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TG-DTA AND FTIR ANALYSES OF PLASTERS FROM BYZANTINE MONUMENTS IN BALKAN REGION
Comparative study

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Historic plasters from wall paintings of Byzantine and post-Byzantine churches situated in the Balkan region were studied. All wall paintings were made with fresco technique and are dated from IX - XVI century. Plaster samples were followed from room temperature to 1000°C by Thermogravimetric (TG) and Differential Thermal Analysis (DTA), and one or two significant temperature regions, corresponding to thermal decomposition mechanisms were observed. The analysis of the plaster samples and the composition characterization was carried out using also, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Although the main components are calcite and quartz (from sand) in different proportions, there are differences between them such as the presence of gypsum being either as a constituent element or due to environmental pollution. The results are examined comparatively taking into account the creation time and place of the paintings.

Keywords: *FTIR, plaster, SEM-EDS, TG-DTA, wall-paintings*

Introduction

As historic plaster is characterized the specially prepared layer that served as a ground for the wall paintings of a historic monument.

Wall painting may be defined any painted design or composition applied directly to the surface of a building. Ranging from simple decorative patterns to more complex figurative or even narrative schemes, wall paintings form integral components of the monument. While some wall paintings can be quite simple in both artistic and technical point of view, the majority consist of a combination of materials applied on a succession of layers. The most common technique in wall paintings during Byzantine period was the fresco technique.

In the present work are characterized comparatively, mainly by thermal analysis methods, the historic plasters of Byzantine and post-Byzantine monuments from Balkan Peninsula, aiming in the study of the applied technique for the complete preparation of wall paintings and its historical continuation. The analytical investigations of archaeological objects or of works of art bring much information on developments in technologies and on the propagation of culture [1–3].

Fresco technique

Fresco is an ancient technique of painting on walls [4]. True fresco entails the application of pigments dispersed in water to fresh, damp mortar referred to also as plaster. The wall is first prepared with a base coat of coarse plaster the arriccio. Pigments are applied to the second layer of finer, smoother plaster the intonnaco which is applied in sections over the arriccio. Each section of intonnaco is called a giornata, the Italian word for day's work, as the painting on each section of intonnaco has to be completed in a single day, before the plaster has set (Fig. 1).

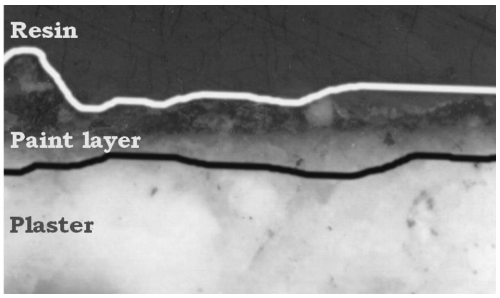

Fig. 1 Typical cross section from a wall-painting (SM)

Mortars and plasters in ancient structures are composite materials which have exhibited excellent durability through time and are constituted of a binder, such as lime (CaO) and/or gypsum ($CaSO_4 \cdot 2H_2O$) and aggregates, such as sand or grit. The composition of mortars and plasters varies greatly and they are commonly divided into lime,

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gypsum and mixed, depending on the binding material and into hydraulic and non hydraulic depending on their ability to set under water. The main steps for lime processing are [5]:

the calcination process

$$CaCO_3 \xrightarrow{850-900^{\circ}C} CaO + CO_2 \quad (1)$$

the hydration process

$$CaO + H_2O \xrightarrow{\theta} Ca(OH)_2 \quad (2)$$

the carbonation process

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

In the case of gypsum plaster, the plaster is produced by the addition of water and an aggregate to the hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and/or the soluble anhydrite ($CaSO_4$). In this way are developed interlocking crystal structures corresponding to calcium sulphate dehydrate [6].

Experimental

The monuments

The monuments from where samples were extracted are:

