



Contemplation of conservation and Painting technique of plaster wall paintings at Church Karas in Deir el-Anba Shenouda Sohag- Egypt

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Abstract: The state of conservation of the frescoes at Church Karas in Deir el-Anba Shenouda Sohag was investigated by integrated physicochemical measurements, particularly optical and scanning electron microscopy, m-infrared spectroscopy, mass spectrometry and X-ray powder diffraction. The frescoes appear darkened and severely damaged owing to the deterioration of surface treatments and to the widespread presence of different salts. These caused significant detachments of the painting layers. The materials used in the painting and preparation layers and in the wall plaster were characterized in order to clarify the painting technique. Different pigments have been identified on the pictorial layers: the original ones correspond to green earth, yellow and red ochre, realgar, bone black and lapis lazuli and others, such as titanium white and cobalt blue, ascribed to recent restoration works. Proteinaceous materials (egg or yolk) have been identified as binders for the pigments, indicating a tempera painting technique. Three different products, belonging to restoration interventions, have been also identified: the natural product shellac, ascribable to next-to-last restoration and scarcely removed during last restoration also because of its insolubility, the synthetic vinyl acetate and acrylic polymers. Particularly the latter one indicates an on-going degradation of the applied fixatives. The extensive deterioration of the surfaces is also due to the widespread presence of salts, such as chloride, nitrate and sulphate clearly identified by XRD measurements. The obtained results give a comprehensive overview on the employed painting technique and its state of preservation and on the causes of the painting deterioration. Therefore, they are a fundamental tool to develop durable and compatible materials and methodologies for a future conservation strategy of this site.

I. Aim of Research

Integrated physico-chemical investigations were carried out on fragments, collected from the pictorial cycle, one of the most important buildings of the Coptic dynasty in upper Egypt, with the aim to obtain useful information about the painting technique, to offer a preliminary scientific view of the state of conservation of these wall paintings, to ascertain the type and the extent of the degradation processes and to detect the materials used in previous interventions. The final goal is to offer scientific tools for a better understanding of this pictorial cycle and to set up a scientific aid and guide for a conscious intervention on these paintings, severely damaged not exclusively by natural decay processes.

II. Introduction

Deir el-Abyad (or the White Monastery in English) (also known as Deir Amba Shenouda or Shenute) is a Coptic Orthodox monastery. It lies about 4 kilometers south-east of the Red Monastery, some 15mi/25km north-northwest of Sohag (Suhag). It was named after Saint Shenouda (Shenute) the Archimandrite who founded it about 332/350 to 451/466. By the time of Shenouda's death, in 466 AD, the population of the White Monastery increased from 30 to more than 2000 monks and 2000 nuns. Although it was burnt in the Arab Conquest (619 AD), the church enclosed inside the monastery is still extant in place. After the Arab Conquest, the monastery began to decline and in 1168. The Monastery was restored during the 13th century, but it began to decline again since the 14th century, until it was burnt by the Mamelukes in 1798, while they were fleeing from Napoleon's army. During the reign of Mohamed Ali, part of the monastery was restored. The Last restoration was committed in 1980. The monastery's architecture is similar to that of the Red Monastery. It is one of the most celebrated and important monasteries in Egypt. Surrounding the monastery is a high wall of white limestone blocks. The church can be entered via a narthex that has an apse at the west end. Noticeably, it is an aisled basilica with a trilobate sanctuary, consisting of a square domed central area and three apses with semi domes. The apses have two rows of five niches alternating with columns. At the north end, there is a second narthex with a pillared apse. Deep down in Egypt, 500 km (300 miles) south of Cairo, just outside the province capital of Sohag, at the

border of the Nile valley and the Western desert, within a stone's throw of the age-old White Monastery, one finds a remarkable new Coptic Orthodox Church.



