CONSERVATION OF THE MURAL PAINTINGS OF THE GREEK ORTHODOX CHURCH DOM E OF SAINT GEORGE, OLD CAIRO-EGYPT

Abd El-Tawab N.
Conservation dept., Faculty of Archaeology,
South Valley Univ., Qena, Egypt
Mahran A.
Institute of tourism, Hotel management and Restoration, Alexandria.Egypt
Gad K.
Conservatore, the Arab contractors, Osman Ahmed Osman, Cairo, Egypt

Abstract

The church of Mary Girgis (Saint George) was built by Athanasius "who also founded the Church of Saints Cyrus and John". The Church was destroyed, and all the rest of the original edifice is a room which covered by huge dome known as the Wedding Hall, dating to the 14th century. The huge dome of the wedding Hall contains several mural paintings represented Coptic arts. The dome mural paintings was darkened and severely damaged as significant detachments of the painted layer and the underneath support lost their cohesion and separated into many pieces, delamination and flaking of the ceiling painting. The most important causes for the monument state of degradation were the environmental condition such as the effects of the groundwater, the presence of salts, the humidity (active in all its forms as infiltration, capillarity and condensation) and the improper previous interventions at the structural level (fillings in the cracks with gypsum mortars). The aim of this study is to characterize the components of the pictorial surface which consists of pigments, the binding media, the plaster layer and its support and introduce the conservation project of the mural painting which was carried out at the dome "between" 2004-20013. Prior to the conservation intervention, the materials were characterized by optical microscopy, polarizing microscope, scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction and X-ray fluorescence. The chemical analyses have determined the nature and composition of the materials used in the painting process (mortars, pigments, binders), have identified the causes of physical and chemical altering processes of pigment layers and provided knowledge on the execution technique. The interior painting was executed according to the Byzantine technique, on a fresco plaster (intonaco) consisting of lime mortar, pigments were obtained by mixing pigments with water. After the material characterization, the conservation and restoration of the mural painting, which including cleaning, injection grouting, fixation of the paint layer, filling of the support gaps with mortar, consolidation, restoration and completion of lost parts, were carried out.

Keywords: Saint George church, mural painting, deterioration, analysis, frescoes, conservation

Introduction

The history of the church

The Greek Orthodox Church of Saint George is one of the most important archeological sites in Egypt cultural heritage. It is one of the few round churches still in existence in the East. It is a historical mark that has its origins to the down of Christianity in Egypt. The present structure is a result of several extensions, modifications and demolitions since the construction of its oldest parts. The history of these church dates back to the 7th century. The original church of Saint George was built in 684 by the same Athanasius who also founded the Church of Saints Cyrus and John" and this church is also mentioned in the biography of the patriarch Alexander II (704 - 729A.D.) (Burmester 1955). It was erected upon the northern tower of the Fortress of Babylon and adjoins the Monastery of St. George. The church can be reached through a long set of steps that lead up to the church that are built on the outer wall of the Roman towers and is crowned by an impressive dome. As one ascend these steps, there can be found a relief of St. George and the dragon wrapped around the outer brickwork of the tower. For centuries, the church alternated between ownership by the Copts and the Greek, but since the 15th century it has remained Greek Orthodox. The church had been burned many times, it was burned in 1904AD. The current structure was built in 1909AD, fifteen meters in length and twelve meters in width. Its central area is lower than its lateral parts. The walls and ceiling show wall paintings and fine stucco decorations (fig.1).

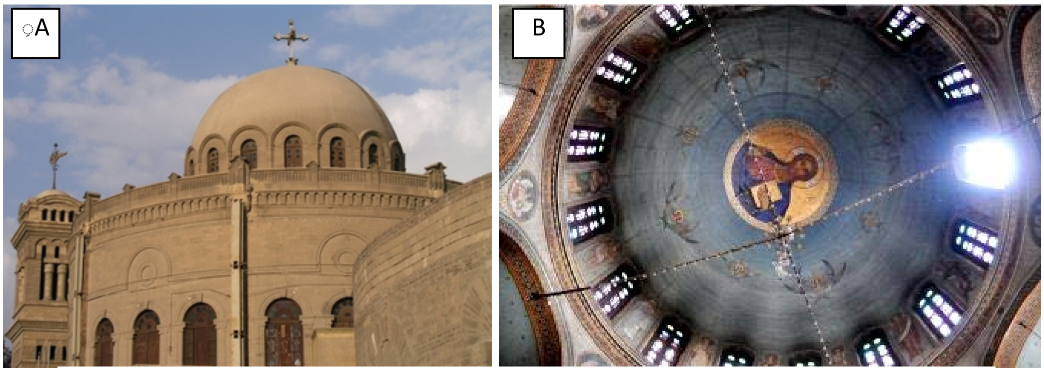

Figure 1: The Church of St. George in old Cairo: a: outside view of the church dome b: inside view of the dome

The figurative elements and the use of pigments

St. George Church is very important in the point of wall paintings it contains. Wall paintings showing the events expressed in the Holy Bible. Wall paintings are located on the dome, drum of the dome and pendentives. Different kinds of wall decoration have been found represented an interesting ensemble of post-Byzantine painting as: The painting of Christ mediates the dome, wearing a blue cloak, holding Gospel and surrounding with decorative frame (fig.2a). Painting of Angels surrounded the Christ (fig.2b). The Barrel of the dome was decorated with the paintings of the full-length portraits of the prophets and each prophet could be identified by his text (fig.2c). Communion of the Apostles is found between arches (pendantives) (fig.2d, e). These paintings are surrounded by stuccos made of colored gypsum (fig.2). The documentation of the figurative elements in the St. George dome has been prepared in (fig.3).In the palette of the wall painting of the St. George Church dome, many different colors were recognized, some of which in two different shades: pale and dark blue. Brown, yellow, black, red, pale and dark green, reddish brown and beige were identified.

Mural painting technique

The technological examination of the mural paintings from St. George church focused on the technical and material elements and determined that. This design layer appears to have been executed according to the oil painting technique on dry plaster, having rough layer (arriccio) made from lime and sand with a thickness of around 3mm which was applied over another fine layer of plaster (intonaco) varying in thickness from 1-2 mm, having in composition lime and inert materials like tow(fig.3a, b). Pigments were executed in oil painting. Oil paintings are executed on directly dry stone or dry plaster. Drying oils have been used as binding media for pigments in wall paintings in the Church of St. George. Oils, which can form solid film layers by reacting with the oxygen in the air, this reaction is known as auto-oxidation with air (Gimeno et al 2001). The final layer is varnish, oil paintings are generally varnished with a natural resin dissolved in mineral spirits and applied to the surface in a thin layer to make it smooth and glossy and helps to protect the painting (fig.4). Physiochemical factors and biological agents play an important role in the deterioration of wall painting of the St. George dome causing remarkable amount of aesthetical and chemical damage. The present study concerns itself with two important aspects of the wall paintings in the dome of the Church of St. George: (a) disclosure and classification of its painting techniques and (b) description of its state of preservation aiming at the consolidation, removal of soot and salts, and restoration of the aesthetic integrity of the murals.

Figure2: the mural painting at the St. George Church dome **a**: Paintings of the **Christ b**: Paintings of the **Angels** around Christ **c:** Paintings of the full-length portraits for of prophets in the barrel of the dome **d**, **e**: Pendentive.

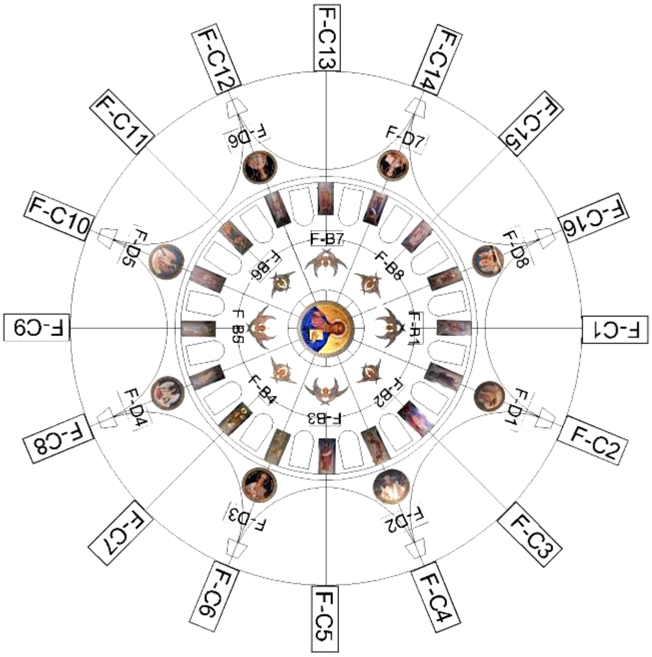

Figure3: distribution of mural painting at the dome of the Church of St. George

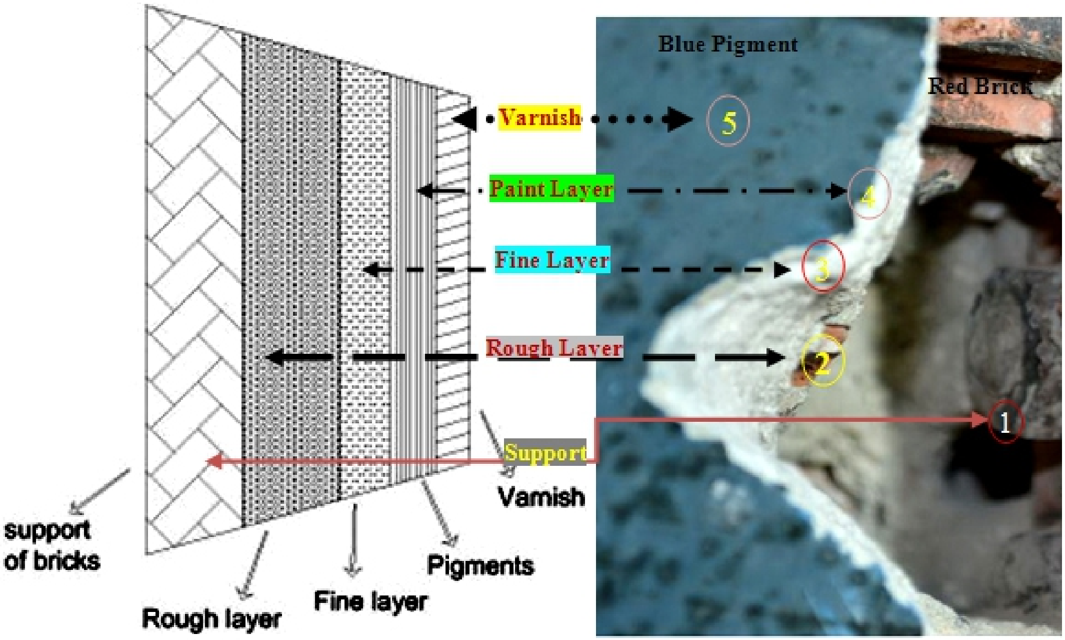

Fig.4 the mural painting structure layer **a**: plane of painting structure layer
b: detail from area of loss on dome

