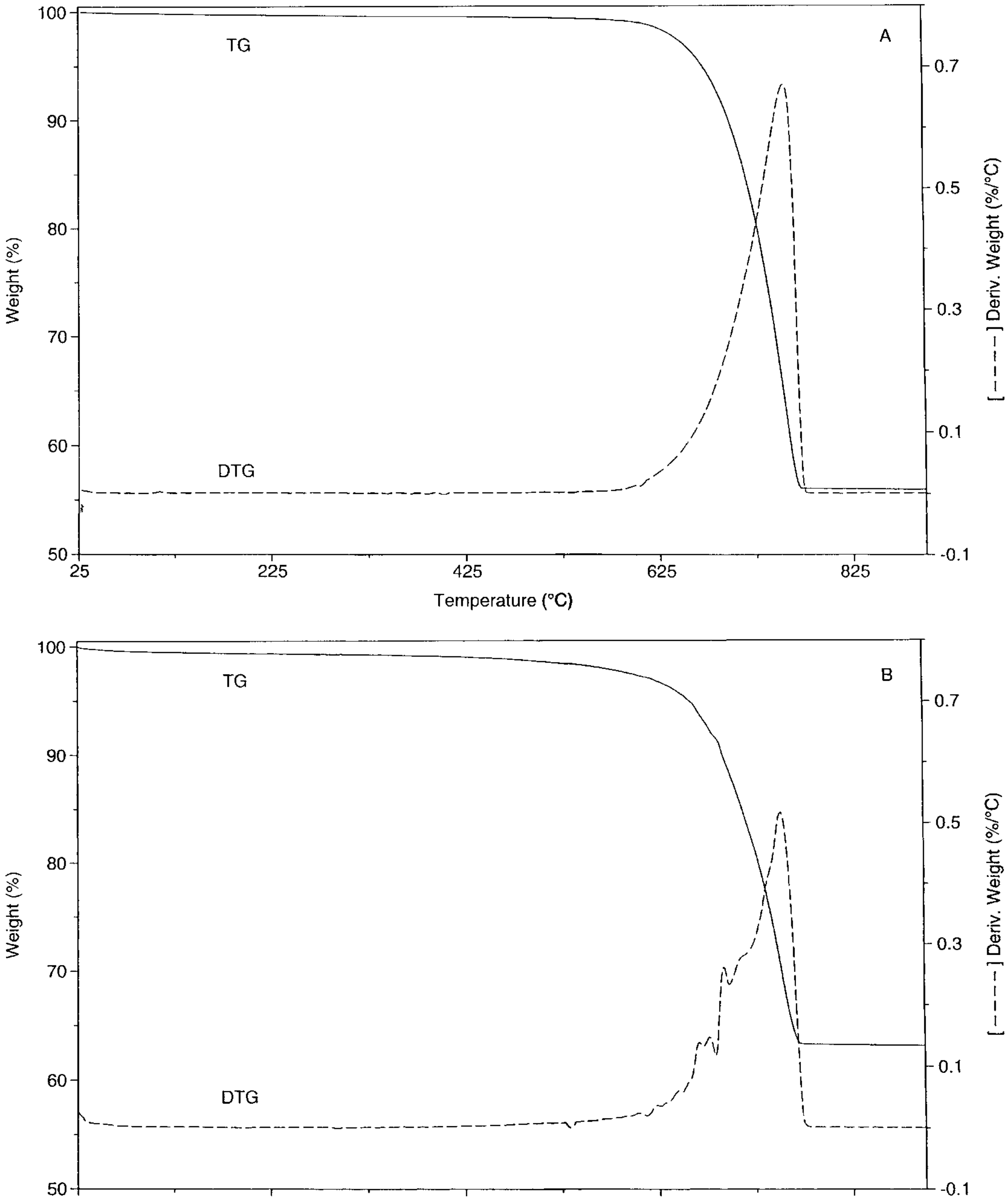


Fig. 3. TG and DTG curves of the grounds studied: (A) YCH; (B) CRE.

