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TECHNIQUES OF THERMAL ANALYSIS APPLIED TO THE STUDY OF CULTURAL HERITAGE

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It is increasingly important that chemistry reaches people who have not studied directly this field of science but that, daily, have practices where chemistry is involved in various extents. This is what happens, for instance, in the activities related with the study and the preservation of cultural heritage. In this sense, the present work is a short review of the particular case of techniques based on the thermal analysis and calorimetry applied within the context of the characterization of art and archeological objects, exemplified by various case studies, as the characterization of mortars, preparatory grounds, ancient painting materials and drying oils.

Keywords: *cultural heritage, thermal analysis*

Introduction

This work presents several cases where techniques based on the thermal analysis and calorimetry are applied within the context of the characterization of art and archaeological objects and materials, providing an example of the interdisciplinary character of the thermal analysis in relation to the chemistry applied to cultural heritage. A description of the principles and methods of thermal analysis is beyond the scope of this text and can be found in various textbooks [1, 2]. The techniques mentioned in the examples below are the thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry coupled with DSC (TG-DSC) and thermomechanical analysis (TMA). One important aspect of these thermoanalytical techniques is that, although being in general destructive, only few milligrams of sample are usually needed – a fact that is very important in the study of objects with historical or cultural value.

Techniques of thermal analysis for the study and preservation of the cultural heritage

The thermal analysis is an example of the analytical methods that find application in the field of art and archaeology [3]. Although not one of the major methods, nor generally used as single technique in a given study, it provides useful information about the compositions of materials that belong to our cultural heritage. In other cases, the results can be related with data obtained by other well-established techniques, confirming the relevant complementary nature of thermal analysis. An important aspect of these studies is to ensure that the samples used are representative, which is directly related with the phase of sample collection.

Historically, thermal analysis was (and still is) an important method in studies related with the determination of the firing temperature of ceramics, particularly archaeological ceramics [4–6]. More recently, thermal methods were successfully applied to other questions related with the cultural heritage. We can mention, for example, studies related to the characterization of the painting media [7, 8], the waterlogged wood recovered in archaeological excavations [9], the parchment used in ancient documents [10], the mortars employed in historic buildings [11], heritage stones [12], the synthetic polymer coatings with high potential for the conservation and restoration of textiles with cultural value [13], or the thermal analysis of model and historic tapestries [14].

In the studies presented in this text, the preponderance of inorganic materials over the organics is mainly due to the greatest complexity that is usually associated to the results obtained with the latter.

Comparative studies on ancient mortars

Thermogravimetry is particularly informative for the study of ancient mortars. The preparation of mortars is

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one of the ancient human-made chemical processes [15]. One type of mortars traditionally used is the lime mortar, whose preparation begins with the calcination of a limestone. The most relevant chemical reaction involved in this process is the decomposition of calcium carbonate, to form calcium oxide, which occurs with the liberation of carbon dioxide. This decomposition begins at 630ºC [16]. Later, at room temperature, the lime is combined with water and slaked lime is formed, that is, calcium hydroxide. On the moment of application to the wall, this calcium hydroxide is one of the main components of the mortar. The subsequent exposure to CO_2 in the atmosphere, for a considerable period of time, in the wall, causes the re-carbonization of the $Ca(OH)_2$ in a reaction that has the water as a by-product. In the overall, this cycle can be described, in a simplified way, by the Eq. (1):

$$CaCO_3 \leftrightarrows CaO+CO_2 \quad (1)$$

Gypsum has also been used in mortars. In this case, natural gypsum ($CaSO_4 \cdot 2H_2O$) is partially dehydrated upon heating to produce a hemi-hydrate ($CaSO_4 \cdot 1/2H_2O$) known as plaster of Paris. Calcination of gypsum at higher temperatures produces anhydrite ($CaSO_4$). The plaster of Paris is the material that is used in gypsum mortars and, when in the wall, it can return to gypsum by reaction with water present in the mortar. So, the overall process is described by Eq. (2):

$$CaSO_4 \cdot 2H_2O \leftrightarrows CaSO_4 \cdot 1/2H_2O+3/2H_2O \quad (2)$$

In addition to water a mortar is, in general, constituted, by a binder, that traditionally is slaked lime (*lime mortar*) or the plaster of Paris (*gypsum mortar*), and an inert or aggregate, usually sand.