Fig. 1. View of Church Karas in Deir el-Anba Shenouda Sohag

Very important mural paintings decorate the central hall and the connected rooms of the building of Church Karas destined to alcoves and baths with tepidarium and calidarium. Although they have been recently restored, the paintings appear severely deteriorated. The low part of the paintings (originally painted as imitation of marbles) are damaged by the rising damp and worsened by writings, incisions and other vandalic actions, that have caused the total loss of significant parts of them. Besides all, chromatic alterations are widely distributed, essentially greyish in colour that could be ascribed to the deposition of soot and other atmospheric fine particulates. Moreover, many areas show an extensive network of micro-cracks associated with a spread darkening of the painted surface and detachments; this peculiar decay pattern is especially localised on paintings subjected to earlier restorations by different organic fixatives. The frescoes of Church Karas show details of the clothes, i.e. the colors and the fabrics, that testified the social and economic life in the Coptic period. Today the visitor must use his imagination to reconstruct the original aspect of the paintings because of the very poor state of presentation of many scenes, as a diffuse dark patina overshadows the restored painted surfaces. An urgent restoration is needed to adequately clean and free from the dirt the wall paintings.

IV. Experimental

Twelve samples areas have been collected from the western and northern walls, side-walls with respect to the main entrance. The sampling procedure deserved difficulty owing to the scarce cohesion of the painting layers and the crumbling of the plaster. The samples were observed as received and as cross-sections. The optical observations on the cross-section were carried out by a microscope Olympus BX51 equipped with UV-light source to prove the organic layers. The cross sections were analysed also by SEM-EDS, after metallization through the deposition of a graphite film. The instrument was Philips Model XL 40 LaB6. Semi quantitative analyses of elemental composition were obtained using an EDAX DX Prime X-ray energy dispersive spectrometer equipped with a thin beryllium window, using an accelerating voltage of 25 keV. By stereomicroscope observation of the collected samples, the different layers of the paintings have been mechanically separated each others and studied separately. The binding media of the painting layers were identified by mFTeIR analyses, performed either on the different crushed layers and on their soluble fractions extracted by solvents (CH_2Cl_2 , H_2O , EtOH, Acetone). IR spectra were collected in reflection mode by a Nicolet Magna IR560 FTeIR Spectrometer and Spectra Tech microscope on the separated layers and the extracted fractions flattened on a gold surface. The IRUG database was used for the identification of the material constituents of the sample. X-ray diffraction (XRD) analyses of the ground samples were performed on a Philips X'Pert PW3710 diffractometer, using Cu Ka radiation (40 kV, 30 mA), high-resolution graphite monochromator, rotating sample holder and proportional detector. Measurements were carried out in the range $50 < 2\theta < 900$ with a step of 0.020; the ICDD data bank of standard X-ray powder spectra was used for phase identification.

V. Results and Discussion

The collected samples have been examined as received and or as cross sections by integrated physico-chemical measurements particularly optical and scanning electron microscopy where possible, by X-ray powder diffraction in order to verify the pictorial technique, the state of conservation of the frescoes the damages caused especially by chemically agents, particularly salts, detachments, repaintings and fixatives also in consequence of the materials employed in previous interventions and to propose an appropriate intervention project. Some Pyrolysis GC-MS measurements have been also included to corroborate the infrared indications about the organic materials. Optical and SEM-EDS microscopies show that the finishing plaster below the painting layers contains calcium carbonate and a small amount of Si, mainly in the form of quartz clusters. Some samples show a superficial finishing layer exclusively constituted by Ca (white lime). Mineral and synthetic inorganic

pigments have been identified on different painting layers: green earth (potassium and iron silicate) bone black, natural lapis lazuli, red and yellow ochres, realgar and white lead (Fig. 2).