Changes following each other very closely cannot be distinguished on the TG curves, as the corresponding stages coincide. However, the DTG curves of the same change indicate by the shape maxima that the thermogravimetric stages can be divided into two parts. In this way, differences in the information provided by TG and DTG curves are found in CRE, YM, SCA and ALP samples.

Table 2
Results of TG–DTG analysis of studied base grounds

Sample	Percentage			Residue (%)	
	$CaSO_4{\cdot}(1/2)H_2O$	$CaSO_4{\cdot}2H_2O$	$CaCO_3$	Calculated	Found at 900 °C
ALP	82.2	–	3.3	79.0	92.0
ANP	19.3	–	–	18.1	98.5
ANP	–	5.6	–	4.5	98.5
BFL	–	–	97.1	54.4	56.8
CRE	–	–	83.6	46.8	63.1
SCA	83.8	–	3.8	80.6	92.1
TA	–	58.1	5.3	48.9	85.6
YB	–	92.1	4.6	75.4	78.7
YCH	–	–	97.3	54.5	55.9
YM	–	95.4	–	75.4	79.8

DTG curve for CRE sample shows two shape maxima which may be ascribed to the calcium carbonate (691 °C) and the DO (752 °C) decompositions. In fact, two peaks for YM at 121 and 135 °C were observed which could be due to the loss of water of the dihydrate which, in this case, would take place in two stages.

Peak temperatures (PT) of the DTG curve for SCA and ALP samples may indicate that the weight loss between 400 and 800 °C was due to the loss of water and carbon dioxide from calcium hydroxide and calcium carbonate, respectively.

Assuming the previous considerations mentioned above, the obtained data are summarised in Table 2. In order to confirm the correctness of the assumption, found residue values were matched with the calculated residues and as it can be observed, there are in good agreement, for YB, YM, BFL, ALP, SCA and YCH samples. The cases in which higher experimental residue values than those calculated for the assignations carried out are obtained reveal the presence of anhydrous salt and/or compounds. In this way, the difference between experimental and calculated residues would be due to these salts.

For these purposes, the morphology and composition were also studied by other analytical techniques, (SEM, XRD and FTIR) and results are reported [8]. FTIR allows to classify the samples as a carbonate or sulphate base ground according to the identifying bands of sulphate (1150 cm^{-1}) or carbonate (1400 cm^{-1}). Several spectra are shown in Figs. 4 and 5. XRD spectroscopy was useful in the detection of the crystalline phases which do not present changes in the course of the heating, such as anhydrous calcium sulphate (anhydrite) as well as to assign the weight loss of water (100–200 °C) to hemihydrate or dihydrate calcium sulphate.

Combined results from TG–DTG analysis with FTIR and XRD allow to deduce the chemical composition of the analysed samples (Table 3).

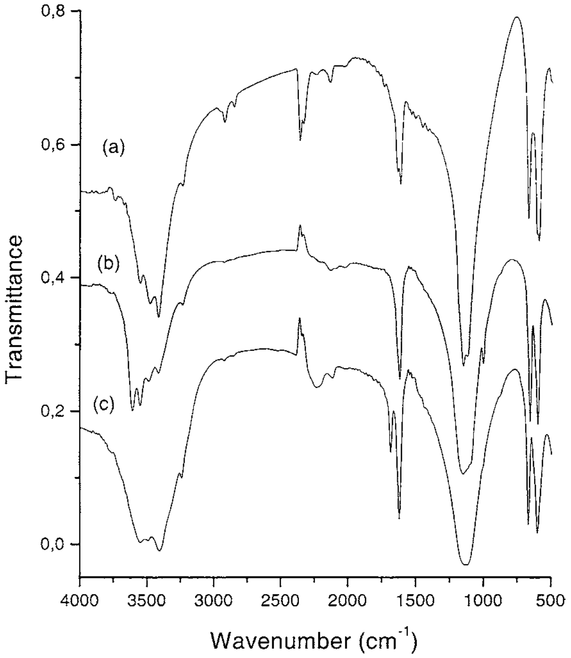


Fig. 4. IR spectra of the grounds studied: (a) ANP; (b) SCA; (c) YB.

