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PLASTERS IN THE CELLARS OF THE VISCONTI CASTLE IN PAVIA
Physico-chemical characterization

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Abstract

An archaeometric investigation on plaster samples taken from the cellars of the Visconti Castle in Pavia has brought out the existence of several layers and colour films of various periods. The oldest plaster spread over the masonry is formed with three main layers. Above them, one film of bluish-black colour can be found on the arcs and on the bearing walls. On this black layer, a white film of calcitic composition, containing also apatite fragments, was spread. These ancient materials were subsequently covered in more recent times with plasters having different compositions and textures.

In the present paper the properties of the three main plaster layers and those of the black film are reported in detail. The thermal behaviour of these materials was studied by means of differential thermal analysis and thermogravimetric analysis. The study was completed with scanning electron microscopy, microprobe analysis and X-ray diffraction on powders.

The results obtained provide interesting clues for advancing reasonable hypotheses both on the methods adopted in ancient building yards, and on the techniques for the production of the pigments employed.

Keywords: aggregate, ancient pigment, ancient plaster, binder, vine black

Introduction

The Visconti Castle as we can see it now in Pavia presents only an impoverished picture of the palace, the construction of which was ordered by Galeazzo II Visconti in 1360–1366. After the destruction of the northern side in the XVI century, the building was used for many different purposes, in particular, as barracks. A thorough restoration was carried out in the periods 1921–1929 and 1930–1940 [1]. In 1932 the Castle was transferred to the administration of the city and at present it is the seat of the town museum (Musei Civici). The premises available on the ground level are now empty and need to be rearranged in order to be devoted to temporary as well as permanent exhibition rooms.

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Thus, the direction of the museum thought it useful to promote a research concerning the materials of construction employed in the building in subsequent historical periods, and their state of conservation. In the framework of this research, a series of samples of mortars and plasters were collected in different places of the cellar of the Castle, and are currently under investigation.

As far as the plasters are concerned, an archaeometric investigation on plaster samples from the walls has brought out the existence of several overlapping layers of various periods. Among the oldest ones, a layer of bluish-black colour can be found on the masonry and on the arches. Above this black layer, a white film of calcitic composition, containing also apatite fragments, was spread. These ancient materials were subsequently covered in more recent times with plasters having different compositions and textures.

Since the first centuries of the Christian era, in which architecture flourished under the Roman Empire, Vitruvius in his well known treatise on architecture 'De Architectura' [2] mentioned a pigment of black colour. In the Renaissance period, Cennini in his Book of Art 'Il libro dell'Arte' [3] reported the technical details for the preparation of a black pigment, the 'vine black', which was employed to make wall decorations 'a graffito', i.e. black and white geometrical drawings. This technique implied coating the masonry with two layers of different composition. On the first layer, deep grey or black in colour, containing carbon fragments, a second one of white colour was spread [4]. The presence of this decoration in the Visconti Castle of Pavia was quoted, in particular, by Albertini Ottolenghi [5] in a study concerning the paintings on the first floor. A black and white decoration of the same kind was applied on external walls in buildings constructed in Pavia in the same period, one example of which is the monastery of Chiara [6].

The present paper aims at reporting the properties of the more ancient layers constituting the considered plasters, with particular attention devoted to the layer of the black pigment.

The thermal properties of the above mentioned plasters taken in the cellars of the Castle of Pavia were studied by means of differential thermal analysis and thermogravimetric analysis. The study was completed with scanning electron microscopy, microprobe analysis and X-ray diffraction on powders. The results obtained provide interesting clues for determining the relative chronology of these materials, as well as for advancing reasonable hypotheses both on the methods adopted in ancient building yards, and on the techniques for the production of the black pigment employed.

Last, but not least, the data collected on the considered materials may give a useful technical basis for planning the choices involved in a consistent restoration programme of the cellars.

Experimental

Techniques

The thermal techniques employed were differential thermal analysis (DTA) and thermogravimetric analysis (TG), both controlled by a TA 5000 system.

DTA measurements were performed at the scan speed of 10°C min^{-1} in static air between room temperature and 1200°C with platinum cups by means of a 1600 high temperature DTA cell mounted on a 2910 MDSC by TA Instruments.

TG scans were recorded at the speed of 10°C min^{-1} under nitrogen flow, between room temperature and 1000°C, by means of a TA Instruments 2950 TGA.