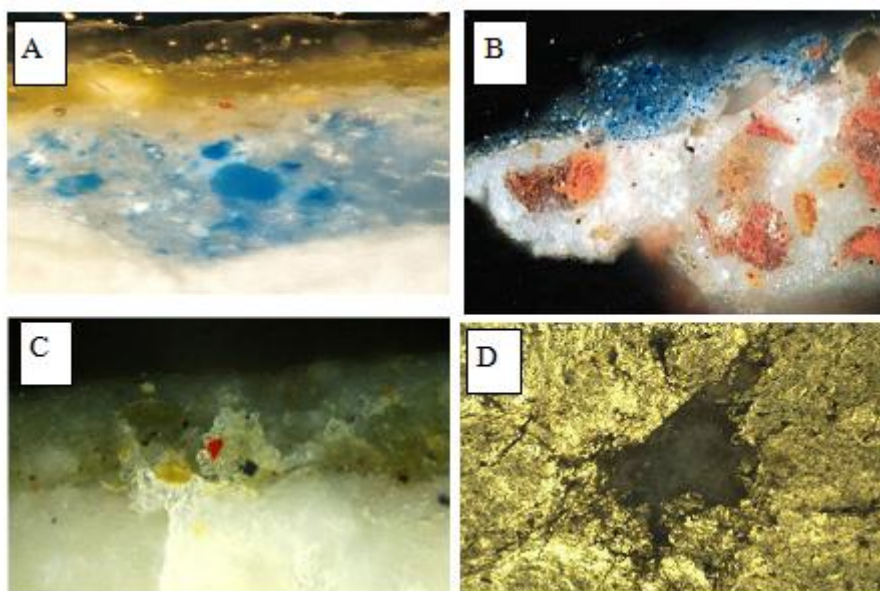


Fig. 2. Cross section of sample magnification 500 (Optical observation shows the finishing lime layer followed by the blue layer composed of calcium carbonate and particles of two superimposed restoration layers (a). (b)Optical micrograph of the cross-section of sample a blue area. (c) Cross section from the olive green zone in the background (d) image showing details of the gilding

With the exclusion of layers containing white lead, the widespread distribution of Ca on the painting layers proves the use of lime as a binder; notwithstanding organic binding as egg tempera, has also been employed as identified by FT IR and GC-MS investigations .Industrial pigments as cobalt blue and titanium dioxide have been also identified; they clearly belong to a pictorial retouching performed during recent interventions .FT IR investigations, carried out on powders collected from the different painting strata, gave quite convincing information on the original binding materials and the organic products applied as restoration fixatives; spectra collected on several samples show a carbonyl ester band at 1738 cm^{-1} ($\nu\text{ C=O}$ stretching) and the protein bands (broad band centred at 3308 attributed to stretching $\nu\text{ N-H}$, 1650 stretching $\nu\text{ C=O}$ amide I and 1543 cm^{-1} bending $\delta\text{ N-H}$ amide II) (Fig. 3a) (The comparison with reference spectra and the data obtained by pyrolysis GC-MS investigations indicate the presence of egg . Absorptions of calcium oxalate bands at 1618 and 1316 cm^{-1} respectively the symmetric and asymmetric stretching of COO group and absorptions of nitrate salts at 1386 and 837 cm^{-1} (Fig. 3b)Respectively the stretching and out-of-plane bending of NO_3 group are clear indication of transformation of constituent materials and salt induced decay processes.

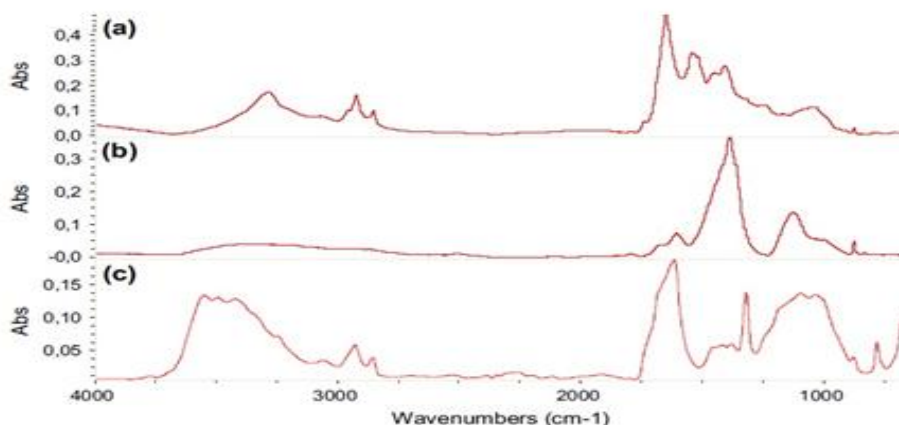


Fig. 3. FT IR spectrum of the CH_2Cl_2 soluble fraction of the sample G3 (a) and of the H_2O soluble fraction of the sample G8 (b, c). Infrared absorptions reflect the composition of proteinaceous binding media (i.e. animal glue, egg) in the painting layers (a) and the presence of nitrates (b) and oxalates (c (due respectively to transformation of constituent materials and salt induced decay processes.