Degradation Causes and Conservation State

The murals painting in the church were in a bad condition at the point of the intervention. The serious damages occurred mainly at the paint layer. The most important causes for the mural painting state of degradation were the natural calamities such as Oxygen in the air, air pollutants, light and changes in temperature accompanied with changes in humidity completed by the lack of maintenance, the humidity (active in all its forms as infiltration, groundwater and condensation) and water leak determined the appearance of salts efflorescence, as well as biological growth, these conditions have had a devastating effect. The salts absorbed in the pores of mural painting tend to dissolve in a humid atmosphere, a process known as efflorescence. The dissolved salts then migrate in the mural painting component and crystallize in different pores creating pressure, which can cause the mural painting to crack. The salts can likewise migrate to the surface of the stone causing considerable damage and posing a serious problem in paint layer such is the case of St. George dome. Additional factors, such as dust, soot, and fungi aid this decay process. Several degradation phenomena were observed on the paintings. Two types of crack formation were apparent: shrinkage cracks, which had formed as the paint layer, and cracks of varying depth and width accompanied with loss of the paint due to blistering and loss of plaster layers (fig.5a, b). There is prevalent intra-layer delamination, as well as significant detachment of these layers from the ground layer, it was loss of cohesion (powdering) and the pain layer start to flake (fig.6), because of the oil content of paint is inadequate (Kabbani 1997). Also humidity, by both infiltration and capillarity, is responsible for the loss and cohesion of the support and paint layers. Liquefaction of some colors on the other colors was noticed (fig.7) due to wash of color by the rain penetration through the cracks or holes in the walls, ceiling and the broken windows. Chromatic alterations (changes in appearance) were observed (fig.8). Unfortunately, oxygen in the air oxidizes the varnish and turns it into a yellow film that dulls the colors that it once enhanced. The paint layer had also suffered scratches (fig.9), which in several places had penetrated the intonaco layer. Mildew discoloration was the common problems at the mural painting of St. George. It showed a phenomenology of alteration varying from white, brown, and black duff patinas (fig. 10a,b). These phenomena might be linked to different microbial colonization. Mildew is caused by forms of stain fungi. The high level of moisture favored the appearance of biological attack on the mural surface, both on Christ and Apostles. According to the analysis, fungal species such as *Penicillium*, *Aspergillus* and *Alternaria* were present on the painting. The dome comprises inorganic and organic materials such as blood of bats (bats dropping), bird's nests, bee's nests…etc. (fig.11a, b). Dirt, impurities stains, insect broods and numerous cobweb nests on the painting surface were registered (fig12), due to the accumulation of airborne deposits from different sources on the surface of the painted dome, this has caused the formation of dark film which obscure and deadens the original pigments (fig.13). The result is a vulnerable, rapidly deteriorating surface that is difficult to read pictorially.

Figure5: The types of cracks occurred in mural painting **a:** shrinkage cracks **b:** cracks of varying depth and width accompanied with loss of plaster.

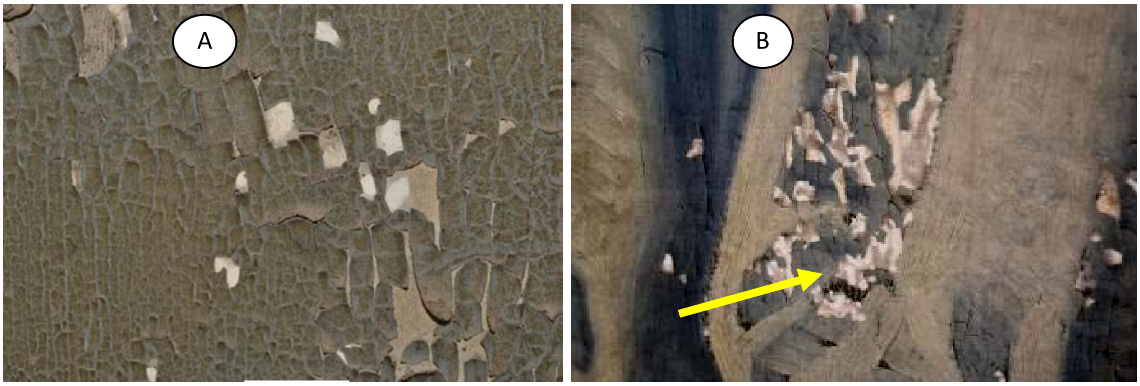

Figure6: Losses of cohesion (powdering), paint start to flake.

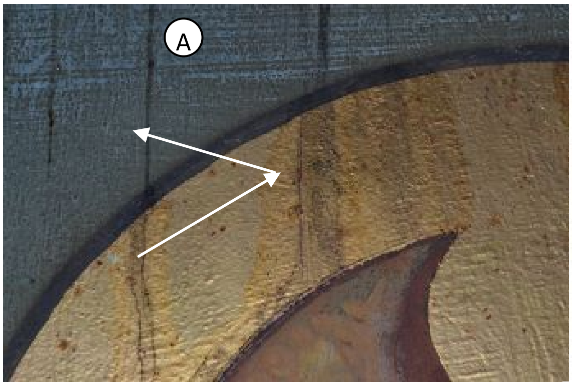

Figure7: Liquefaction of the paint layer at the other colors

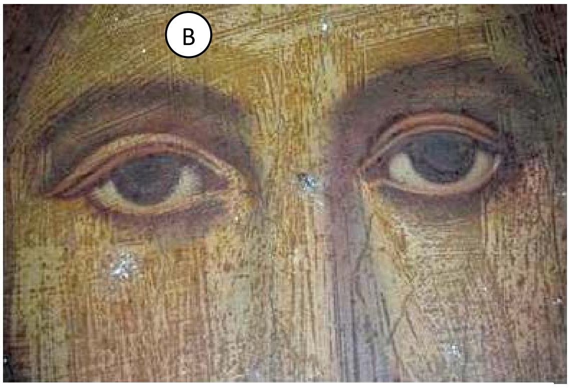

Figure 8: Chromatic alterations (yellow film that dulls the colors)

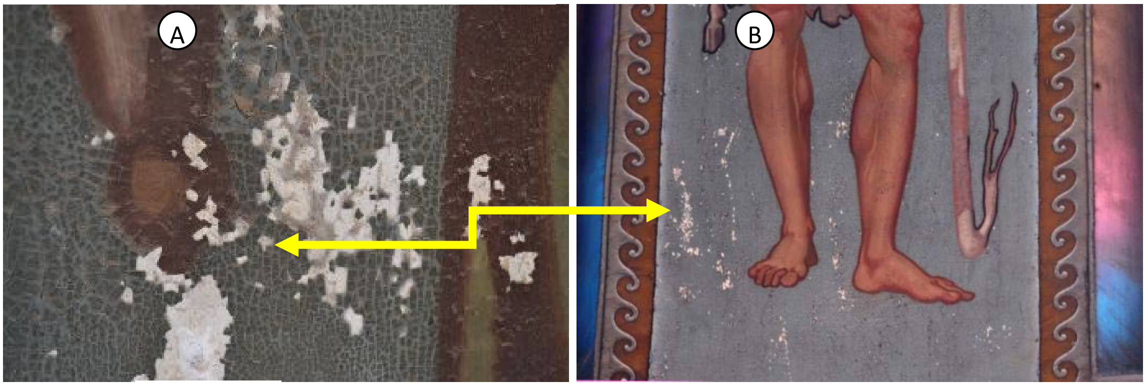

Figure 9a,b: scratches, which in several places had penetrated the intonaco layer

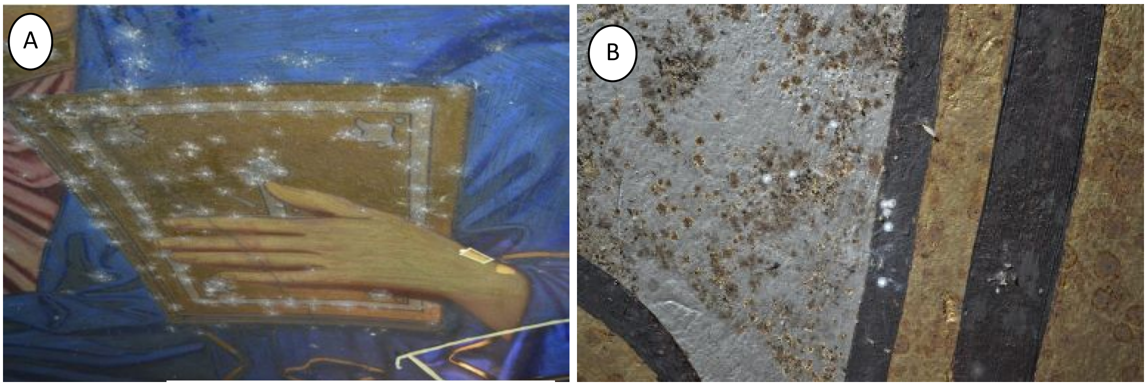

Figure 10a,b: Mildew discoloration at mural painting on St. George dome.