The instruments for thermal measurements were calibrated as previously reported [7]. The uncertainty in the T measurements was ±0.5°C.

Moreover, the present investigation was carried out combining microtextural observations and compositional analyses. Microtextures were investigated with a Leitz Laborlux 12 POL S optical microscope and with scanning electron microscopy (SEM) on polished thin sections. Analytical work was performed combining the use of 'bulk' techniques, i.e., X-ray diffraction (XRD) and thermal techniques, with that of an 'in situ' technique, electron microprobe (EMP) analysis.

For X-ray diffraction, a Philips PW 1800 diffractometer, CuK_α graphite-monochromatised radiation, was used under analysis conditions 40 kV and 20 mA, in the scan range between 2 and 65° 2ΘCu, scan speed 1° 2ΘCu min^{-1}. The collected diffraction data were analysed considering the intensity of the reflections for each mineral; the semi-quantitative percentage of the various mineral phases was checked using a home made software derived from the 'Siroquant Software Package' [8].

Electron microscopy was performed with a JEOL JXA 840A electron microanalyzer, equipped with three wavelength dispersive spectrometers (TAP, PET and LiF analysing crystals) and one Si(Li) energy dispersive spectrometer (EDS) with a Be window. Analytical conditions of 20 kV of accelerating voltage and 20 mA of beam current have been employed with a spot size of about 5 μm. Data collected by EDS have been processed with the semiquantitative programme provided by the manufacturer of the microscope.

Materials

The first sampling of mortars and plasters was performed in August, 1998, in the western side of the cellars and in the western tower. In Fig. 1 a mapping of the ground level spaces, drawn in 1921 by architect Aschieri by appointment of the Superintendence [1], is illustrated. In this map, the subdivision of these spaces in two parallel cellars is apparent. The external one is enlightened by windows and subdivided by arcs into a series of wide rooms. It underlies the official premises of the first floor and is larger than the internal one, which corresponds to the gallery of the first floor. Samples of plasters taken in six different places in both cellars looked rather similar and were submitted to the same procedure of analytical investigation. In the present section, a preliminary morphological description of these materials is given.

The plaster is constituted by three technical layers, separated by well-defined surfaces of discontinuity. It has an overall thickness of about 3–5 cm. A typical stratigraphy is illustrated in Fig. 2A. The more ancient coarse layer (TL1) is directly supported by the masonry and looks like a yellowish material with thickness ranging between 20 and 30 mm. The second technical layer (TL2) is also a coarse plaster of whitish colour with thickness varying between 3 and 12 mm. In that layer the aggregate is more abundant than in the technical layer 1.

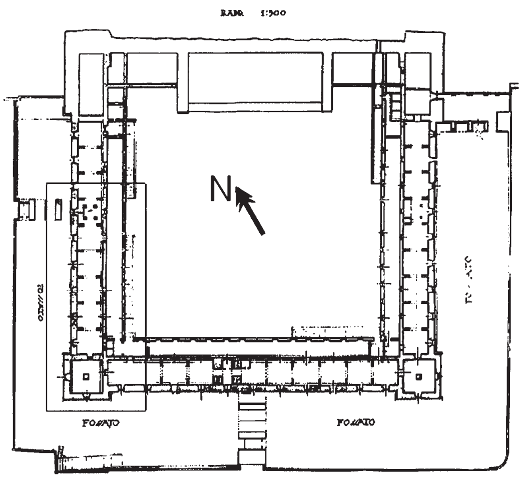

Fig. 1 Mapping of the cellars of the Visconti Castle in Pavia (after a drawing of Aschieri, 1921). In the grey area, which is now under restoration, samples of plasters and mortars were taken in August 1998