- The Archbishopric church of Drustar (Bulgaria), a basilica building first built in the IXth century, with walls decorated with colourful murals. The number of the fragments found suggests that not the whole church was covered with murals.
- The Karagach-Teke Monastery (Bulgaria), a monastery active between the IXth and XIVth centuries and dedicated either to Theotokos or to St Archangel Michael. Its wall paintings are probably dated to the Xth century.
- The monastery of Mileseva (Serbia), erected in 1234, with wall-paintings of the XIIIth and the XVIth century. The frescoes examined in the present study belong to the first painting of the XIIIth century.
- The church of Saint Trinity in Berat (Albania) built in the form of a Greek cross with narthex, not later than the first half of the XIVth century. The existing fragments of wall-paintings indicate that the whole church has been decorated from the time of its construction while the author of the paintings is anonymous.
- The church of Saint Theodori in Berat (Albania) built during the first half of the XVIth century on the foundations of an older one. Fragments of wall paintings still exist on the walls around the apse. The wall-paintings on the northern and southern walls are attributed to an anonymous painter, while those on the eastern wall are painted by the famous Onoufrios during the first period of his activity.
- The church of Saint Nikolaos in Shelcan (Albania) first built probably in the XIVth century and reconstructed in the XVIth century. The wall- paintings on the eastern walls (apse), iconostasis and a small part of the northern and southern walls close to the iconostasis are painted by Onoufrios (there is an inscription that mentions his name but not the date) while those on the northern, southern and western walls are probably painted in 1625 by an anonymous painter (as mentioned in a second inscription).
- The church of Saint Paraskevi in Valsh, with wall-paintings painted by Onoufrios and dated in 1554 (there is an inscription) [7, 8].

Sampling

The samples from the seven monuments can be coded into nine categories regarding their origin and are shown in Table 1. For Saint Theodori and Saint Nikolaos churches two types of samples were collected in every church in order to examine the differences of the plaster between the two iconographers (two periods). In the Serbian and the Albanian churches the plaster was taken from already damaged areas of the wall paintings while from the Bulgarian

Table 1 Description of the plaster sample types

a/a	Code number	Century	Location
1	BD	IX–X	Drustar, Bulgaria
2	BKG	X	Karagach – Teke, Bulgaria
3	SM	XIII	Mileseva, Serbia
4	ATr(8)	XIV	Saint Trinity, Berat, Albania
5	AP(1)	XVI	Wall paintings of Onoufrios Saint Paraskevi, Valsh, Albania
6	AN(1)	XVII	North wall, Saint Nikolaos, Shelcan, Albania
7	AN(9)	XVI	East Wall, Wall paintings of Onoufrios, Saint Nikolaos, Shelcan, Albania
8	ATh(1)	XVI	North wall, Saint Theodori, Berat, Albania
9	ATh(18)	XVI	East Wall, Wall paintings of Onoufrios, Saint Theodori, Berat, Albania

ones the plaster was removed, with the use of a micro-scalpel, beneath the pictorial layer.

Due to the destructive nature of sampling, the samples were carefully chosen from areas that had no aesthetic or iconographic value for future reconstruction.

Methods

TG-DTA simultaneous analyses were performed using a SETÁRAM SETSYS 1750 TG-DTA system. Samples (7.5–23 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 1000°C, with heating rate 10°C min^{-1}, in N_2 atmosphere.

For the FTIR measurements a small amount from the plaster of the samples, was removed with a sharp tip of a micro-scalpel and placed on a freshly prepared KBr pellet. The FTIR spectra, in transmittance mode, were obtained from different areas of the specimens. The same pellets were analyzed by SEM-EDS after being coated with carbon. Scanning electron microscopy (SEM) was carried out using a JEOL JMS-840A scanning microscope equipped with an energy-dispersive X-ray (EDS) Oxford-ISIS 300 micro analytical system. FTIR spectra were obtained in the region 4000–550 cm^{-1} using a Perkin-Elmer FTIR Microscope model i-Series, equipped with a nitrogen cooled MCT detector. For each spectrum 64 scan were recorded with resolution 4 cm^{-1}. A database of FTIR spectra with reference inorganic and organic materials was used to characterize the unknown materials of the samples.

Results and discussion

Thermal analysis (TG-DTA) involves measuring the thermal variations associated with the physical and chemical transformations (such as dehydration and decomposition) which occur during the heating of the specimen. For the examined samples typical thermal curves obtained by DTG/TG analysis are shown in Fig. 2.

For the thermal characterization of the materials, the temperature range, can be divided in four regions corresponding to the mass loss in the thermal curve [9]: *i*) <120°C, *ii*) 120–200°C, *iii*) 200–600°C, and *iv*) >600°C. The first region is attributed to absorbed water (hygroscopic water), while the second to chemically bound water of the hydrated salts, such as gypsum. The third region refers to the water chemically bound to hydraulic compounds - probably calcium silico-aluminate hydrates – (200–600°C) [9–12]. Finally the fourth corresponds to the carbon dioxide developed during the decomposition of carbonates. The endothermic peaks after 750°C correspond to calcite decomposition (Eq. (4)). While pure calcite decomposes near 840°C, the lower degradation temperature for the plasters is characteristic of the CO_2 loss from $CaCO_3$ formed by recarbonation reaction of lime with atmospheric CO_2 (Eq. (3)) [10, 11].

