INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 7, Issue 4, October-December 2016: 1031-1046 www.ijcs.uaic.ro

SUBMERGED VILLAGES. RECOVERING WALL PAINTINGS FROM THE CHURCH OF ATANCE (GUADALAJARA, SPAIN). TECHNICAL STUDY, EXHIBITION, AND 3D DISPLAY

Marta PLAZA BELTRAN *

Complutense University of Madrid. Faculty of Fine Arts. c/ Pintor El Greco 2. 28040 Madrid, Spain

Abstract

The construction of a dam often means losing the heritage of the villages that are caught beneath the rising waters. In the case discussed here, the inhabitants of the village of Atance (Guadalajara, Spain) saved their church and its contents by relocating it to the city of Guadalajara (Spain). The removal of an altarpiece in the church revealed a hidden niche covered in frescos. The niche had been walled up to erect the altarpiece. When the frescos were detached, they were found to have been laid on top of another painting, estimated to be as old as the church itself. We designed a novel system for displaying both sides of the detached frescos (with the impression left by the earlier work), preserving the shape and dimensions of the niche. This structure shows both the original and later paintings, together with the impression left by the original fresco on the back of the later depiction. Using virtual 3D imaging, the structure can now be viewed from all angles.

Keywords: *Mural; Polychromy; Conservation; Exhibition; 3D photogrammetry*

Introduction

The village of Atance (Guadalajara, Spain) was lost beneath the waters of the river Salado following the construction of the Salado dam. The church of Nuestra Señora de la Asunción, located in the centre of the village, dates from the 16th century and contains many historical objects of great artistic value.

The organization in charge of constructing the dam, the Confederación Hidrográfica del Tajo, relocated the entire building and its contents to the Aguas Vivas district of the city of Guadalajara, where it is now known as the church of San Diego de Alcalá. During this process, a partially walled-up niche was uncovered behind one of the lateral altarpieces, revealing part of a mural. When the wall was removed, the interior of the niche, including the jambs and arch, was seen to be covered in paintings. After the outer paint surface was removed (back panel, jambs and arch), another earlier fresco was found underneath (Fig. 1). This was also detached using special removal techniques (Fig. 2). The niche is currently on display in the central patio of the Diocesan Museum of Ancient Art in Sigüenza (Guadalajara, Spain), and is one of the museum's central exhibits for many years (I+D project).

Both murals share a similar theme: the final judgment, with the Archangel Michael thrusting his spear into the dragon, the image of Jesus surrounded by angels, the depiction of various souls suffering in purgatory and the images of the saints San Roque and San Anton in the later paintings (Fig. 3a), and San Sebastian in the older work (Fig. 3b and 3c). The main

* Corresponding author: mplazabe@art.ucm.es

difference between the two murals lies in the decoration of the jambs and the arch. In the older paintings, these show the Instruments of the Passion, or *Arma Christi*. In the later work, however, they are covered with a series of brightly coloured decorative motifs with floral scrolls [1].

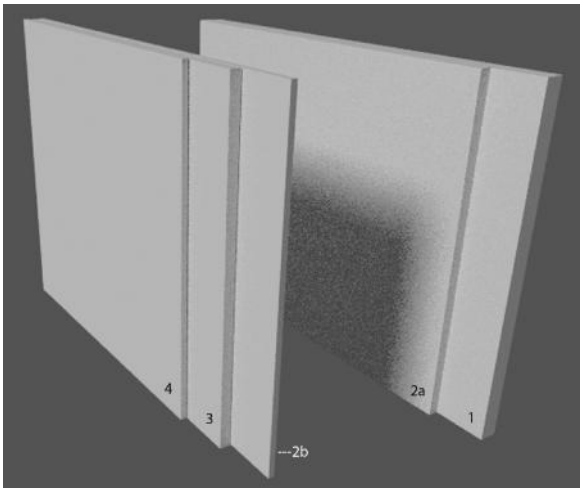

Fig. 1. Laminate wall paintings: 1 - Original mortar; 2a - Original wall paintings;
2b - Imprint of the original paintings on the back of the later paintings; 3 - Post mortar; 4 - Later murals

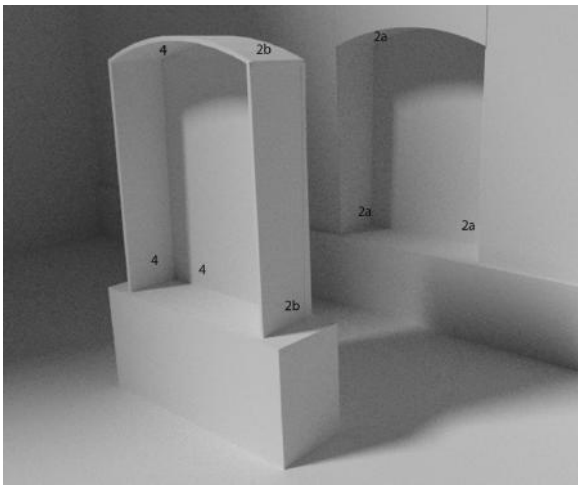

Fig. 2. 3D reconstruction. Murals situation in the original niche and back structure: 2a - Original wall paintings; 2b - Imprint of the original paintings on the back of the later paintings after starting; 4 - Later murals.