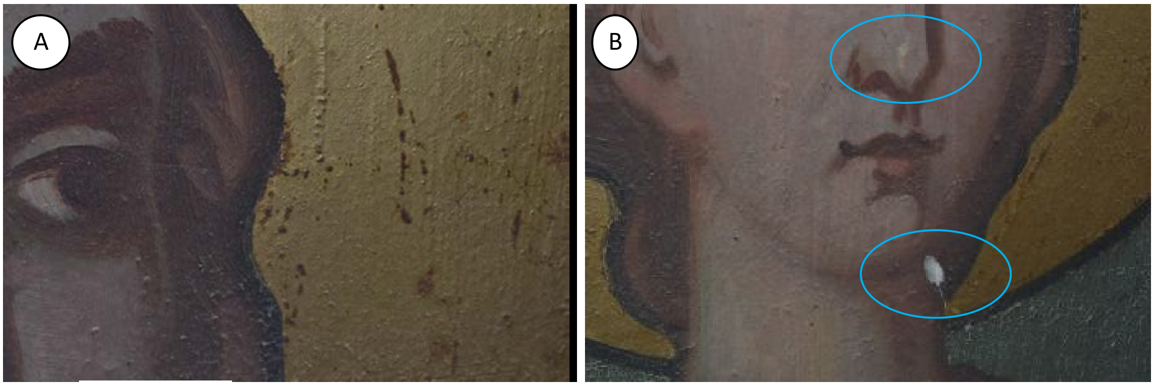

Figure11a,b: organic materials at the surface of mural painting **a:** bat droppings **b:** extracts of birds

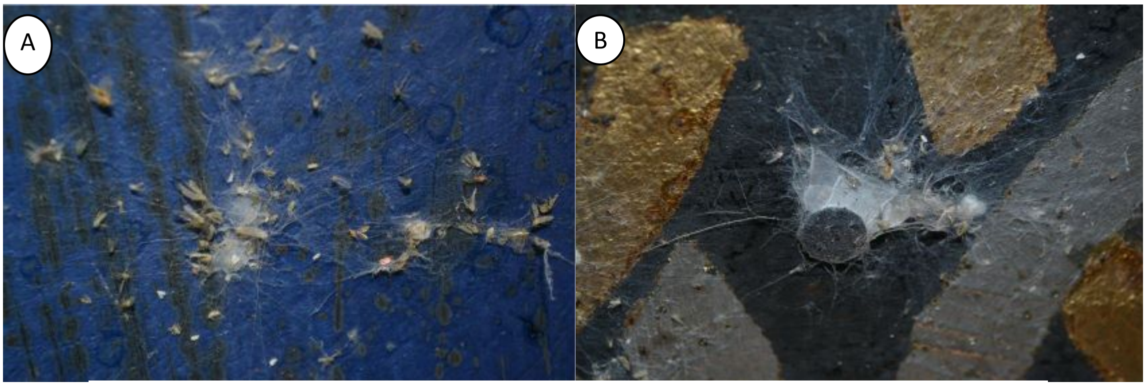

Figure12a,d a, b Dirt, impurities stains, Insect broods and numerous cobweb nests on the painting's surface.

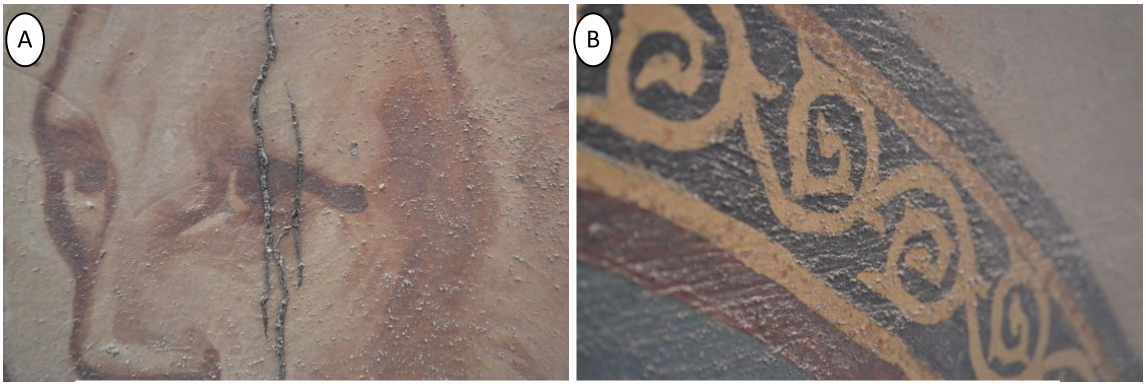

Figure13a,d a,b: due to the accumulation of airborne deposits from different sources on the surface.

Experimental

Samples

The samples under investigation were acquired from a variety of scenes and zones in the dome of the church and were chosen for the purpose of identifying the material elements that make up the redbrick support, plaster, pigments and the residual salts on the wall painting surface. Painted plaster samples were collected from detached parts of the paintings, it was cared to collect samples as small as possible in size. Moreover, attention was given to locate and describe the painting techniques (stratigraphy, pigment). Samples of all layers of wall painting were collected by using scalpel and forceps. During sample collection it was cared not to damage the wall paintings. Each of the samples was labeled with abbreviations considering the section of the church they collected from, and the type of the sample (support, plaster or paint sample) (table 1). Parts of these samples were used for cultivation to determine the fungi and bacteria grown on it. The other samples were used for various analysis and examination.

Table 3: Description of sampling position

No. of Samples	**Point in the church**	Scene	Sample
FA.ON	neck of Christ	Christ	Brown pigment
FA.BF	The drum of the dome	background	Blue pigment
FA.BD	Clock of the Christ	Christ's tunic	Blue
FB.BB	Angel N.5	Angel	Blue Angel
FB.BG	Prophet No.11	Prophet	Green Angel
FA.OF	Christ's tunic	Christ	Silver
FA.G	Prophets N. 14	prophets	Gold
FA.S	Around Christ	Apostles wear	Yellow pigment
FA.ON	Coarse layer	background	Coarse layer (arriccio)
FA.B	Fine layer	background	Fine layer (intonaco)

Methodology

Different series of laboratory tests was applied to each layer of painting samples in order to determine their basic characteristics.

Light Optical Microscopy (LOM)

The stratigraphic characterization of polychrome surfaces was done through the observation of samples by Light optical microscopy (LOM) using Leica DM 1000 stereoscopic microscope with a Leica EC3 camera under a magnification of 40x to 100x, to determine the number and sequence of layers and to characterize each one of them with respect to matrix heterogeneity, particle size, color, shape and transparency, among other aspects (Carolina et al 2008).

Scanning Electron Microscopy and Microanalysis (SEM/EDX)

Chemical compositions and microstructural properties of support, plasters and paints were determined by JEOL JSM 6400 Scanning Electron Microscope (SEM). Robinson detector of back-scattered electrons was used under the constant pressure conditions (0.5 mbar) without the necessity of surface metallization equipped with X-ray Energy Disperse System (EDS). SEM-EDS with an energy dispersive X-ray spectrometer (EDX) system with accelerating voltage 200v-30K.V., magnification 500x up to 2500x.

Powder X-ray Diffraction (PXRD)

Mineralogical composition of lime plasters were determined by X-ray diffraction (XRD) analyses performed by PW 1840 diffractometer equipped with a conventional X-ray tube (CuKα radiation, 40 kV, 25 mA, point focus), an X-ray monocapillary with diameter of 0.1 mm, and a multichannel detector X'Celerator with an anti-scatter shield. Diffractograms were taken between 5.025 and 73.96° 2Θ with 0.0300° step and 2200 s counting time per step that produces total counting time of about 23 hours.

FTIR spectroscopy

The chemical composition of the binding media and varnish layer were determined by using FT-IR. FTIR in the study of pigments can be particularly useful for identifying organic that are missed using techniques such as EDS and XRD. FTIR is able to recognize inorganic compounds containing complex anions (such as carbonates, sulfates, silicates) (Michele 1999). The binder was finely ground on an agate mortar. 0.5 mg of this mixture was then dispersed and further ground in about 70 mg of KBr and pressed into pellets under about 10 tons/cm2 pressure. Spectral measurements were carried out on a JASCO FT\IR–460 spectrophotometer. Spectra were acquired between 400 -5000 cm^{-1}.

Petrographic examination

The minerals characteristics, texture, cement materials and digenetic features of redbrick sample were further examined by using a polarized optical microscope. Petrographic thin sections were prepared and optically analyzed by using a Leitz polarizing microscope.

Biodeterioration study of the wall painting

A survey of biodeterioration phenomena was performed in mural painting at the church dome by swap technique. For each sample, 1g was diluted with 9 ml of sterilized distilled water. Samples were shaken vigorously to form uniform solution of 10-1 concentrations. The decimal serial dilutions (10-1 to 10-5) were prepared using the method of (Ejifor & Okafor 1985). For the isolation of fungi, plate count method (Raper & Fennell, 1965) was used as follows: a known volume of the diluted sample, from sampndle serial dilutions, was used to inoculate the used medium in plates. The plates contained Czapek's agar medium. The plates were incubated at 28ºC for 5-7 days during which the developing fungi colonies were counted and identified (Domsch et al., 1980). The microbial population in the original compost sample was then calculated using the following equation: Organisms /g compost= number of colonies/ (amount plated x 1/dilution). The same method was used for the isolation of bacteria, by using nutrient agar medium (NA) instead of Capek's. The inoculated plates were incubated at 37°C from 24 to 48h. The evaluation of microorganism total concentration in each sample was determined by plate counting of serial dilutions according to the equation: Colony forming units (CFU)/g = Number of colonies X 1/dilution.

Results and discussion

The structure of the wall paintings and the pigments used Support

Mineralogical compositions of brick were determined by X-ray diffraction (XRD) (fig.14) indicated that they were mainly consists of quartz (SiO_2), Orthoclase ($KAlSi_3O_8$), Silicone oxide (SiO_2), Calcite ($CaCO_3$) in addition to halite (sodium chloride), iron oxide (Hematite Fe_2O_3) and cly minerals. Their elemental composition analysis carried by SEM-EDS revealed it was consisted of high amounts of Quartz (37.82), Aluminum (Al) (17.30), Calcium (Ca) (13.43), iron (Fe) (9.7), magnesium (Mg) (7.27) and minor amounts of K (3.43) and Ti (1.11) (fig. 15). Considering the above results, it can be claimed that the brick consisting of high amounts of Quartz, Clay minerals, Calcite and iron oxide. These results confirmed the XRD results. SEM and Optical microscope observation of bricks shows that there are some cracks, gaps and voids, which led to the disintegration, separation, thus erosion and weakness of the brick internal structure. Also, dissolving of some brick components and crystallizing some types of salts were detected (fig.16, 17). Petrographic study of bricks shows that it consists mainly of clay minerals and quartz, in addition to a percentage of iron oxides.