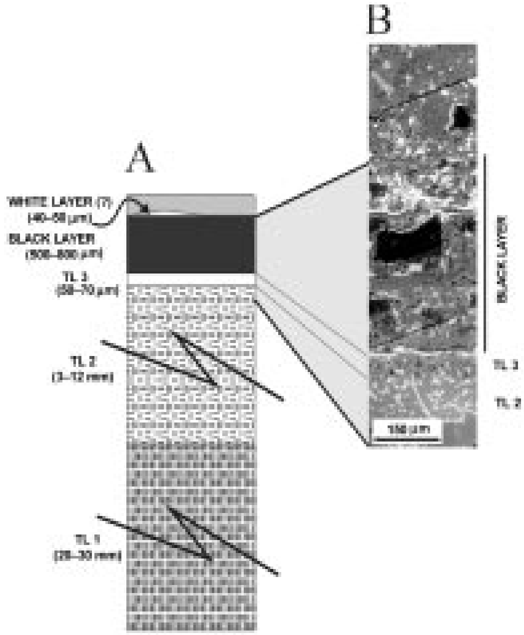

Fig. 2 Stratigraphy of a plaster sample of the cellars. A – sequence of the technical layers and colour films as observed in optical and electron microscopy; B – detail of the texture of the black colour film (image taken with secondary electrons)

The third technical layer (TL3) displays limited thickness (50–70 μm) and a homogeneous texture with extremely fine grain size.

The film of black colour has a thickness ranging between 500 and 800 μm and is organised in thinner levels (80–100 μm), separated by surfaces of discontinuity, as illustrated in Fig. 2B. The course material of black colour is opaque to the transmitted light; its size ranges from 150 to 1 μm. The binding material displays very fine grain size and represents about 50% of the total composition.

Above this black layer, a somewhat fragmentary white film about 40–50 μm thick can be found. Numerous layers of white paintings were subsequently laid over the black layer. These more recent films of white colour will not be taken into account in the present work.

The first technical layer of the plaster, present only on the load-bearing walls, is made of a coarse aggregate having the size of a medium-fine sand (0.1–0.5 mm). Among the minerals present in it, quartz, feldspar (K-feldspar and plagioclase) and micas (biotite and muscovite) are predominant. Mafic minerals are also represented, i. e. green amphiboles and garnets; less represented are the pyroxenes. Lithic fragments are mainly due to the presence of metamorphic rocks and fine grained sedimentary rocks. The binder is not homogeneous and displays an opaque aspect when observed by optical microscopy: fine grained aggregates of pure calcite alternate with more complex areas where at least two phases of different composition are present. For the aggregate/binder ratio, one can approximately estimate values close to 3.

The second technical layer is also a coarse material with abundant aggregate and carbonate binder. The grain mineralogy and the kind of lithic fragments are fully similar to the above described ones of TL1. The aggregate/binder ratio displays a value close to 4.

In Table 1 the list of the rock fragments and of the minerals observed by optical microscopy in the aggregates of both the mentioned technical layers is provided.

As for the third technical layer, it is always less than 100 μm thick. The SEM pictures taken with secondary electrons show an extremely homogeneous texture and chemical composition. This material is highly porous. The above mentioned characters and the carbonate composition of the material allow to indicate this layer as lime putty.

In the black colour film, the layers are well separated by surfaces of discontinuity which are apparently well defined and continuous over all the thin section area (Fig. 2B). The coarse fraction is made with black elements, sometimes with a translucent surface, having extremely varying sizes. Pictures taken by means of scanning electron microscopy show that these elements display a regular internal structure, formed with small-sized tubules arranged in a parallel order (Fig. 3B), whereas in transverse sections the regular arrangement of these tubules creates a hurdle structure. In transmitted light at the optical microscope, these elements are fully opaque. This morphology looks like that of partially burnt vegetal fragments. The binder is mainly a fine-grained carbonate displaying a heterogeneous distribution. The binder : pigment ratio is about 1:1 (Fig. 2B).

The subsequent layers are of white colour. The very fragmentary one which is in contact with the black film may be considered of particular interest. In this material, the carbonate binder holds angular fragments of porous apatite. The following white layers were made with fine carbonate materials and contain only rare fragments of quartz and feldspar.