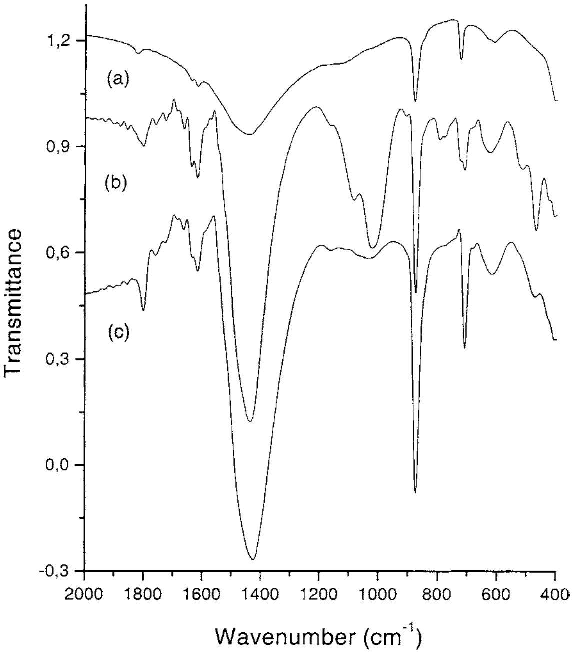


Fig. 5. IR spectra of the grounds studied: (a) DO; (b) CRE; (c) BFL.

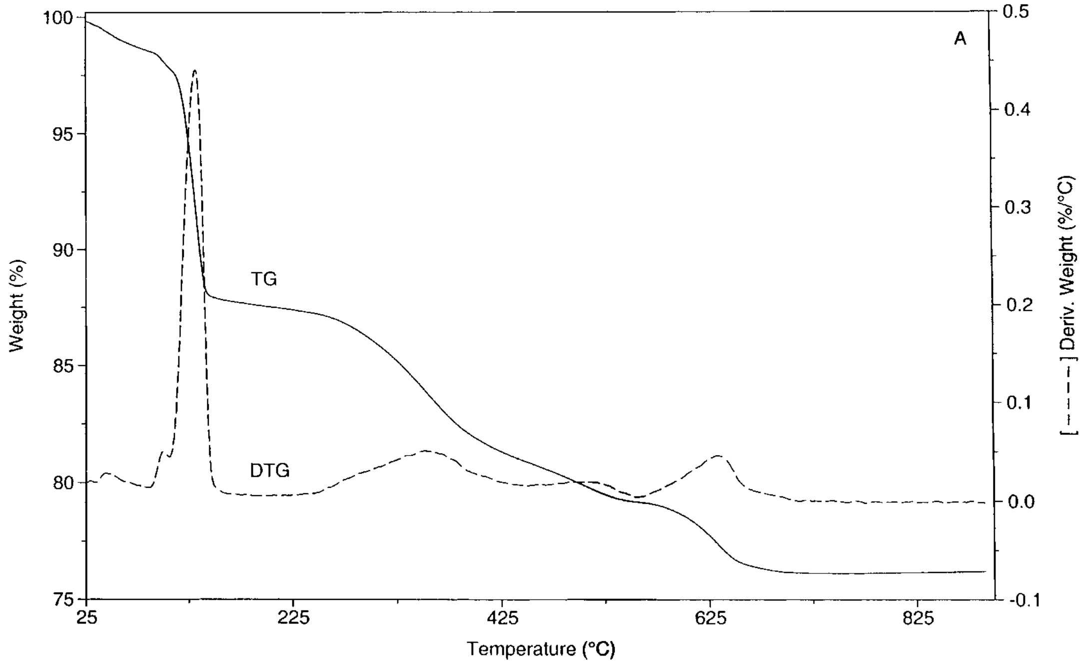
Thus, it was determined that Anhydride Plaster corresponds to anhydrous calcium sulphate (94.6% (w/w)) with impurities of dihydrate calcium sulphate (5.6% (w/w)). The weight loss between 100 and 300 °C was attributed to dihydrate calcium sulphate (confirmed by XRD) and anhydrous calcium sulphate was calculated from the residue at 900 °C. YB and YM are basically composed of dihydrate calcium sulphate and, in a smaller amount, of anhydrous calcium sulphate as it can be concluded from their XRD analysis and percentages calculated as in the previous sample. From the weight loss between 500 and 800 °C the calcium carbonate percentage was determined for the YB sample. TA presents the same composition than that of YB sample but with a larger anhydrous calcium sulphate content. BFL and YCH happened to be calcium carbonate with a high degree of purity. From the loss of CO_2 and using pure DO as standard the percentage of magnesium and calcium carbonate was attributed and from the residue at 900 °C the silicon dioxide percentage was calculated.