Moreover, presences of some gaps as a result of high porosity were noticed, (fig.16)

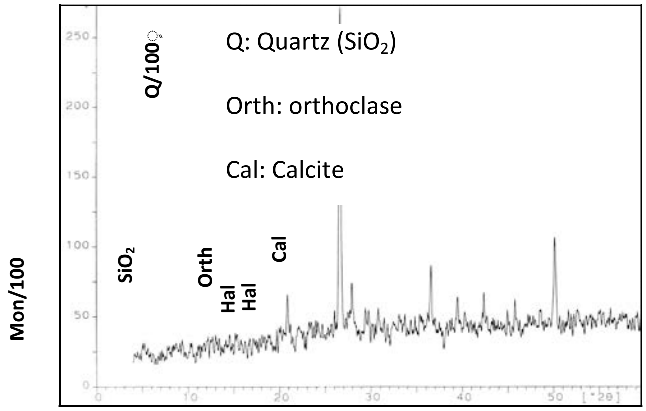

Figure14: XRD pattern of redbrick samples

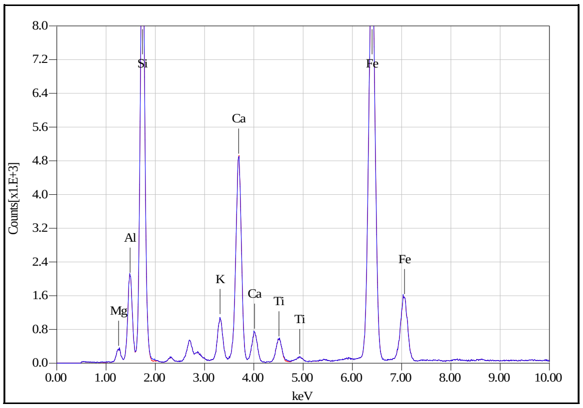

Figure15: EDX pattern of redbrick samples

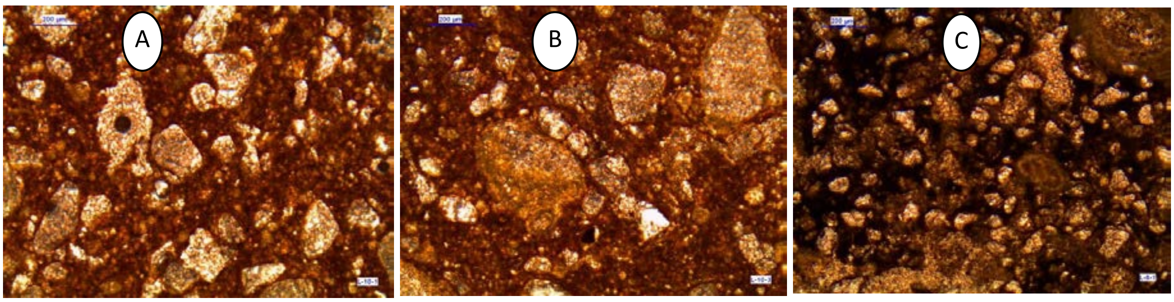

Figure16: optical microscope photograph of brick showing clay minerals, grain of quartz and iron oxide, also micro cracks, cavities and pits can be observed, 40-60x.

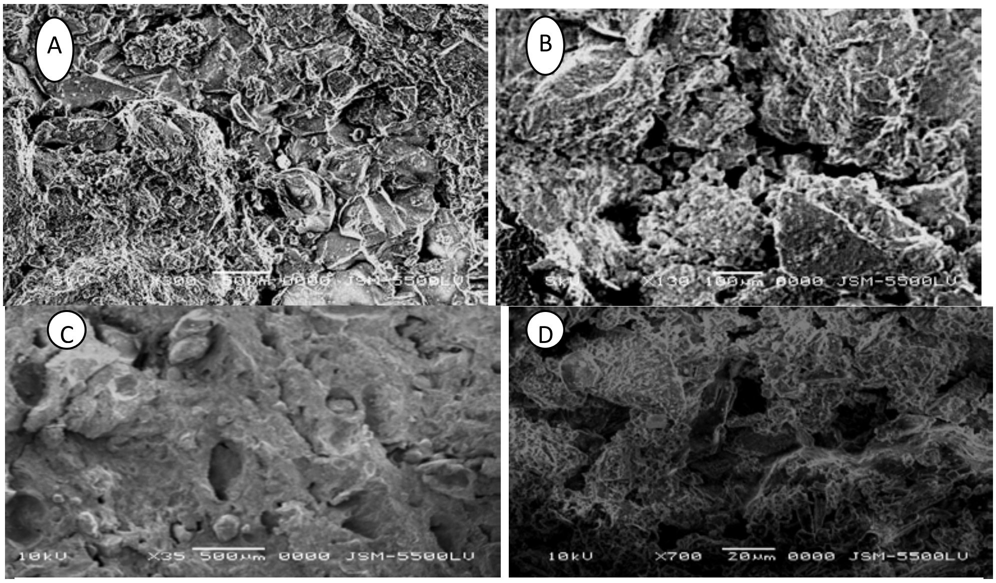

Figure 17: SEM photomicrographs showing the collapse of internal structure, voids, loose of binding material and salts crystallization between mineral grains**.**

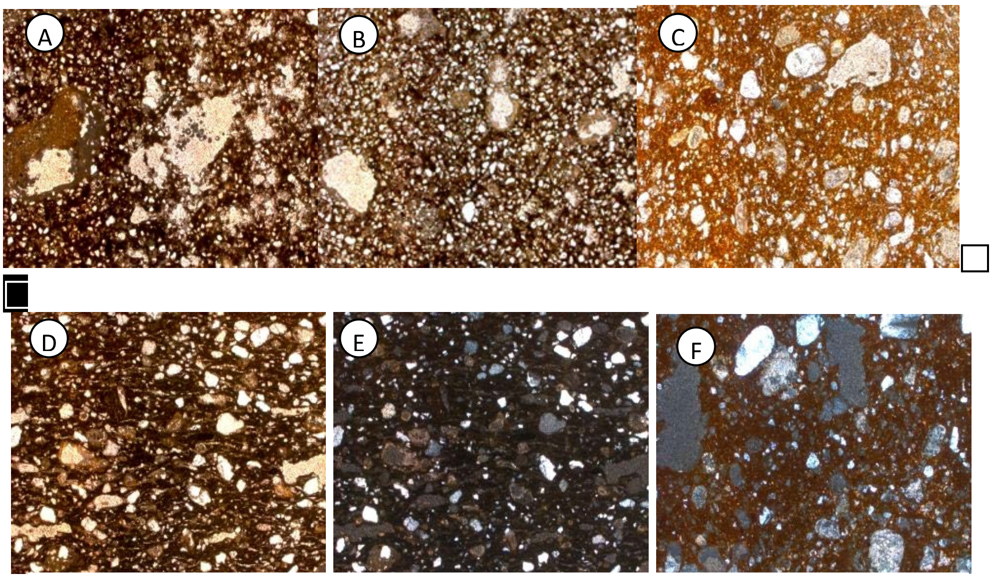

Figure 18: thin sections photomicrographs of bricks showing quartz grains, iron oxides, clay minerals and crystals of orthoclase 64 X.

Ground layers

Microscopical observation of cross section of paint plasters in St. George Church, (fig.19) shows the painted layer approximately 5m thin and was applied in two underlying layers of plaster with micritic texture. The inner (bottom) layer which was applied over the wall structure is rough (arriccio) and second layer (upper) over this layer is finely smooth (intonaco). Mineralogical composition of plaster layers were determined by X-ray diffraction (XRD). XRD patterns of the rough plaster (figure20a) indicated that it was mainly consists of calcite, quartz, zincite and halite. Calcite is originated from lime and quartz from aggregates, zinc oxide from zinc and halite from salts, while the fine plaster layer (fig.20b) was composed of calcite, bigger ratio of zinc and low ratio of quartz than the rough samples. It is elemental composition analysis carried by SEM-EDS revealed that it was consisted of high amounts of carbon (c), calcium (Ca), zinc (Zn), aluminum (Al) and magnesium (Mg) (fig.21).Considering the above results, it can be claimed that fine plaster layers were prepared by using lime containing magnesium hydroxide as binder, zinc and sand as a filler. Sodium is found as halite NaCl whose presence is due to materials used in the ground layer or salty water which leaked through the ceiling and the wall. The high percentage of Carbon and Oxygen are mainly originated by the use of vegetable oil.

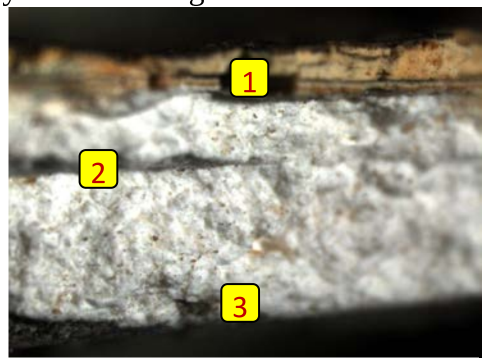

Figure19: LOM photograph of cross section stratigraphy of painted layer

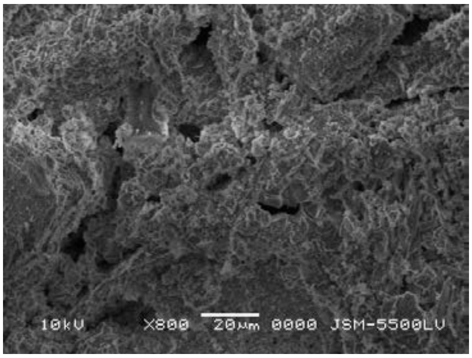

Figure20: SEM photograph of ground layer

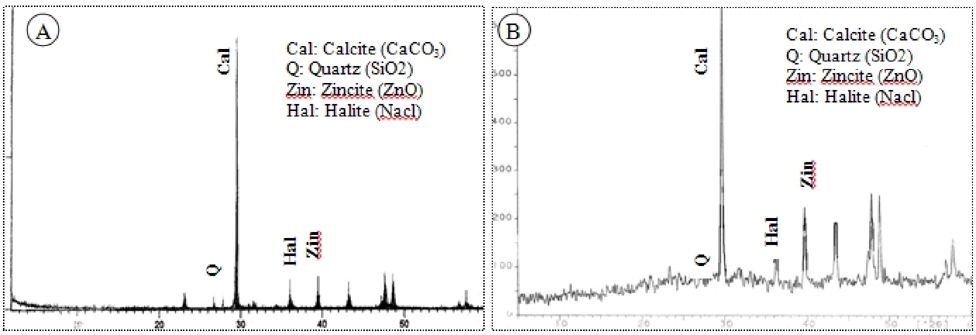

Figure20: XRD patterns of ground layer a: pattern of coarse ground layer b: pattern of fine preparation layer.