Table 1 List of the rock fragments and of the minerals observed by optical microscopy

	Rock fragments	Minerals
	quartz+biotite	quartz
	quartz+illite	K feldspar
	epidote+chlorite	micas
	quartz+chlorite	epidotes
	albite+chlorite	garnets
TL1	K feldspar+quartz+biotite	green hornblende
	quartz+rutile	red hornblende
	K feldspar+quartz+rutile	ilmenite
	green hornblende+plagioclase	rutile
	K feldspar+plagioclase+quartz+micas+apatite	clinopyroxenes
	ilmenite+garnets+quartz+albite+epidote	
	quartz+epidote+zircon	quartz
	quartz+illite	K feldspar
	epidote+chlorite+apatite	micas
	quartz+chlorite+apatite	epidotes
	quartz+chlorite+albite	garnets
TL2	K feldspar+plagioclase+biotite	green hornblende
	ilmenite+zircon+chlorite	red hornblende
	K feldspar+quartz+rutile	ilmenite
	quartz+K feldspar+albite	rutile
	quartz+biotite	clinopyroxenes
	magnetite+ilmenite+sphene	allanite

In order to check whether the fragments of the black pigment could come from remainders of combustion of vine shoots, it was decided to try to reproduce the so-called 'vine black'. Some dried vine branches were burnt in a pit, after having been covered with vine leaves. The combustion process was stopped after some hours to produce coal, whereas it was continued for a longer time to obtain ashes. The fragments obtained were observed with SEM (Fig. 3A). Their behaviour as a function of temperature was investigated by thermal techniques.

Some experimental mixtures were also prepared and analysed with DTA to compare their properties with those of ancient materials, to get a better definition of the nature of the binder employed in the plasters of the cellars. These mixtures were made using the following natural minerals: quartz, calcite, kaolinite and gypsum, which were purchased in a mineral shop.

The compositions of the experimental mixtures were chosen taking into account the results of the X-ray diffraction patterns obtained on two plaster layers TL1 and TL2. Besides pure calcite and pure kaolinite, five binary mixtures of these components with calcite content of 50, 60, 70, 80 and 90 mass% were prepared, as well as two ternary and two quaternary mixtures with different concentrations of the four mentioned minerals.

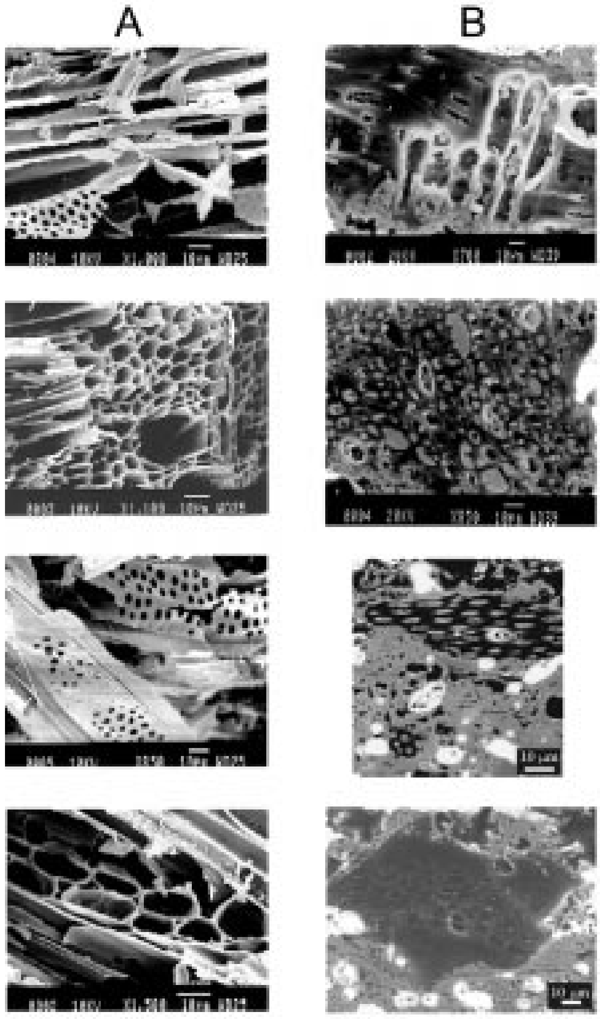

Fig. 3 Comparison between the morphology of the charcoal made with vine shoots (A) and that of the fragments of the pigment in the colour film (B). (SEM images taken with secondary electrons)

Results and discussion

The plaster layers described in the experimental section were separated, when possible, and analysed by means of X-ray diffraction on powders. In Fig. 4, the compositions of the technical layers as determined from the records of the diffraction patterns are illustrated. It was not possible to single out the layer of lime putty (TL3) due to the fact that this layer was too thin: thus, the composition of this material was investigated with the electron microprobe only.