The XDR analysis for ALP and SCA samples indicates that bassanite ($CaSO_4 \cdot (1/2)H_2O$) was the main component. Consequently, when the weight loss between 100 and 200 °C was attributed to water from hemihydrate calcium sulphate, the chemical composition which appears in Table 3 may be assigned. From the residue at 900 °C the $CaSO_4$ amount was calculated. Moreover, the chemical composition of ALP and SCA samples may be expressed as the addition of total water weight loss, anhydrous calcium sulphate and calcium carbonate. Results obtained may be expressed as 6.2% of H_2O; 3.3% of $CaCO_3$ and 90.3% of $CaSO_4$ (w/w) for ALP sample and 6.2% of H_2O; 3.8% of $CaCO_3$ and 90.1% of $CaSO_4$ (w/w) for SCA sample.

Fig. 6 shows the TG–DTG curves of two different grounds belonging to artworks. Four steps may be observed. No significant differences were found among samples for steps 1, 3 and 4. However, the height of the TG steps is different. In fact, a very large TG step between 100 and 200 °C occurs in B sample

Table 3
Results of base grounds by FTIR, XRD and TG–DTG analysis

Percentage							
Samples	H_2O	$CaSO_4$	$CaSO_4 \cdot (1/2)H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	$MgCO_3$	SiO_2
ALP	1.1	13.2	82.2	–	3.3	–	–
ANP	–	94.6		5.6	–	–	–
BFL	–	–	–	–	97.1	–	–
CRE	–	–	–	–	53.5	25.5	21
SCA	1.0	12.1	83.1	–	3.8	–	–
TA	–	36.6	–	58.1	5.3	–	–
YB	–	3.3	–	92.1	4.6	–	–
YCH	–	–	–	–	97.3	–	–
YM	–	4.6	–	95.4	–	–	–