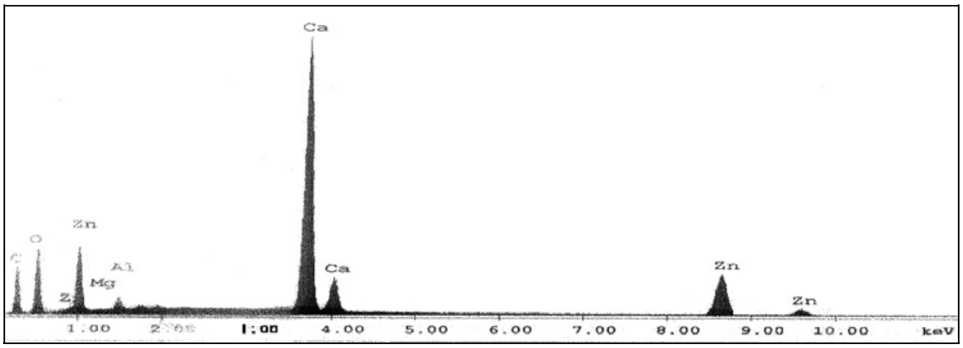

Figure21SEM-EDX spectrum of ground layer

Mineralogical and chemical compositions of paint layer Composition of the Binder and varnish layer

The chemical composition of the binding media of the paintings was determined by FT-IR analysis in this study. In the IR spectrum of the binding media, vibrations bands due to the hydroxyl (O-H) at 93436.53, 3639.98, 3446.17cm-1), fatty acids (CH_2) at (2860.88, 2863.77, 2868.59 cm-1), esters (C=O) (1797.33, 1798.3, 1798.3 cm^{-1}), carbonate (CO_3^{-2}) at (1428.03, 1420.32, 1420.32 cm^{1}) and sulphate (SO4 $^{-2}$) at (708.712, 708.712, 708.712 cm^{-1}) were detected. This result was compared with new sample of linseed oil (Michele 1999). According of this study, the medium used in the paint layer is linseed dry oil (fig. 5.17 and table2).

Chemical composition of the varnish layer

Analysis of the varnish layer by FT-IR spectroscopy showed that the varnish is Dammar (natural resin) that proved through comparing with new resin (fig.22d & table2). Dammar resin is a natural resin obtained from the *Dipterocarpaceae* family of trees in India and East Asia The soft, viscous, highly aromatic resin oozes readily from incisions in the bark and dries to become transparent, brittle, odorless lumps that are sorted into the following grades: pale (A), yellow (B), amber (C), and dust (Scalarone et al 2005).

Table 4: FTIR results of paint & gilded layers in St.George church.

Function group	**Characteristic IR Absorption Bands**					
	Dammar	Varnish	Linseed Oil	blue pigment	golden pigment	silver pigment
hydroxyl O-H	3600-3200 cm^2	3408.75	3600-3200 cm·'	3436.53	3639.98	3446.17
fatty acids CH_2	31 00-28OO cm^2	2923.56	3000-2800 cm·'	2860.88	2863.77	2868.59
C=O (ester) stretching	1 740-1 640 cm^2	1624.73	1 750-1730 cm·'	1797.33	1798.3	1798.3
C-H bending bands	1 650-1 600 cm^2		1 480-1300 cm·'	1428.03	1420.32	1420.32
carbonate	1 48O-1300 cm^2	1408.75	1 300-900 cm·'	1172.51	874.56	873.596
C-H torsion band	1 300-900 cm^2	1118.51	750-700 cm·'	708.712	708.712	708.712

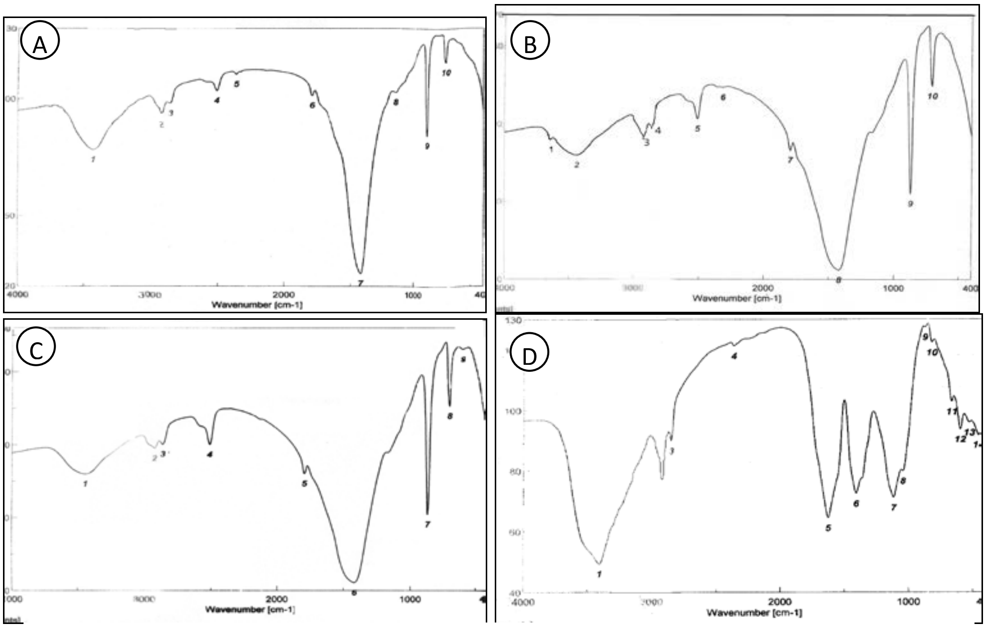

Figure22: FTIR spectra paint layer of St. George church dome A: blue pigment B: silver pigment C: gilded layer. D: Varnish layer.

Pigments identification

Optical microscope was used to inspect the different pigments (Fig.23) The LOM results shows the severe damage (disfiguring) of pigments, which are covered by a thick layer of dirties, LOM observation also revealed network of micro cracks.

Mineralogical, chemical and microstructural properties of the paint layers have been determined by SEM- EDS analysis. The mineralogical composition of the pigments was not determined by XRD due to their low concentration in the thin films over priming layers. Hence, SEM-EDS analysis was carried out to find the elements which were present in the painting layers. The pigments of mural paintings have been analyzed and the results are summarized in (table 3).

The **Dark blue** pigment sample has been collected from Christ clothes. In the EDX analyses of the dark blue pigment (Fig.24a) the presence of Na, Al, Si, S, C and Zn were detected, this leads to characterize the blue color as blue pigment consists of sodium aluminum sulfide silicate, ultramarine blue, $Na_8.(S_2)$ $(Al_6Si_6O_{24})$. The pigment ultramarine can be prepared from a natural semiprecious stone, lapis lazuli. The pigment is composed of silicon, aluminum, sodium, sulfur, and oxygen (Edwards et al 1997). Zn related to zincite and Ca related to calcite, so the presence of zincite and calcite are related to preparation layer. The presence of cl is related to Halite salt.

Light blue pigment sample has been collected from the ground around the Christ. It represents one of the few blue painted areas which have been mentioned by archaeologists. However, no chemical element imputable to blue pigments been detected with EDX analysis. On the contrary, it has been found the same composition of dark blue (Na, Al, Si, S, Ca, Ti, Fe and Zn). (fig.24b)

EDS analyses of the **Green pigment** (fig.24c) reveals the presence of Na, As, Al, Ca, Ba, Cr, Fe, Cu, Zn, Pb which leads to characterize the blue color was formed by mixing Veronese green $Cu_3(AsO_4)2·4H_2O$ with Viridian $Cr_2O_3·2H_2O$.

In the EDX analyses of the **yellow pigment** sample amounts of lead (Pb),Cr, Ba, Zn, Al, Si and calcium (Ca) were observed (Fig.24d). Yellow color may be produced by lead chromium oxide, crocoite, $PbCrO_4$.

The elemental composition analysis of the **Brown pigment** indicate that they are mainly composed of zinc (Zn), iron (Fe), K, Cl, S, Si,) and aluminum (Al) (fig.24e).The less amounts of iron may show the use of iron containing pigments such as iron oxide. The aluminum in the paint layer can be explained as impurity found in the iron compounds or from dirt layer which covered the surface. According to (Buxbaum 1998), variation of the zinc to iron ratio gives light to medium brown pigments.

The EDX analysis of **Beige pigment** which has been collected from Christ's neck reviles amount of Zn, Fe, Si Ti, S and Cl. According these results, the beige color may be produced by mixed of titanium zinc and iron, (fig.24f).

The EDX analysis of **Silver pigment** which has been collected from the ground around the Apostles on the barrel of dome reviles high percentage of aluminum (Al), sulphure (S), chloride (Cl), calcium (Ca), zinc (Zn) which leads to characterize the silver color formed by aluminum sulfate ($Al_2[SO_4]_3$). Aluminum sulfates are described in the chemical and pigment literature as white or silver color, the Color Index (1971) gives CI 77002/Pigment White 24 as 'aluminum hydroxide with varying amounts of basic aluminum sulfate (Eastaugh 2004).The presence of Ca related to preparation layer, the presence of Al related to the accumulation of airborne deposits and the presence of cl related to salts, (fig.24g).

The examination of the **gilded layer** in the dome of St. George church by EDX showed high percentage of Au (35.22) and Zn (9.53) and low percentage of Ca, Ag, K, Fe and Cl (fig.24h). Sample indicating that the gilded layer may be gold paper containing copper and Au as impurities. Most gold-leaf samples were alloyed with silver and gold, and just one contained only copper in addition to the gold (Payer et al 1994).