As an example of study, we can mention the work of Reller and Wilde [17] about some ancient Egyptian mortars, from Sphnix, which showed by thermal analysis that significant differences on the compositions of mortars of the same edifice can be found. Namely, they identified mortars made from gypsum, sand and lime and others made only from sand and lime. In fact, the sample prepared with gypsum was collected near the exterior surface of the building and the sample made without it was collected from walls in the interior, at about 4 m inside the building. The same authors made a parallel study with mortars from a site in Nevali Çori, Turkey, where a culture was developed in 10000–8000 B.C. From samples of mortar obtained in three different situations of a terrazzo floor, namely (*i*) embedded, (*ii*) from the surface and (*iii*) from the bottom, the thermogravimetric curves were obtained. The first relevant observation from these experiments [17] was that the three curves were not superimposed. The thermal stability of the samples decreased from the situation (*i*) to (*iii*). Moreover, the curves resembled well those of $CaCO_3$ which implied that the samples (*i*) to (*iii*) suffered re-carbonization, but to different extents. As emphasised by the authors, the re-carbonatization of the mortar, in principle, allows ^{14}C dating, but the existence of different levels of carbonization in different samples that belong to the same site, as well as the presence of not fully calcined limestone, in general prevent any radiocarbon dating attempt.

In another example, Biscontin *et al.* [18], using a large number of mortar samples from Venice, correlated the ratio CO_2/H_2O, that is, the ratio between the mass loss above 600ºC, due to CO_2 released by decomposition of the carbonates, and the mass loss in the range 200–600ºC, due to the loss of water bound to hydraulic compounds, with the hydraulic nature of the mixtures. This correlation allowed the conclusion that, in the studied Venetian mortars, the indoor masonry binders were characterized by different compositions and various CO_2/H_2O ratios, with no apparent relation with the historical construction phases but, conversely, the foundation binders showed homogeneous CO_2/H_2O ratios, attesting similar original mixtures and conservation conditions.

The curves obtained in the thermal analysis for ancient mortars sometimes are more complexes than it may be expected for a specific mortar. For example, in the same study, Biscontin *et al.* [18] showed by TG-DSC the effect of the presence of soluble salts, as sodium chloride, in a Venetian calcium carbonate based mortar. In fact, when NaCl is present, instead of the expected one-step decomposition of the $CaCO_3$, the TG-DSC curves showed a four-step decomposition process. In overall, the presence of NaCl resulted in a decomposition of the mortar at lower temperatures than what happened after removing the sodium chloride by washing the mortar with distilled water. Other authors reported also the decrease in the decomposition temperature of carbonates, due to the presence of soluble salts [19, 20].

The characterization of historical mortars, namely its composition, is frequently difficult due to various aspects, namely: (*i*) the variable chemical composition of materials of the same type, as a result of variable technology; (*ii*) the chemical transformations that occur with time; (*iii*) the double function (binder and aggregate) often carried out by the same substance; (*iv*) the conservation and restoration actions. In this way only several and complementary studies, with information from different techniques, can give an appropriated insight on the composition of a historical mortar. The information so obtained can be used in the reconstruction of a given mortar, namely for conservation purposes [18, 19, 21].

Characterization of grounds

In painting and polychromed sculpture it is common the application of a thick layer of an inert powder material bind by a glue, directly over the support. This provides a smooth surface for the subsequent layers with pigments. This preparatory layer, or ground, frequently is a gypsum or a chalk (calcium carbonate) layer, although in some periods of the history of painting the use of coloured grounds was common.

Useful information on the component materials, and their purity, of grounds used in works of art can be obtained by thermal studies, as illustrate by the work of Genestar and Cifre [22]. These authors studied several commercially available calcite or gypsum-based grounds and confronted the TG-DTG results with those obtained in high purity calcium carbonate, di- and hemi-hydrated calcium sulphate, and dolomite. The authors observed different situations, that could be attributed to high purity gypsum grounds (mass loss between 120–135ºC) – Fig. 1 – or to gypsum grounds contaminated with a fraction of calcium carbonate, were a second transformation occurred above 600°C (Figs 1a and c). High purity calcium carbonate grounds were found also (Fig. 2a). In some situations the DTG curve allowed a more detailed analysis of the mass loss curve, revealing that dolomite, which presents a decomposition temperature of 750ºC, can also be mixed with some $CaCO_3$ base grounds (Fig. 2b). The same authors also showed that, when analyzing works with similar grounds, some steps are found in the TG curve, for the temperature range 200–600ºC. In this range of temperatures, inorganic components of the grounds do not present significant mass losses and, consequently, the observed transformations were attributed to the oxidation of organic matter, particularly glue [22].