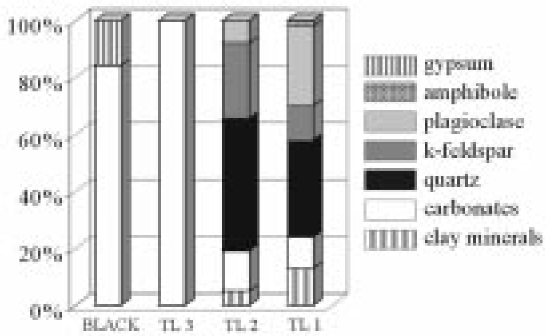

Fig. 4 Mineral composition of the different technical layers as obtained from the X-ray diffraction patterns taken on powders

XRD data summarised in Fig. 4 are in fair agreement with the description obtained from the observations made with optical and electronic microscopy.

In the first layer of the plaster, TL1, the aggregate is mainly composed with quartz, K-feldspar and plagioclase, these phases representing 75 mass% of the layer. The plagioclase (28 mass%) is more abundant than K-feldspar (12 mass%); the amphiboles are present in a lower content, always <5 mass%. The fraction corresponding to the binder is formed partly with carbonates and partly with clay minerals, the ratio between these phases being about 1:1.

The identification of such phases is important to define the technical characters of the binder employed. Actually, the coexistence of carbonates and silicates raises the question if the binder had hydraulic properties, or if it were made up with a mixture of an air-setting binder with clays.

In order to determine the chemical composition of the heterogeneous phases making up the binder, areas displaying different properties at the optical microscope were analysed by microanalysis. The results are reported in the ternary diagram (CaO+MgO)+SiO_2+Al_2O_3 shown in the scheme of Fig. 5. The phases of the binder are divided into two composition groups: one close to the (CaO+MgO) corner, the second one containing high concentrations of SiO_2 (about 50 mass%) and different (CaO+MgO)/Al_2O_3 ratios, some compositions only being similar to those of the clay minerals.

Non-stoichiometric compositions, such as those resulting from the diagram in Fig. 5, may be justified taking into account the extremely small size of the phases studied, lower than the diameter of the electron beam (5 μm). In cases like this, microanalyses must be interpreted as ‘microbulk’ analyses, which cannot give a definite resolution in determining the composition of the binder phases.

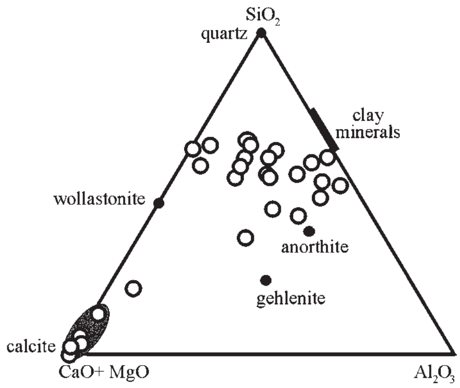

Fig. 5 Composition data of the binder in TL1 and TL2, obtained with electron microprobe analysis (EMP) in the ternary system $(CaO+MgO)+SiO_2+Al_2O_3$. Empty circles: compositions of the binder contained in TL1; grey area: compositions of the binder contained in TL2

In the second layer of the plaster, TL2, the aggregate displays a mineral composition very similar to that of the technical layer 1: quartz is prevailing (>40 mass%); among the feldspars, the K-feldspar (26 mass%) is more abundant than the plagioclase (8 mass%). This proportion is similar to the one outlined above in the analysis of the thin sections (Table 1). It may suggest a common source of supplying of the sand used as aggregate in two coarse layers.

The binder is lime-based (14 mass%) with a content in clay minerals always lower than 10 mass% (Fig. 4). The chemical composition of the calcite is very homogeneous (Fig. 5) and rich in CaO.

As for the film of black colour, the crystalline phase present in it is calcite. The presence of gypsum, in concentration lower than 20 mass% (Fig. 4), may be due to alteration processes which occurred after the colour film was laid down.