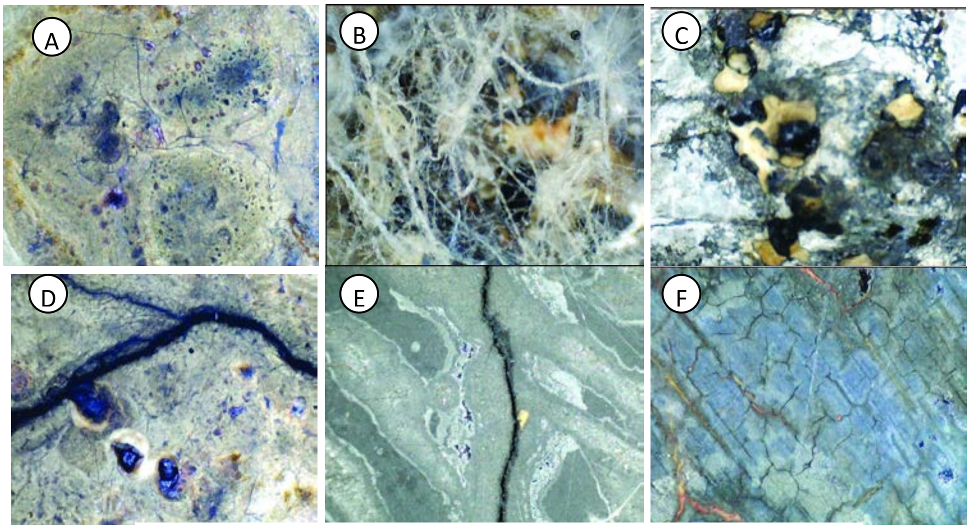

Figure23a: f Optical Microscope investigation of pigments samples

Table 3: Results of (EDX) analysis of pigments samples from St. George Church

Sample / Elements	ground layer	blue of ground layer	Angel blue	Blue robe of Christ	Angel Green	neck Brown	brown of ground layer	gilded parts	Silver pats
C	38.58	82.35	22.77	86.20	21.50	70.56	29.04	27.28	34.37
O	40.94	11.37	14.74	6.55	15.89	11.34	24.16	21.65	23.44
Mg	0.26	-------------	-------------	-------------	-------------	-------------	-------------	-------------	-------------
Al	1.42	0.15	1.95	1.02	1.01	0.56	2.67	-------------	23.21
Ca	13.30	0.39	1.43	0.10	1.83	0.79	5.24	3.33	4.64
Zn	5.50	4.49	4.49	3.48	3.92	11.84	21.64	9.53	11.56
Na	0,82	-------------	-------------	0.11	1.94	-------------	-------------	-------------	-------------
Si	-------------	0.19	1.76	1.38	-------------	1.15	3.35	-------------	
S	-------------	0.68	-------------	1.00	-------------	1.52	2.44	-------------	2.16
Cl	-------------	0.08	-------------	0.05	-------------	0.38	8.34	0.09	0.63
Sn	-------------	0.03	-------------	0.02	-------------	-------------	-------------	-------------	-------------
Ti	-------------	0.17	-------------	-------------	-------------	0.28	-------------	-------------	-------------
Fe	-------------	0.08	-------------	0.06	0.36	1.57	2.74	0.68	-------------
Co	-------------	0.03	0.18	0.02	-------------	-------------	-------------	-------------	-------------
Ba	-------------	-------------	9.62	-------------	3.19	-------------	-------------	-------------	-------------
Cr	-------------	-------------	0.13	-------------	7.10	-------------	-------------	-------------	-------------
Pb	-------------	-------------	42.92	-------------	37.83	-------------	-------------	-------------	-------------

As	-------------	-------------	-------------	-------------	3.58	-------------	-------------	-------------	-------------
Cu	-------------	-------------	-------------	-------------	1.84	-------------	-------------	------------	-------------
K	-------------	-------------	-------------	-------------	-------------	-------------	0.38	0.92	-------------
Ag	-------------	-------------	-------------	-------------	-------------	-------------	-------------	1.31	-------------
Au	-------------	-------------	-------------	-------------	-------------	-------------	-------------	35.22	-------------

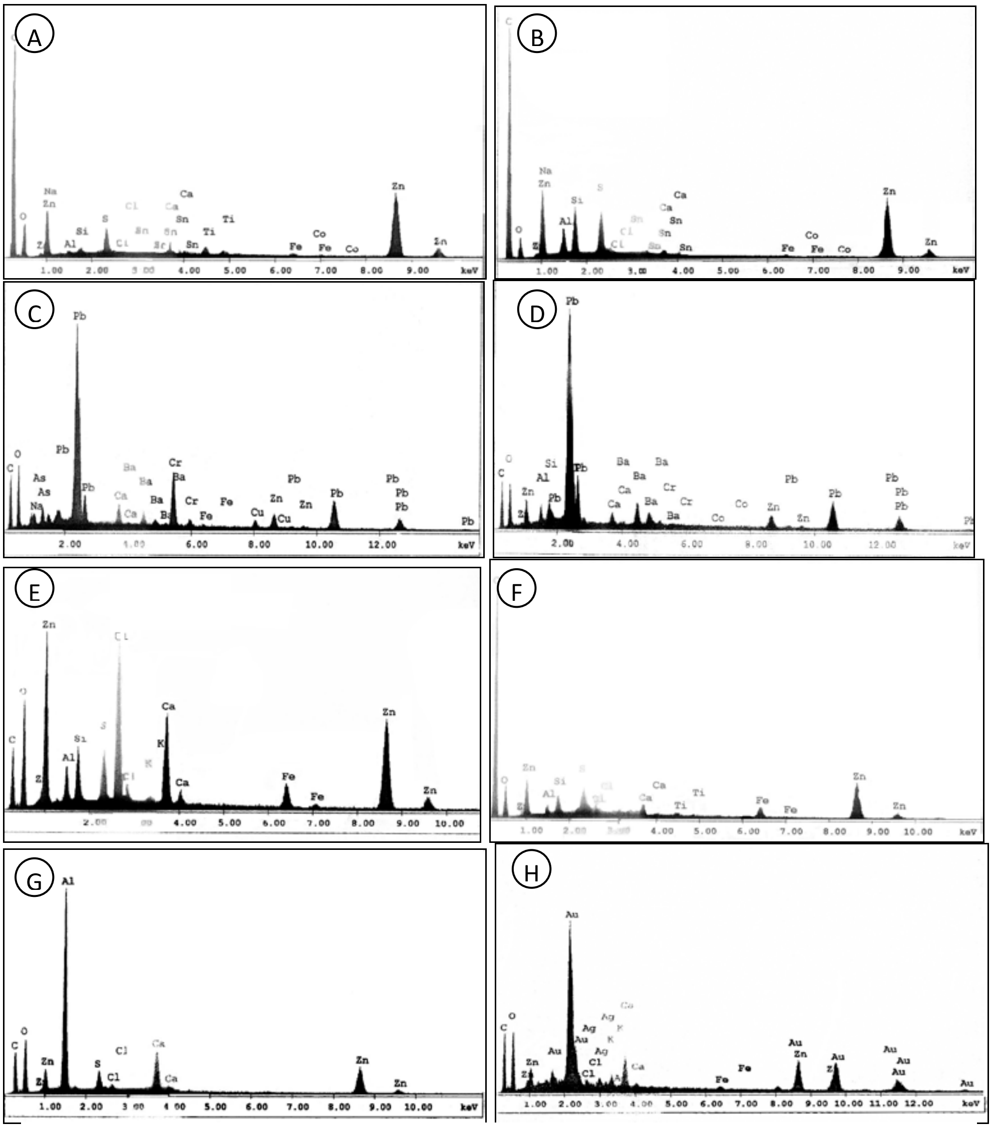

Figure 24: DEX pattern of mural painting structure at St. George Church A: dark blue B: light blue C: green pigment D: yellow pigment E: brown pigment, f: beige pigment, G : silver pigment H: Golden layer.

Biodeterioration study of the engraved limestone

During the present investigation numerous fungal floras were identified that caused deterioration of the mural painting in the dome of the St. Gorge church. The results of the qualitative microbiological analysis of air samples for fungi are shown in (table 4). The fungal species *Aspergillus flavus, Aspergillus humus, Aspergillus niger, Aspergillus terreus, Alternaria alternate, Penicillium notatum.* A summary from around the world of the fungi found on mural painting to reveals many species in common. Biodeterioration problems in historic buildings and churches are well recognized and during the past few decades the role of the microbes in biodeterioration processes has been acknowledged (Saarela et al 2004). Growth of microorganisms on mural painting can result in visible aesthetic and structural damage. Some examples of visual damage on mural paintings at the dome are given in (fig.10a, b). On such substrates aesthetic damage implies pigment discoloration, stains and formation of a biofilm. Structural damage is observed as cracking and disintegration of the paint layer, formation of paint blisters, and degradation of varnish and binders resulting in detachment of paint layer from the support.

Table 4: **Various types of microbiological growths found over wall painting at of St. George church.**

Sample	Microorganisms	Total Fungal Count (CFU/Sample)
FA.ON	*Aspergillus flavus* Syn A.humus	6
FA.BD	*Pencillium notatum*	2
FA.G	*Aspergillus niger* Syn. A. fuscus	2
FA.BG	*Aspergillus terreus* Syn. A. venetus	3
FC.10	*Alternaria alternate*	4

Treatment and Restoration

The conservation project described in the previous article had started in 2011 and is still ongoing. The project started with the research of the building condition and the conservation state of the walls and paintings. The causes of damage were identified and documentation drawings were made to map the different areas (fig. 25).

Ultraviolet fluorescence was used to elucidate the state of conservation of the painted surfaces, and to characterize the presence of fixatives, either at the level of the paint layer or on the surface. UV diagnosis showed, as it was expected, that the pigments were the usual ones and no old treatment intervention were carried out (fig. 26).

Firstly preventive treatments for addressing the causes of damage or decay of the murals and the architectural systems they embellish were preferred. A number of measures were taken to modify the building in order to prevent water infiltration, including repair the roofs of the dome and the repairing of some windows in the barrel of dome.