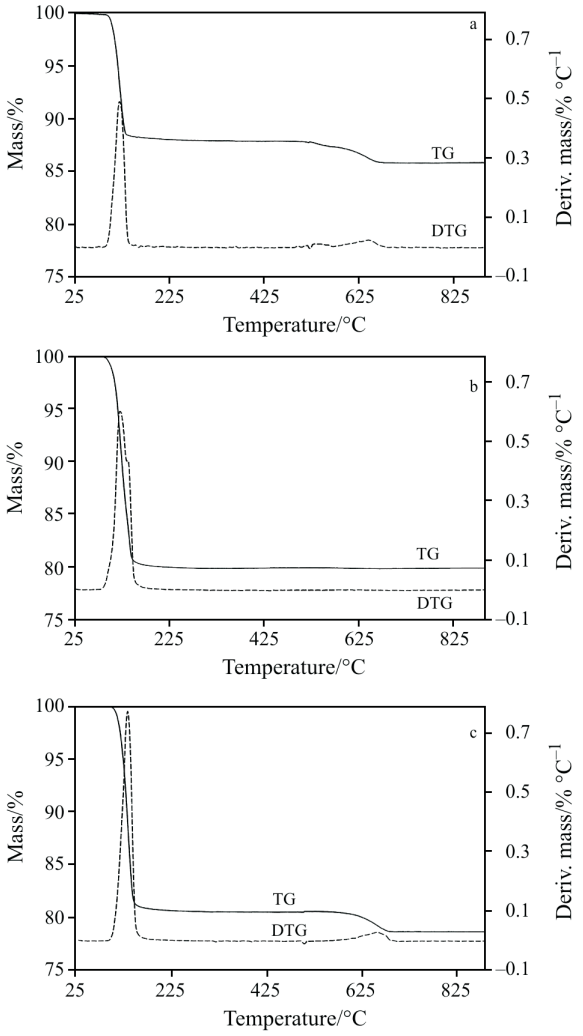

Fig. 1 TG and DTG curves of various grounds (mainly calcium sulfate as dihydrate form). Reprinted from [22], Copyright (2002), with permission from Elsevier (a to c, see text)

Ancient sculptures and bricks

An army of thousands of normal size terracotta warriors, with more than 2000 years, was found in China in 1974 [23]. These terracotta sculptures were individually modelled from clays containing feldspar, quartz and some carbonate [24]. One question that was object of study was whether those sculptures were fired at high temperatures. Wiedemann *et al.* obtained the TG, DSC and TMA curves of Chinese terracotta of the Qin dynasty [24]. TG curve showed a continuous variation until 600ºC that was interpreted in terms of the water loss and the thermal decomposition of the clay. The DSC curve showed a broad exothermic peak near 350ºC, that the authors assigned to the combustion of organic material, and a sharp endothermic peak at 578ºC due to the β-quartz formation. In the TMA curve, an expansion of the material was observed until 600ºC, followed by contraction, which is compatible with the carbonate breakdown followed by sintering. The same authors compared the TMA curves of the Chinese terracotta with the TMA curve of the quartz. The TMA curves were obtained in two cycles and showed that, after the first heating program, the results obtained with terracotta sample match those obtained for quartz. These observations were interpreted in the sense that the expansion behaviour of the heated terracotta approached the behaviour of quartz, supporting the idea that the terracotta was hardly fired.

Another evidence in this sense was obtained in the same work by recording the TG curves of the Chinese terracotta with and without a magnetic field of about 100 Gauss. In fact, due to the existence of ferromagnetic components, the magnetic field displaces the TG curve to high mass values. Above a given temperature the two curves coincide. This temperature,

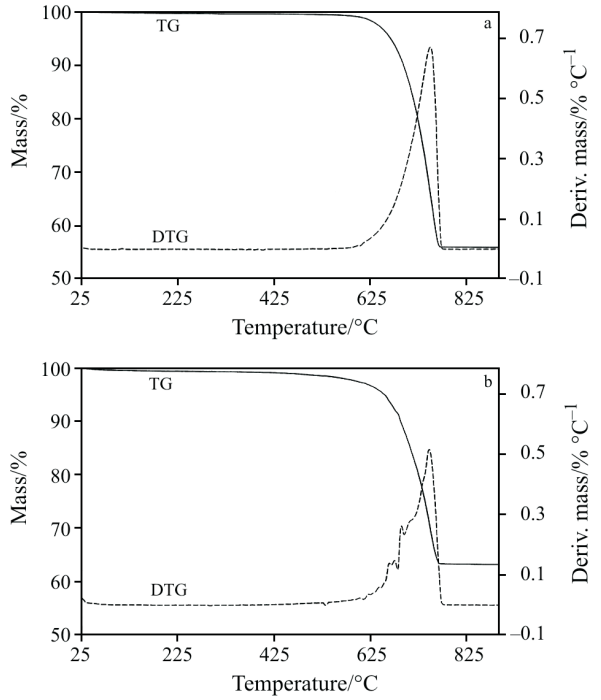

Fig. 2 TG and DTG curves of various grounds (mainly calcite). Reprinted from [22], Copyright (2002), with permission from Elsevier

about 600ºC, is near the Curie temperature of magnetite, which is oxidised to hematite at 1000ºC and turns to be antiferromagnetic. The authors interpreted these observations, as further evidence that the terracotta, most probably, was not fired at elevated temperatures. It should be noticed, however, that different views exist about this question [24].