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (4)$$

The main difference between the examined samples is located in the temperature range 120–200°C. The Bulgarian and Serbian samples do not show any peak in

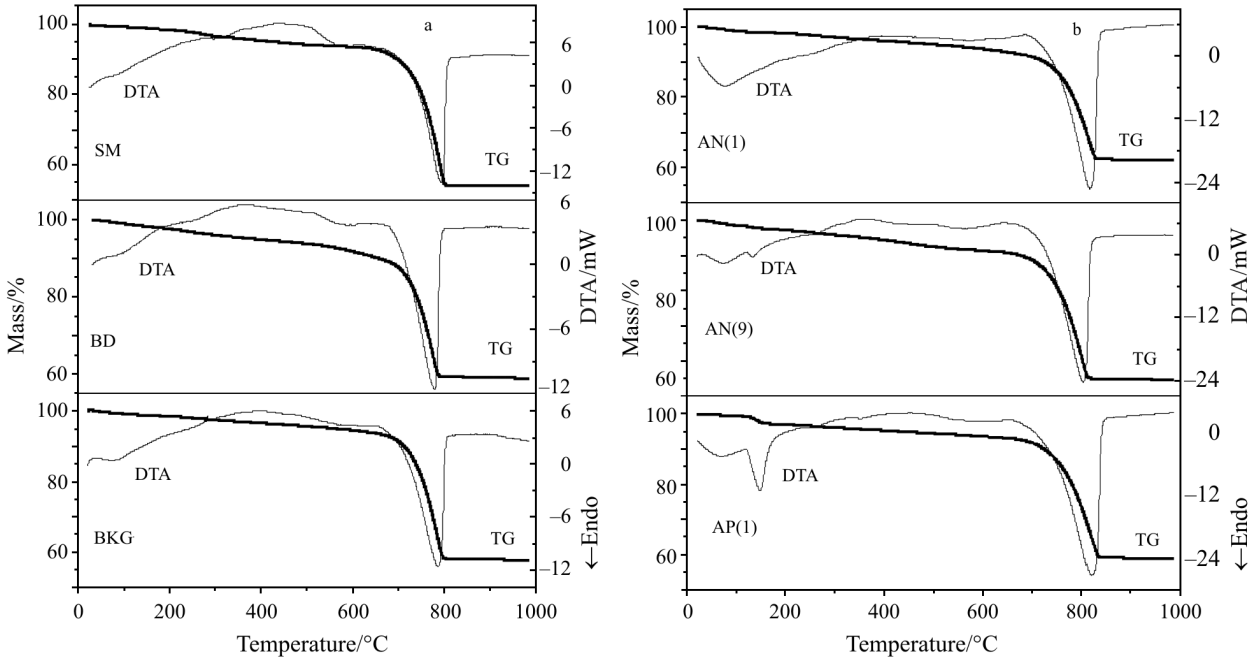

Fig. 2 Thermal curves of studied plaster samples, a – SM, BD, BKG and b – Albanian samples AN(1), AN(9) and AP(1)

this region (Fig. 2a). On the other hand AN(9) and AP(1) show endothermic peaks with the minimum at 132 and 149°C, respectively. This peak is attributed, besides a loss of moisture, to the dehydration of the gypsum ($CaSO_4 \cdot 2H_2O$), which takes place in two stages (Eqs (5) and (6)), between 130–160°C [10, 11, 13].

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2\ H_2O \quad (5)$$

$$CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4 + 1/2H_2O \quad (6)$$

Consequently it is clear from the thermal curves that in samples AN(9) and AP(1) there is a gypsum participation. The presence of gypsum in these plaster samples is also verified by the FTIR and EDS measurements as it is shown below.

Beyond the use of gypsum as a binding material of the plaster, gypsum can be formed during sulfation, as a result of Eq. (7), which involves the dry deposition reaction between limestone ($CaCO_3$) and sulphur dioxide (SO_2) gas, in the presence of high relative humidity, an oxidant and a catalyst (Fe_2O_3 or NO_2). In that case gypsum is primarily detected close to the surface, especially in cracks and voids [14].

$$CaCO_3 + SO_2 + 2H_2O + 1/2O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \quad (7)$$

In our case AN(9) and AP(1) are samples taken from St. Nikolaos and St. Paraskevi both frescoes painted by Onoufrios (XVIth century). AN(1) which is sample from the same church of AN(9) but from another place, painted by a different artist (XIVth century), has no traces of gypsum. This means that gypsum was not a deterioration result but Onoufrios used it as a component in the initial mixture of the plaster.