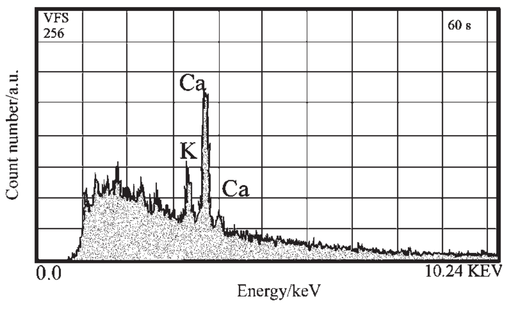

Fig. 6 EDS spectrum of a fragment of organic black pigment. Ordinates: count numbers; abscissas: energy in keV

The EDS spectrum of Fig. 6 was recorded by positioning the electron beam on a vegetal fragment of the black film. In such a material only small amounts of Ca and K are present. The low-level counting and the rather high background of the EDS spectrum are features typical of an organic material, such as the combustion products of vegetal fragments.

The morphologic comparison of the SEM imagery between the vine charcoal fragments (Fig. 3A) and the elements of the black pigment of the colour film (Fig. 3B) shows close analogies of forms and sizes. In our opinion, this indicates that the pigment used to obtain the black colour was the vine black.

The results of some analyses performed with TG are illustrated as an example in Figs 7 and 8, where a comparison is suggested between the thermal behaviour of the samples of ancient plasters and those of the freshly prepared mixtures of similar chemical composition.

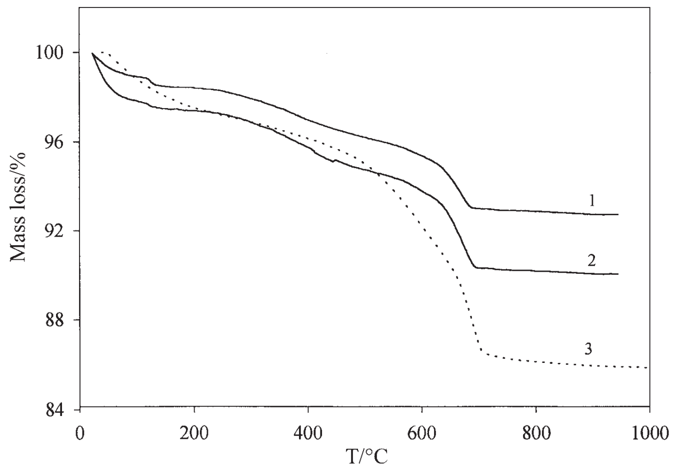

Fig. 7 TG curves recorded on selected samples. 1 – first layer of the plaster, TL1; 2 – second layer of the plaster, TL2; 3 – sample of pure cement

The thermogravimetric records of the first and second technical layers (TL1 and TL2) are shown in traces 1 and 2 of Fig. 7. They look rather similar and display three main mass losses: the first one below 200°C is due to moisture elimination, with a reproducible small step at ~130°C. It is followed by a second continuous mass decrease effect not properly resolved between 300 and 500°C, and by a third sharp one above 600°C, which can be ascribed to the decomposition of calcite. In Fig. 7, trace 3, the thermal decomposition of a recently prepared sample of cement is also reported. Its behaviour looks more similar to that of the old plasters, but for the fact that the mass loss between 500 and 700°C is much higher.

For the purpose of comparison, Fig. 8 illustrates TG thermal traces of four experimental mixtures prepared from available natural minerals. They reproduce the compositions of the TL1 and TL2 layers in section a) and b) of the figure, respec-

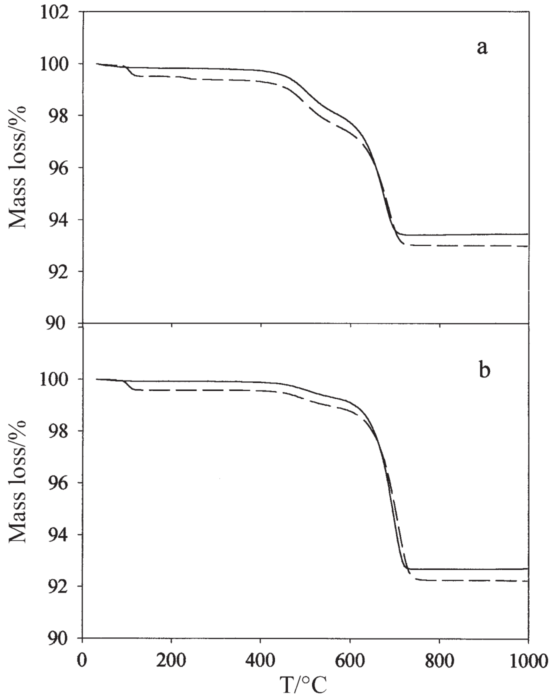

Fig. 8 TG curves recorded on samples of: a – quartz-calcite-kaolinite mixture 75-10-15 mass%, solid line; the same after the addition of 2 mass% gypsum, dashed line; b – quartz-calcite-kaolinite mixture 80-15-5 mass%, solid line; the same after the addition of 2 mass% gypsum, dashed line