This study will focus on the analysis of the plaster and pigments used in these paintings, the restoration of the murals, and the structure devised for displaying the frescos. For this purpose, a rigid, detachable framework was built to exhibit the niche from all angles, showing the front and back of the panels, with the impression left by the original fresco. Using 3D photogrammetry, we also created a virtual model of the niche and frescos to disseminate the find and give a clearer understanding of the paintings [2].

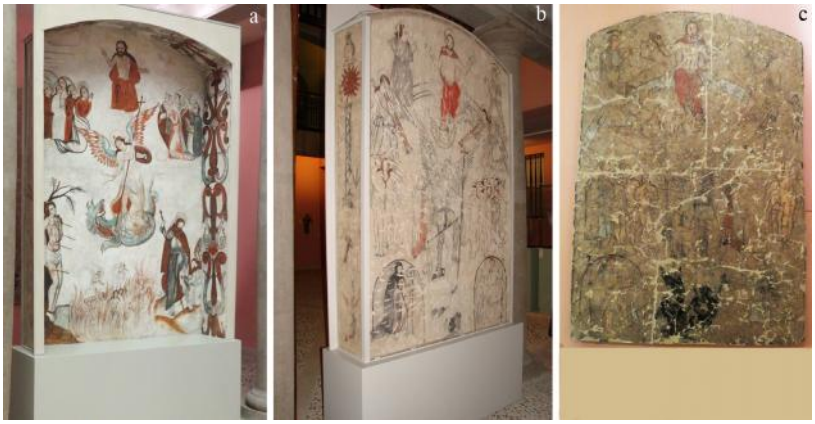

Fig. 3. The image of Jesus surrounded by angels with Archangel Michael, San Roque, San Anton, and San Sebastian: a - Front of the niche with the later murals; b - Reverse niche with the imprint of the original paintings, older painting; c - Original paintings, older painting.

Materials and methods

Removing the frescos

Murals are, by definition, an integral part of the underlying structure. On the understanding, therefore, that the removal of a mural can jeopardize its integrity, preservation *in situ* must always take precedence over any other course of action. The case of the frescos discussed here, however, was exceptional, as urgent action was needed to save these murals. We chose the *stacco* technique to remove the murals, which allowed us to detach the paint surface together with the underlying plaster, thus preserving all the characteristics of the fresco [3]. The jambs and arch were removed *in bloc* (Fig. 4a), while the back panel, which measured 230 × 165cm, had to be divided into two interlocking sections (Fig. 4b). This system was chosen to facilitate the subsequent reassembly of the two pieces. Detaching the paintings from the arch was the greatest challenge, as this required building a frame of exactly the same size and shape as the original structure in order to preserve the original curve of the mural.

As mentioned, removal of the first paint surface revealed another, a much older painting underneath. The image of this painting was imprinted on the back of the overlying fresco (this is because in fresco painting, the pigments bind with the lime plaster, making it extremely difficult to separate one layer from the other) [4]. Once the first paint surface was removed, the second layer (the earlier work) was detached from the underlying surface using the same *stacco* method.

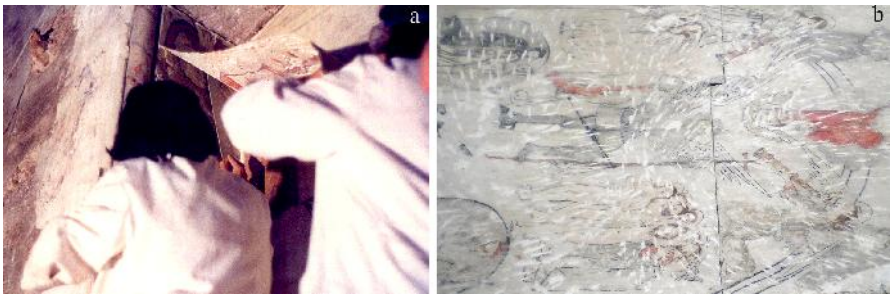

Fig. 4. Extracting mural: a - Starting the first layer of wall paintings with stacco method; b - Detail of the back panel with two sections

Study of the materials and painting technique

Several micro-samples were taken from both the plaster and pigments in order to ascertain their age and to study the method and materials used in painting the frescos. The aim of this study was to identify the composition of the plaster and the binding material used on the paint surface, the layers of paint, and the chemicals contained in the pigments used. The following analytical methods were used in the examination of the study materials:

- *Optical microscopy (OM):* This technique was used for the preliminary analysis of the samples, observing the different colours, textures and morphology of the strata comprising the paint surface. In optical microscopy, samples are encased in colourless, transparent resin mounts that are sliced and polished for study under polarized light. This technique is used for stratigraphic analysis of the specimens. It shows the painting technique and the kind of pigments used. OM of samples containing geomaterials, meanwhile, shows the morphology and texture of the component parts [5]. It can be used to quantify the composition of the plaster (sand: binder ratio), and classify the type and mineral composition of the geomaterials contained in the sample on the basis of their optical properties [6, 7].