The FTIR characterization of powders and CH_2Cl_2 extracts from the superficial layers of painting samples shows different absorption patterns: some spectra, collected from the outmost layers, show a strong absorption at 1739 cm^{-1} due to the $\nu\text{ C=O}$ carbonyl stretching of an ester group, intense bands at 1235 cm^{-1} corresponding to the C-O stretching band of the acetate $\text{CH}_3\text{-CO-OR}$, and at 1021 cm^{-1} corresponding to the O-C stretching of the acetate group O- CH_2 (Fig. 4a). This characteristic absorption pattern is ascribable to a vinyl acetate polymer, in good agreement with the reference spectrum of the commercial synthetic resin poly(ethylene/vinyl-acetate) (BEVA 371), widely employed in the recent past as fixative for mural paintings and canvas . Acrylic polymers have also been identified on superficial layers of few samples) Fig. 4b), these may be ascribed to the commercial product Primal, applied during the last restoration work. More remarkably, the IR spectrum of the acrylic polymer shows a weak band occurring at 1776 cm^{-1} related to stretching absorption of γ -lactones (Fig. 4b), a common feature of polymer photo-oxidative degradation , indicating the applied product is undergoing severe deterioration processes .

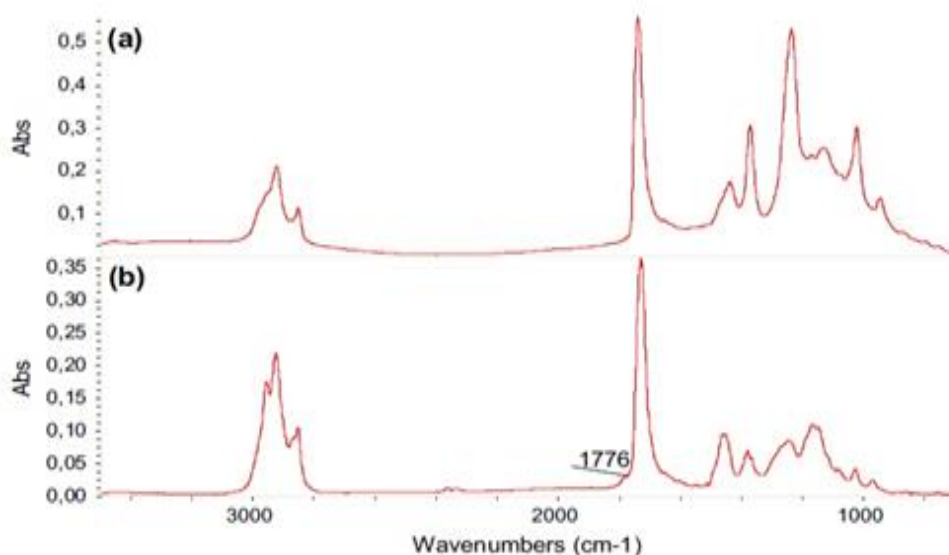


Fig. 4. FT IR spectrum of the CH_2Cl_2 soluble fractions of the sample G4. Both spectra indicate the presence of restoration polymers applied in the recent past: a vinyl acetate polymer, in good agreement with the reference spectrum of the commercial synthetic resin poly(ethylene/vinyl-acetate) (BEVA 371) (a) and an acrylic polymer tentatively ascribed to the commercial product Primal (b). The latter is undergoing severe deterioration processes as indicated by the absorption at 1776 cm^{-1} ascribable to γ -lactones, a common feature of polymer photo-oxidative degradation.

Several samples also show a brownish superficial layer, which appears bright fluorescent by UV light observation of cross sections) Fig. 2b) and consequently not ascribed to a polymer used as restoration material. So far, it has been mechanically separated from the painting fragments and characterized by FT IR. All attempts to solubilise it with different solvents (CH_2Cl_2 acetone, H_2O , $\text{CH}_3\text{CH}_2\text{OH}$) failed. The IR spectra collected on the insoluble brownish product, show a strong band occurring at 1712 cm^{-1} with a shoulder at 1732 cm^{-1} related respectively to antisymmetric C=O stretching of a carboxylic acid and to $\nu\text{ C=O}$ stretching of an ester group. Other bands in the range $1300\text{e } 1150\text{ cm}^{-1}$ can also be attributed to different stretching modes of the ester and acid groups, while absorptions at 2929 and 2856 cm^{-1} are related to asymmetric and symmetric stretchings of CH_3 and CH_2 groups (Fig. 5.)