Table 2 summarizes the results from the thermal treatment. It is obvious that in all samples the main constituent is calcite as can be seen from the mass loss in the temperature range >600°C. SM has the greatest mass loss 39.44% in this temperature area. AN(9) and AP(1) perform in the second region mass loss of 1.05 and 2.27% respectively due to gypsum dehydration, which means that gypsum was in greater proportion in the mixture of the plaster AP(1). BD has a mass loss almost 1% in the temperature range 120–200°C, but the heat flow curve shows no peak corresponding to gypsum.

In Fig. 3 are presented thermal curves of the sample ATr(8), where is followed an endothermic peak with a minimum at 142°C, due to gypsum dehydration and the respective mass loss is 1.07%. The sample was collected from an area where the painted layer was damaged so the plaster was exposed to the air. In the FTIR and EDS measurement there is no evidence of gypsum in the plaster studied below the pictorial layer in painted samples. On the contrary it is identified gypsum on the external surface of the painted layer. Therefore, the presence of gypsum can not be attributed to its inclusion in binder but is more likely to be related to the sulfation of the carbonate component, due to environmental pollution [12].

The FTIR and EDS results are in good agreement with the TG-DTA analysis. In particular, FTIR analysis gives information about the presence of characteristic atom groups of the components that co-exist in the plaster. In the FTIR spectra the bands at 1445, 866 and 712 cm^{-1} are attributed to the CO_3 group of calcite [15, 16] while the existence of gypsum is identified from the bands at 602, 668, 1146, 3406 and 3550 cm^{-1} [16]. When silicates or alumino-silicates materials are added to the plaster, the FTIR spectrum reveals the most characteristic bands of the SiO_4 tetrahedra at the spectral regions 1200–900 and 500–400 cm^{-1} [9, 17, 18].

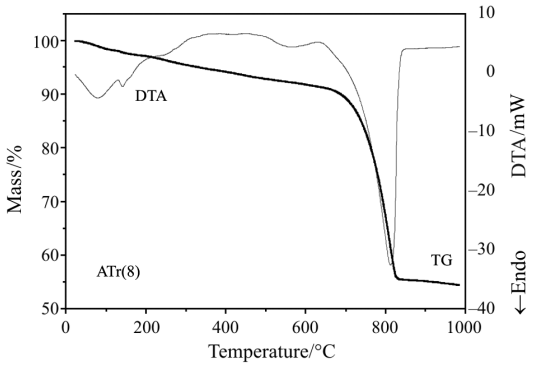

Fig. 3 Thermal curves of the Albanian sample ATr(8), with the typical peak of gypsum

Table 2 Mass loss in each temperature range (%) and CO_2/H_2O ratio

Sample	<120°C	120–200°C	200–600°C	>600°C	CO_2/H_2O
BKG	0.87	0.50	3.98	36.76	9.20
BD	1.34	1.01	5.84	32.81	5.60
SM	0.95	0.70	4.76	39.44	8.28
ATr(8)	1.87	1.07	5.29	37.33	7.05
AP(1)	0.68	2.27	3.42	34.71	10.14
AN(1)	1.36	0.44	4.48	31.51	7.03
AN(9)	1.62	1.05	5.86	32.71	6.26

Table 3 EDS results from the analysis of monuments samples

Sample	Ca/%	S/%	Al/%	Si/%	Mg/%
BD	32–34	0–0.08	–	18–20	0.1–0.2
BKG	24–25.6	0.3–0.46	15–17	41–43	1–1.6
SM	37.3–41.4	–	–	0–0.4	0–0.6
ATr(8)	3.5–33.3	–	0.6–2.6	0.4–9.9	0.5–0.9
AP(1)	20–31	0.7–8.3	0.4–2.9	0.5–3.8	0.7–0.9
AN(1)	85–91	–	1.2–2.3	3–5.7	1.8–4.2
AN(9)	28.9–34	1.1–8.3	1.1–2.6	0.3–1.5	0.8–2.6
ATr(1)	82.4–89	–	4–7.1	1.2–1.7	0.8–1.5
ATh(18)	32–62	0.5–9.2	0–1	0.5–5.3	0.3–1.6