In a recent study, López-Arce *et al.* [25] used X-ray diffraction and DTA to study samples of bricks from the 12th to 14th centuries, from historical buildings of the city of Toledo (Spain), to ascertain on the temperatures at which the original bricks were prepared. By the systematic re-firing of the original samples, at temperatures successively high, and using the mentioned techniques, the authors were able to establish different ranges of temperatures for the firing of the original samples.

Ancient painting materials

Thermal analysis can also provide some useful information about ancient painting materials, as it can be illustrated by the work by Wiedemann *et al*. on some Egyptian mural paintings with about 3000 years old [26]. For example, chromatographic/mass spectrometric measurements made in this study, suggested the use of a composite material made from a mixture of carbon black pigment and bee wax in the black pupil of the Nefertete Queen depicted in one of the paintings. The authors prepared in the laboratory a

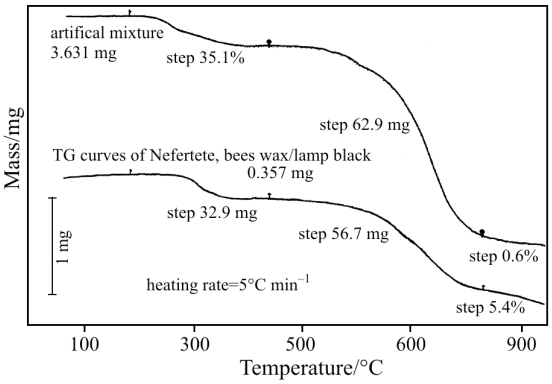

Fig. 3 Comparative thermoanalytical measurement of the thermal degradation of the carbon/bee wax mixture collected from Nefertete's eye and prepared as imitate made up of oil lamp black and ancient bee wax. Reprinted from [26], Copyright (2002), with permission from Elsevier

mixture from 3000-year-old bee wax and ancient soot from oil lamp, and compared the thermogravimetric results obtained with this material and the original pigment of Nefertete's eye. Analogous TG curves were obtained between 100 and 900ºC for both samples (Fig. 3) and, so, the authors conclude that the ancient black material was prepared in the same way as the modern one.

Drying oils

Drying oils, like linseed oil, have been used for centuries as binding media for the pigment particles in paintings. Those substances show a change in their chemical and physical properties during the drying process, that is, during the polymerization, that originates a vitreous material. The use of methods of thermal analysis at sub-ambient temperatures can be informative on the properties of thermosetting materials [27]. For example, when the fresh walnut oil is rapidly cooled at temperatures below –140ºC several transformations occur during the rise of temperature until the room temperature. The first is the glass transition of the amorphous component at about –110ºC. At –83ºC and at –65ºC there are two exothermal peaks that can be assigned to the melting of some minor crystalline fractions. Finally, the more important crystalline fraction of the walnut oil melts at –36ºC. As the walnut oil dry through a crosslinking process as time goes by, high temperatures will be required to liquefy the material, because large molecules are formed. Therefore, with the drying processes, the peaks shift to high temperatures [27, 28]. This effect is more pronounced in poppy and, above all, linseed oils because they dry faster than the walnut oil.

However, pigments as white lead, a basic lead carbonate, clearly accelerate the process of drying of

the walnut oil (and also the poppy and linseed oils), as shown by the DSC results, where the intensity of the endothermic peak, related with the fusion, is much less intense. Titanium white, that is, titanium oxide, a known oxidant of organic molecules when exposed to radiation in the range 300–400 nm, has a similar accelerating effect. Zinc oxide, in the form of a zinc white pigment, has an opposite effect. In fact, it is a drying inhibitor since the endothermic peak of the melting for the walnut oil continues to be clearly seen, even after 17 days of drying. Poppy and linseed oil gave results similar to those obtained with the walnut oil [27].

Conclusions

In this text necessarily not all the works, where the techniques of thermal analysis and calorimetry were applied to the study and the conservation of the cultural heritage, were reviewed. However, the selected examples are a contribution to point out the main advantages, and also some limitations, of these types of techniques and, mainly, their interdisciplinary and complementary character in a field which, in spite of its growing importance, the divulgation of the potentialities of the thermal analysis and calorimetry is probably not as intense as it could be.

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