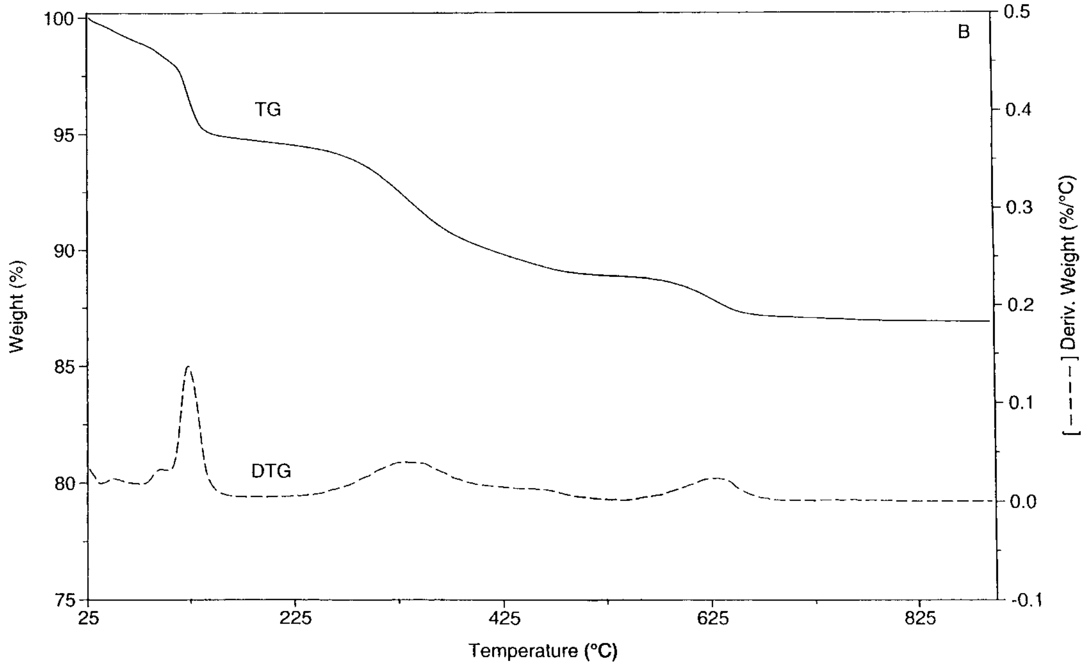


Fig. 6. TG and DTG curves of ground samples belonging to (A) St. Peter's sculpture and (B) a gothic Predela being both from Mallorca, 17 and 15th centuries, respectively.

(10.7% of weight loss), whereas for sample A only 2.3% of weight loss is observed in this temperature interval. From the results previously obtained, steps 1, 2 and 4 have been well recognised. The thermogravimetric step observed between 200 and 600 °C can be reasonably explained in terms of oxidation and combustion of organic matter present in the samples as glue.

Consequently, for a ground coming from canvas, sculpture and/or altarpiece, from the results previously obtained the following changes in weight may be assigned to the following steps: at temperatures below 100 °C the weight loss can be attributed to hygroscopic water (i.e. physically adsorbed water), whereas between 100 and 200 °C the loss of water due to hydrated salts takes place. The thermogravimetric step observed between 200 and 600 °C can be attributed to the combustion of the glue and, finally, weight losses which take place at temperatures over 600 °C to the decomposition of carbonates.

From TG–DTG curves (Fig. 6) relevant information may be deduced. First, the qualitative composition of the ground layer, in this case composed of hydrated calcium sulphate, glue and calcium carbonate (the latter probably due to the impurities of gesso employed). Furthermore, from the weight loss belonging to the third and fourth steps, percentages of glue (as gelatine) and calcium carbonate may be deduced. On the other hand, important differences in the water loss step (between 100 and 200 °C) were found, which implies differences in the hydration degree of the calcium sulphate employed. In this way, work on a detailed study of grounds from different sculptures, canvas and altarpieces is in progress to characterise and determine the composition of the samples.

4. Conclusions

The components of the analysed samples can been characterised in most cases exclusively by TG–DTG analysis. Thus, from thermal analysis, ALP and SCA samples may be assigned to hemihydrate calcium sulphate, ANP to anhydrous calcium sulphate, YM and YB samples to dihydrate calcium sulphate and BFL and YCH correspond to calcium carbonate. However, the difference between experimental and calculated results for the residue of TA and CRE samples, implies that a complete characterisation by using only thermal analysis is not feasible for these samples and that further XRD and/or FTIR analyses, are then necessary.

Consequently, samples containing both calcium carbonate and dihydrate calcium sulphate (weight loss about 20%) or hemihydrate calcium sulphate (weight loss about 5%) may be resolved by using only thermal analysis. However, for mixtures of both and/or anhydrous calcium sulphate an additional XRD analysis would be required.

The application of thermogravimetric analysis to the base grounds from works of art as paintings, sculpture and altarpieces, would provide valuable information about their composition and the nature of the ground layer employed.

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