TECHNIQUES OF THERMAL ANALYSIS APPLIED TO THE STUDY OF CULTURAL HERITAGE

J. Pires[1*] *and A. J. Cruz*[2]

[1]Departamento de Química e Bioquímica and CQB, Faculdade de Ciências, Universidade de Lisboa, Edifício C8
Campo Grande, 1749-016 Lisboa, Portugal
[2]Departamento de Arte, Conservação e Restauro, Escola Superior de Tecnologia de Tomar, Estrada da Serra
2300-313 Tomar, Portugal

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

* Author for correspondence: jpsilva@fc.ul.pt

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].