During visual documentation highly paint layer areas have been detected. When the condition survey was complete and while the scientific studies were still underway, it was decided to undertake emergency treatment on the most endangered areas of the wall paintings in order to prevent the loss of original material. The goal was to stabilize the paintings using a fully reversible minimal intervention such that the paintings would be secure. This treatment consisted principally of securing loose fragments and cracks with small strips of Japanese paper. These were adhered to the wall at both ends with Paraloid B72 (15% solution in trichloroethane). This treatment imparted sufficient strength and cohesiveness to permit cleaning.

The immediate step was the biological treatment of the surface. A solution of Cedial (3%) was applied by brushing or spraying through Japanese paper. The areas affected by biological attack were monitored during the entire intervention.

When the treatment was complete, the treatment plan was carried out. On the basis of the damage assessment the following conservation steps for the mural painting are considered necessary: removing of old varnish layer, cleaning, consolidation of powdering paint and disaggregated plaster, injection of preparation layer, salt reduction, and application of repair mortar and surface protection by new varnish layer.

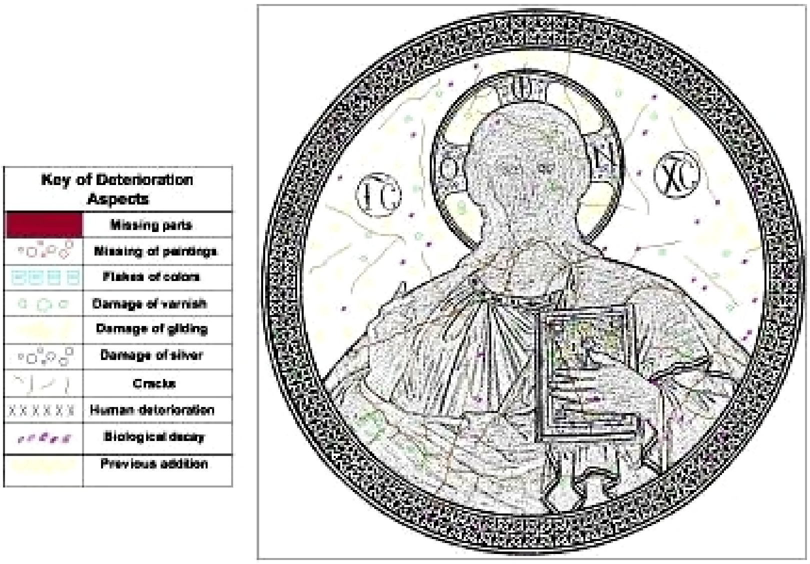

Figure 25: damage mapping documentation was prepared as a base for conservation interventions

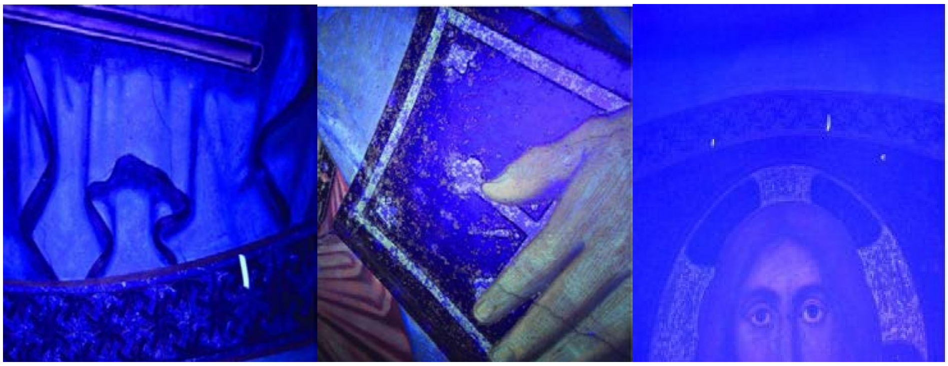

Figure 26: The analyses and UV diagnosis showed, as it was expected, that the pigments were the usual ones

Cleaning and removing of old varnish

According to above analysis, the mural paintings of St. George were carried out by oil painting technique, its surfaces was coated with varnish layer of dammar resin, the varnish layer was the original one and it was unique and no other coatings or additional layers were observed on the painted surface. The varnish layer was in an extremely terrible condition and thick with several physical damages such as severe scratches and detachments at discrete sites of the surface. In addition, it had an intense yellowish hue indicative of its oxidative and polymerized state. Apart from the damaged structure layers, the varnish was also affected. In addition, the existence of soot on the varnish layer proclaimed that it was slightly burnt, possibly from candles. The application of varnish layers has been shown to play a significant role in protecting painted surfaces (Stolow 1985). During aging, the varnish degrades through oxidation, auto-oxidation and crosslinking processes, catalyzed by the absorption of light (De La Rie1988). Owing to preservation reasons, the artwork must be relieved from the degraded varnish that can affect the inner layers (Theodorakopoulos & Zafiropulos 2003). Mechanical and chemical cleaning was used to remove the old degraded varnish. Scalpels were used for removing the thick parts of varnish layer as shown in (fig.28a). The solubility tests of the varnish layers were performed on the basis of finding the least concentration of solvent in an inert medium, which would marginally dissolve the residual varnish. For the particular mixture of the solvent system, a series of solutions of varying concentrations were prepared. Mixture of Isopropyl alcohol, Spirits of Turpentine and acetone (1:1:1) proved to be the most useful solvent for the old varnish layer which the mechanical cleaning failed to remove (fig. 28b).The chemical cleaning showed, that the varnish removal from all zones (fig.28c,29).

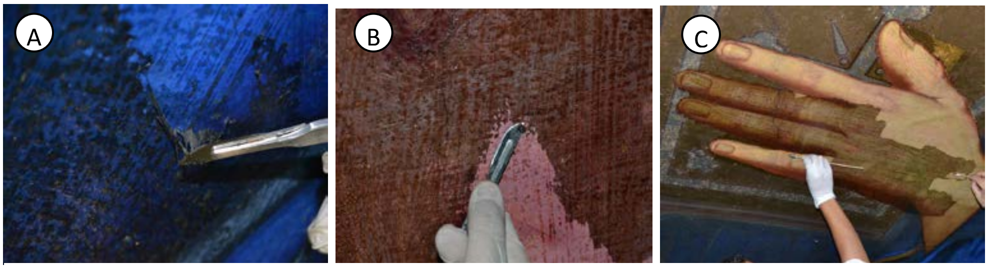

Figure 27: Different aspects during the removing of the varnish layer from mural painting at St. George dome.

Figure 28: mural painting before, during after removing varnish layer.

The cleaning revealed the colorful original paintings and focused substantially on the removal of extraneous substances which were impossible to distinguish for so many years due to the dirty covering layers, soot and stains. A wide range of techniques is available for cleaning mural painting, ranging from mechanical cleaning to chemical cleaning. Considering the paint layer's sensitivity to water, we used mainly dry **mechanical methods** using cotton swabs, different types of brushes, scalpels and wishab sponges until the expected result was obtained(fig.29). We tried to improve the results of the dry mechanical method using in parallel chemical cleaning. **The chemical cleaning** was completed where necessary. Several solvent mixtures were tried but the best results were obtained with mixture of ethyl alcohol, acetone, toluene and trichloroethylene used for removal of dirt. Some initial tests were carried out prior to the intervention for setting up the right methodology specific for each color and gold layer (fig.29). It was applied two or more times, for very short periods, usually from two to four minutes. With this method, however, it was difficult to actually lift the dirt off the surface. A poulticing system was then tested. This consisted of small cotton-wool compresses, wetted with the same solvent mixture, placed on an intervention layer of Japanese tissue, and left in contact with the paint surface for ten seconds. Poulticing was repeated two to three times, if necessary (Fig.29). This proved to be highly effective in removing the dirt and the coating without affecting the sensitive paint layer (fig.30, 31).

Figure 29: some initial tests were carried out to assess potential treatment options**.**

Figure 30: Different aspects during the cleaning of the mural painting at St. George dome.

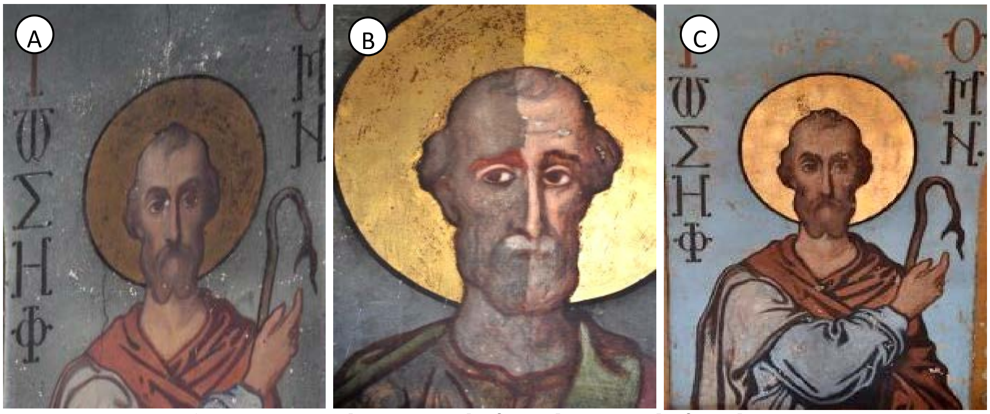

Figure 31: prophet No. 14 before, during and after cleaning.

Fixation and Consolidation of the paint layer

The fixation of the paint layer was imperative due to the high degradation level which would definitively have led to large losses. For the powdering areas the Paraloid B.72 was sprayed on the surface (fig. 32a, b). Depending on the absorption level of the paint layer some alcohol was sprayed before for a better penetration. After the fixative was totally absorbed by the paint layer the surface, the surface was pressed back into its original position using a protective sheet of silicon paper and cotton sheets (fig.32c). Observing the behaviors of the surface after the treatment, sometimes the operation was repeated. Very good results were obtained with this method. In cases where fragments were almost completely detached from the support, a drop of Primal AC33 was placed at the center on the fragment and then the surface was laid down on the support by means of a spatula.