tively. In a) the solid line represents the behaviour of the mixture containing 75 mass% quartz, 10 mass% calcite, and 15 mass% kaolinite (close to the composition of TL1). Similarly, in b) the solid line concerns the mixture with 80 mass% quartz, 15 mass% calcite and 5 mass% kaolinite (close to the composition of TL2). In both a) and b) the dashed lines correspond to the mentioned mixtures in which a 2 mass% of gypsum was added. The solid lines do not show any mass loss below 400°C, and the samples start decomposing at relatively high temperature, i.e. around 450°C, since they do not contain hydration water.

The small mass loss occurring in curves 1 and 2 of Fig. 7 at about 130°C deserves a further comment. This effect, not observed in the traces drawn as solid lines in a) and b) of Fig. 8, could be detected above 100°C in the freshly prepared mixtures to which some gypsum was added, as illustrated by the dashed lines in Fig. 8. From this experimental evidence one can conclude that the two layers of old plaster contain some gypsum.

The thermal behaviour of the black layer is shown as an example in Fig. 9, in which both DTA and TG curves are reported. The DTA trace evidences a tiny endothermic peak around 100°C, which can be ascribed to the evaporation of the adsorbed

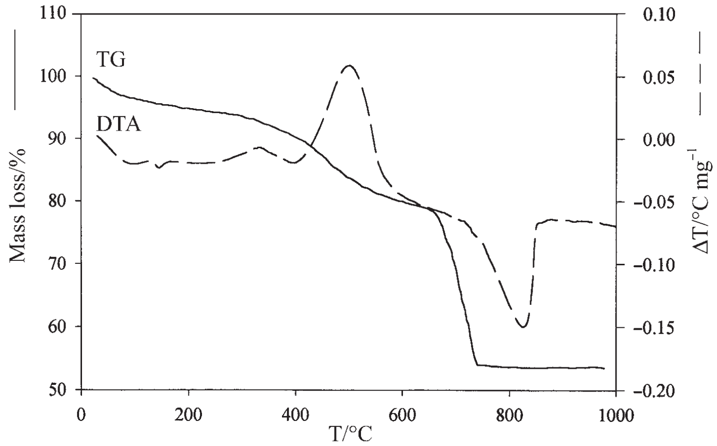

Fig. 9 DTA (dashed curve) and TG (continuous curve) records of a sample of black colour film

water, followed by two exothermic effects at about 250 and 450°C, respectively, both related to the thermal decomposition of vegetal fibres, accompanied by a partial burning. The final endothermic effect starting at ≅700°C is associated with the decomposition of carbonates present in the sample. In the TG curve, at least three mass losses can be detected: a first small one, due to adsorbed water, occurring at temperatures <200°C, is followed by a more important loss between 300 and 600°C due to the decomposition of vegetal fibres. The last and larger loss around 650–700°C is easily attributed to the release of CO_2 from the carbonated phases.

The records of Fig. 9 can be compared with the curves illustrated in Fig. 10, where the TG and DTA traces recorded on vine charcoal are shown. The good agreement between the two curves is clearly brought out.

A comprehensive view of the results obtained in the present investigation allows one to outline the following general comments of historical as well as technical character.

The sequence of the layers in the examined plaster samples is very similar to that of a typical painted wall, such as the one described in a general way by Baglioni *et al.* (1997) in a paper concerning the techniques of conservation of lime-based wall paintings [9].

In spite of the fact that in the existing archives no historical documents going back to the early period of the construction of the castle have been found so far, and no detailed description of the activities in the building yard is available, the above illustrated characters of the plaster seem to be consistent with those of a wall prepared for a further painted decoration.