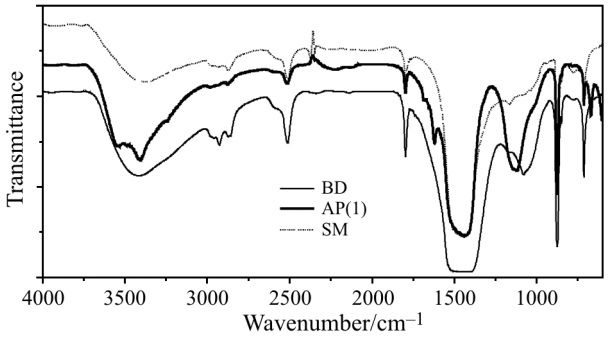

Fig. 4 Representative FTIR transmittance spectra from studied plasters

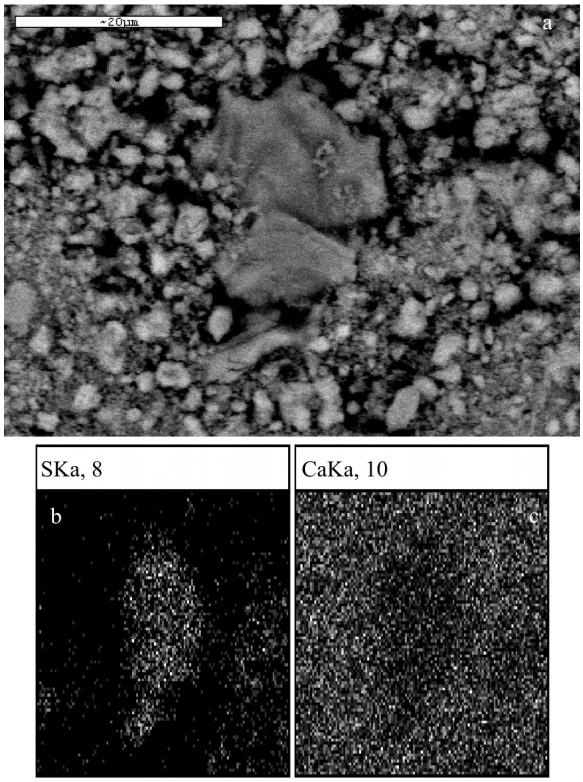

Fig. 5 SEM image of the AP(1) sample showing large gypsum's grains in the center (a). EDS analysis of the same sample and area showing sulfur (b) and calcium (c)

In Fig. 4 three characteristic FTIR transmittance spectra, obtained from samples, are presented. The spectrum from SM sample is dominated by the characteristic peaks of calcite while a weak broad band at about 1100 cm^{-1} is an indication of silicate traces. On the contrary the spectrum from BD sample presents the peaks of calcite but also presents a strong band at about 1080 cm^{-1} guiding us to conclude that the sample contains a significant amount of silicon containing compounds. Finally the spectrum obtained from AP(1) sample except from the peaks of calcite presents a strong contribution of gypsum, while the shoulder at about 1020 cm^{-1} is attributed to silicates whose the absorption band is overlapped by the strong peak of the gypsum (1140 cm^{-1}). Finally the main elements that are identified by EDS analysis are presented in Table 3.

The small participation of gypsum was not always detected by the FTIR spectra, obtained from different areas of the specimens, fact leading to the belief that a small amount of gypsum was probably mixed with lime and aggregates rather than being applied above the smoothest plaster (the intonnaco) as a separate layer.

Results obtained from the SEM-EDS analysis of AP(1) sample, show gypsum's grains scattered in the layers of plaster, without showing any larger topical concentration beneath the pictorial layer. Careful observation at ×2300 magnitude showed a differentiation in the size between the gypsum's and the calcite's grains, ranging between 8–10 and 2–3 μm respectively (Fig. 5).

Conclusions

The historic plasters studied can be classified in two distinct groups depending on their thermal behavior. Each plaster type formed a more or less compact group of samples.

Thermal Analysis seems to be a reliable method for plasters' discrimination. The adhesion of the pig-

ment to the plaster is better in the case of lime plasters as compared to gypsum plasters. In the first case the pigment penetrates well (fresco technique) into the lime plaster and is thicker, whereas it is thinner on the plaster with the gypsum participation.

The results give useful information on the understanding of the technology of historic plasters and on planning syntheses for restoration of wall paintings. Our work allows a consistent approach to the wall paintings conservation and repair to be achieved.

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