The mixture of esters and acids resembles the composition of the natural product shellac, whose reference IR spectrum fully agrees with the analysed unknown product .Shellac's good adhesive power and penetration made it widely employed as fixative for wall painting, notwithstanding the yellowing and increasing insolubility with ageing that darken the treated surfaces and strongly reduce the removability. XRD analyses of samples collected from the widespread efflorescences, prove the presence of sylvite and halite, respectively a potassium and sodium chloride, apthialite, a mixed sodium and potassium sulfate, and, finally, nitratine, sodium nitrate. Macro-evidences of pulverization of the wall painting, detachments and superficial incrustations, induced by the disruptive effects of these soluble salts, have been also highlighted by micro morphological SEM observations on samples collected from these deteriorate areas.

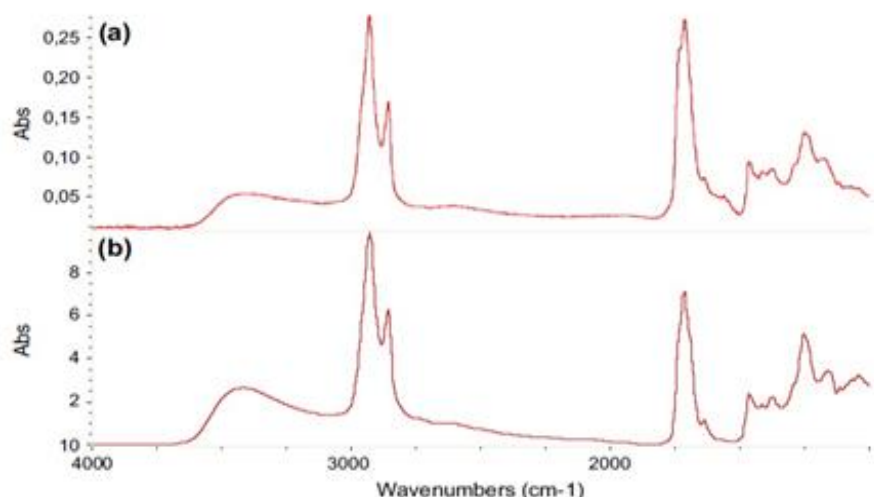


Fig. 5. FT IR spectrum of powdered superficial brownish layer of painting sample G8 (a). The infrared absorption can be inferred to a mixture of esters and acids, resembling the composition of the natural product shellac. Its spectrum fully agrees with IRUG reference IR spectrum (b)

VI. Conclusion

The physico-chemical investigations, carried out on a series of fragments, collected from the wall paintings of Church Karas in Deir el-Anba Shenouda Sohag allowed a comprehensive characterization of the pictorial technique and of the nature and the degradation degree of the wall paintings. Different pigments have been identified on the pictorial layers: the original ones, corresponding to green earth, yellow and red ochre, realgar, bone black and lapis lazuli and those ascribing to recent restoration works, such as titanium white and cobalt blue. In disagreement with other studies FT IR and GC-MS analyses identified a proteinaceous medium, i.e. egg or yolk employed as binder for the pigments. FT IR spectroscopy has also identified three different fixatives. The natural product shellac has been found in several samples ascribable to next-to-last restoration and scarcely removed during last restoration also because of its insolubility in the most common solvents. It could be responsible of the widespread and severe darkening of the wall paintings. Also vinyl acetate and acrylic polymers have been identified on the painted surfaces and the decay products, especially of the acrylic polymers clearly indicate an on-going degradation of the applied fixatives. The pictorial cycle is indeed severely damaged also by soluble salts transported by rising damp and ground water; chloride nitrate and sulphate salts have caused remarkable surface alterations efflorescences and detachments of painting fragments. The present work must be considered as a preliminary assessment to quantify and qualify the degree and type of damage suffered by wall paintings, to evaluate the current effectiveness of the fixatives applied during the previous restoration and their possible alterations. The obtained results clearly show the severe deterioration that are suffering both the original materials and the applied products and must be use as a starting point to develop durable and compatible materials and methodologies for a future conservation strategy of this site.

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