Studies on plasters of the Renaissance period are not numerous in the scientific literature dealing with the conservation of architectural monuments. However, the results of the present work may be compared with those reported in a technical examination of the plasters of an ancient farm, Cascina Pozzobonelli, built near Milan by the end of the XV century, which was carried out by Alessandrini and co-workers

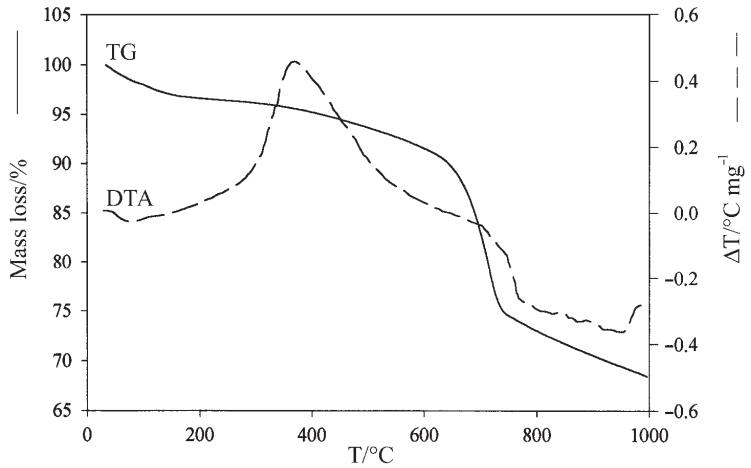

Fig. 10 DTA (dashed curve) and TG (continuous curve) records of a sample of freshly prepared charcoal from vine shoots

(1989) [4]. This paper provides an accurate analysis of the internal decoration of the farm chapel, which 'is of particular interest from an artistic point of view, including, as it does, graffito and geometric designs'. According to the mentioned authors, the 'mixture of magnesian lime and sand with the addition of vegetable-based charcoal' forms the black layer of the graffito decoration of the chapel.

As for the Visconti Castle of Pavia, the film of black colour investigated in this work was laid down with a different preparation technique, inasmuch as i) the pigment is much more abundant and of much finer size; ii) the colour film is organised in several layers, and is remarkably thick; iii) the material treatment and the technique adopted suggest a rather refined style of yard work, in comparison with the coarse and relatively poor characters of the black decoration reported in [4].

Concerning the first plaster layer, TL1, the use of a clay containing binder may be considered as appropriate for the microclimate of the Pavia Castle cellars. Actually, not only this material displays a good ability to absorb moisture, but also the clay minerals included in it resist to the volume withdrawal during the binder carbonation, and favour the stabilisation of the mixture. Findings in fair agreement with this observation were reported in a recent study on some mortars and plasters in ancient buildings of Cremona [10], in which it was brought out that a fraction of 10 mass% of clay is probably sufficient to insure the accuracy of the surfaces without decreasing the quality of the mechanical performance of the plaster.

Finally, it is worthy of remark that, thanks to their high sensitivity, differential thermal analysis and thermogravimetric analysis allow one to detect the presence of minor components in complex mixtures which display significant thermal phenomena.

Conclusions

In the cellars of the Visconti Castle of Pavia, a major part of the plaster spread over the masonry is formed with three technical layers. Two of them are rather rough, one is fine-grained and made of lime putty. Further films of colour are present above these layers.

The two coarse layers TL1 and TL2 are characterised by different values of the aggregate/binder ratio, 3 and 4, respectively, and different binder composition. The technical layer 1 was manufactured with an air-setting binder mixed with clay, whereas the technical layer 2 was made up with the air-setting binder only. These features witness different preparation techniques of the materials, which aimed at fulfilling the specific function the material had to perform.

It was shown that the sandy material used as aggregate in the two layers presents the same mineralogical composition and the same kinds of lithic fragments.

The presence of a thin film of lime putty in the technical layer 3 and the traces of a white colour film containing apatite, overlapping a thick film of black pigment, lead one to assume that even in the cellars some kinds of graffito decorations could have been executed, similar to those of the first floor.

From the comparison between the vegetal charcoal obtained burning vine shoots and the black colour film included in the plaster it was proved that the latter was produced making use of an organic pigment, the so-called vine black.

The multi-analytical approach here adopted was proved to be particularly successful to investigate both compositional and technical aspects of ancient building materials. The data collected in the present work allowed us to reproduce the materials by starting from natural minerals, and to define their technical properties.

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