The choice of a material for consolidation was conditioned by several factors. As with any consolidant, it was important that it had good penetration, and would not reduce the porosity, alter the color, or compromise future treatment. In addition, it was essential that the consolidant would not in any way adhere the salts to the substrate or impede the passage of the liquid water necessary for their extraction (Hammer 1987).To determine the most suitable consolidation method, a number of synthetic consolidants were evaluated by applying them to small, detached pieces of the paint layer. Therefore it was decided to the consolidation of the friable areas of the paint layer with a solution of Ethyl silicate + Acryloid B.72. The operation was performed by repeated brushing or spraying the solution at time intervals until the expected results were achieved. The consolidant was applied several times a day, on each of four days, at two-week intervals. The process was applied by spray method; firstly, ethyl silicate was applied several times until the paint surface was consolidated, after that Paraloid B.72 was applied at the surface. Very good results were obtained with this method (fig.30).

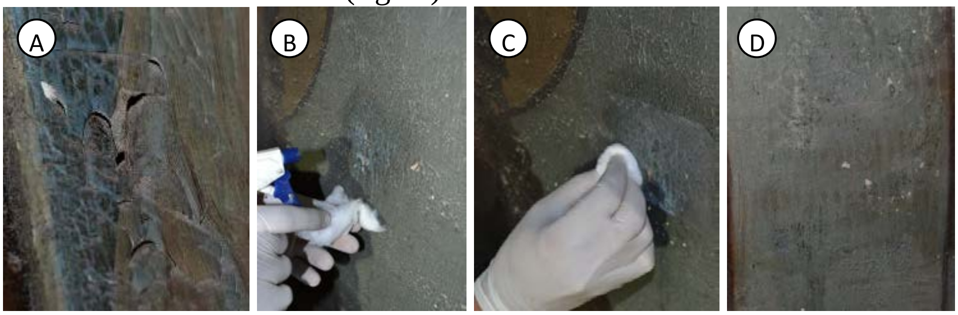

Figure 32: Fixation of the paint a: after b: fixative with B.72 c: the surface was pressed back into its original position using a protective sheet of silicon paper and cotton sheets d: the surface after fixation.

Injection

The mural painting at the St. George dome suffered from cracks of varying depth and width accompanied with loss of the parts of ground layer and some areas where the paint layer was detached together with parts from the preparation. The consolidation of the detached areas of the ground layer by injection was performed; using the Plexisol (Degalan) P 550. Plexisol P 550 is a 40% solution of an acrylic resin based on Butyl Methacrylate in benzene 100°/140°C. It is used as a consolidant of ground and paint layer. It was appropriate to use due to both its better adhesive power and its capacity of creating a thin layer which could provide a better ground for pasting of thick layers. The very fine cracks that could represent outlets for the injected consolidant were temporarily secured by the application of white cotton and the detachment area was pressed with a spatula (fig33).

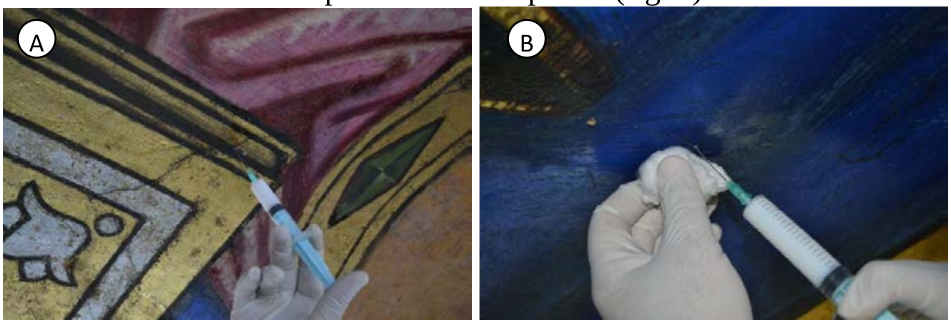

Figure33: injection process of cracks using Plexisol P 550

Filling Gaps

We proceed to the filling of the cracks and deep gaps of the ground layer. The fillings done using a lime mortar consisting of 2coarse sand + 1 lime + ½ zinc dissolved in primal AC33 1:8 with water. A coarse mortar was applied in in several layers so that it would evenly remain below the level of the paint layer. This surface difference allowed the ulterior application of a finer mortar layer. The fill material was applied by a spatula to flatten the putty and smooth and then the surface was smoothed by using different sizes of soft sandpaper to remove all products from the surface and prepared for the work necessary frills color (fig.34).

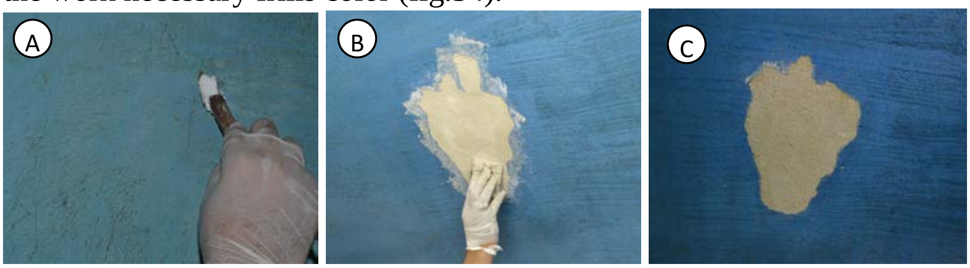

Figure34: filling gaps process a: filling lime mortar by spatula b: smoothed surface by sandpaper d: after filling

Retouching and Varnishing

Most unsightly gaps were retouched by means of oil pigments applied in a stippling technique (fig 35). Oil colors were used for the whole retouching treatment due to their same type of original color and their resistance in time. Also linseed dry oil was used as binding medium. As a result, the white spots of the paint gaps were optically pushed backwards leaving the original readable (fig.35). Gold paper was used to repair the gilded areas (fg.45).

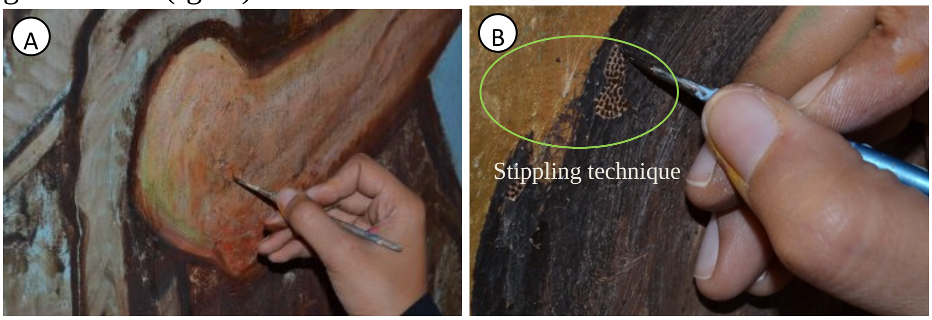

Figure35: Retouching treatment with stippling technique.

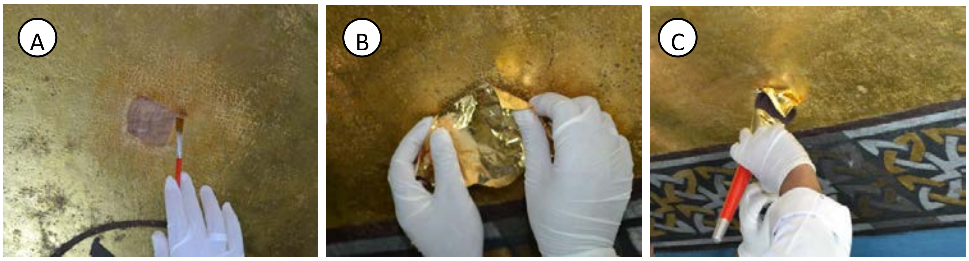

Figure36: Gold paper was used to repair gilded areas

There was final application to protect or saturate the painting. 3% solution of spray Paraloid B72 was applied onto the painted surfaces. These served as an isolating barrier to separate in painting and later protective varnishes from the original surfaces (fig.37). In addition, it consolidated areas that suffered from fine cracks and detachment parts. B72 was chosen for its well-known properties of reversibility and stability and thus allowing for its future removal. In addition to protecting from dust and dirt and this coating optically saturated the paint colors of both the original paint and the inpaint.

Figure36: final application of Paraloid B.72as new varnish**.**

Figure38: mural painting after restoration.

Conclusion

- This study was carried out in order to form a database of the application technique, material properties and deterioration problems of the wall paintings of the St. George Church and introduce the conservation process to this mural painting at the dome of the church.
- Wall paintings in the St. George Church were executed by oil painting technique over lime plasters by using vegetable oil.
- Plasters of the dome Church are lime plasters. It is composed of a two layered, rough plasters which are composed of lime, sand, zinc and organic materials between2 :1: ½. Fine plaster layers do not contain sand. Rough plaster layers have a denser structure than fine plaster layers.
- The binding medium is composed of linseed oil, linseed oil mixed with several pigments.
- The pigments identified by chemical analyses are; ultramarine as dark blue, mixing of Veronese green $Cu_3(AsO_4)$ $2.4H_2O$ with Viridian Cr_2O_3.2H2O as green pigment, lead chromium as yellow, iron oxide as brown pigment, titanium zinc and iron as beige color, aluminum sulfate $(Al_2[SO_4]_3)$ as silver color and gold paper containing copper and Au was used as gilded layer.
- The murals painting in the church were in a bad condition. The serious damages occurred mainly at the paint layer.
- The main problem in the wall paintings is the loss of paint layers due to the loss of adhesion between the binding layer and the lime plaster and there is a clear detachment between the fine layer and the coarse layer. Deteriorations observed on the wall paintings are formed by the dampness in the building. Also Dirt, impurities stains, insect broods and numerous cobweb nests on the painting surface were registered as conservation problems.

- The treatment plan was carried out. On the basis of the damage assessment the following conservation steps for the mural painting were carried out: removing of old varnish layer, cleaning, consolidation of powdering paint and disaggregated plaster, injection of preparation layer and application of repair surface protection by new varnish layer.

Recommendation

After restoration, illumination, environmental control and control of the dampness sources are very important for the sustainability of the conservation. Continuous monitoring of wall paintings and environment and permanence of conservation must be provided. Reaction of wall paintings to present conditions after restoration must be observed continuously. Following preliminary studies, plans must be advanced for the installation of equipment to control and correct the potentially damaging temporary fluctuations caused by the large number of visitors .

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