- *Scanning Electron Microscopy (SEM).* This technique uses electromagnetic instead of light waves to examine samples in 3 dimensions; in other words, it reveals a detailed image of the topography of the specimen. This allowed us to examine the morphology and texture of each sample in high definition. SEM is also used to make elemental maps of micron-sized areas.

When combined with energy dispersive X-ray spectrometry (SEM-EDX), SEM can identify the chemical composition of regions as small as a few cubic micrometers. SEM-EDX extends the magnifying power of SEM, but the images are only displayed in grayscale. In this case, the device was used in back-scattered electron (BSE) mode. With the SEM, we were able to identify the pigments contained in each paint layer, while EDX enabled us to quantify the chemical composition of the pigments in each sample [7].

- *Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).* ATR-FTIR uses molecular spectrometry to show the qualitative and quantitative composition of a given material [8].

Original murals

Plaster

We used ATR-FTIR to analyze the composition of the plaster. The findings were complemented with the corresponding EDX elemental map.

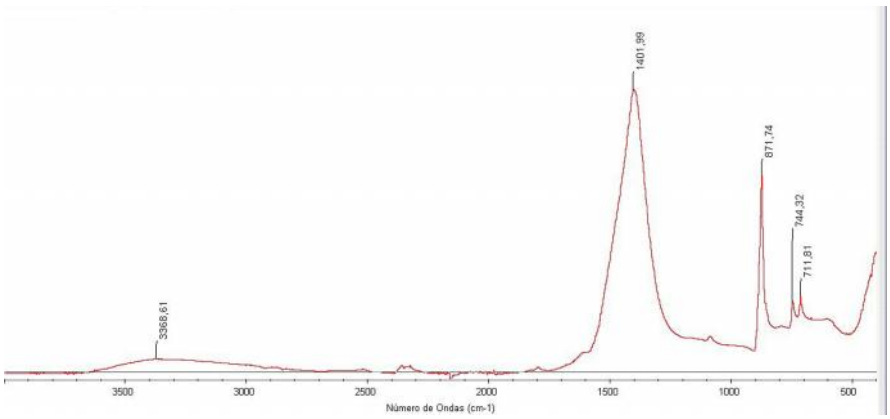

Fig. 5. Composition of the plaster. Spectrum FTIR - ATR sample mortar.

The ATR-FTIR spectrum showed the characteristic spectral bands of calcium carbonate ($CaCO_3$): stretching vibration band of the CO_3^{2-} group (ca. 1411cm^{-1}) (wide, intense band) and the bending band of the group (O–C–O) (ca. 872cm^{-1}) (narrow and intense). Another characteristic band shown is cca. 712cm^{-1} (weak and narrow). The band at 744cm^{-1} has been assigned to dolomite ($MgCO_3$). EDX analysis of the plaster identified mainly calcium (Ca) and magnesium (Mg), with a smaller amount of silica (Si) (Fig. 5). The presence of these materials clearly shows that the paint was applied using the fresco or mezzo fresco technique, confirmed by OM.

Paint layer

EDX analysis of samples obtained from the paint layer identified the presence of calcium (Ca) and magnesium (Mg), together with calcium carbonate to bind the pigments [$CaCO_3 + MgCa(CO_3)_2$].

Stratigraphic analysis showed poorly defined layers, also indicating the use of fresco techniques, where the pigment is applied to the wet plaster and the carbonation process takes place for both at the same time. The colours used in the paintings are: red, brown, black and flesh-pink. These are described below, together with an analysis of the pigments contained in each layer of colour.

Red: vermilion/cinnabar

Red was used on the cloaks of some of the figures depicted on the back panel of the niche and in the *Arma Christi* represented on the jambs and the inside of the arch.

Under OM (500X), the sample of red pigment showed small particles of pigment mixed in with plaster (typical of fresco painting). The depth of the layer was 30µm. Under SEM, we observed a moderately high density pigment which, under EDX particle analysis proved to contain elements such as sulphur and mercury. This confirmed the pigment to be vermilion/cinnabar (HgS, mercury sulphate), mixed with dolomitic calcite [$MgCa(CO_3)_2$] as the binding agent (Fig. 6).

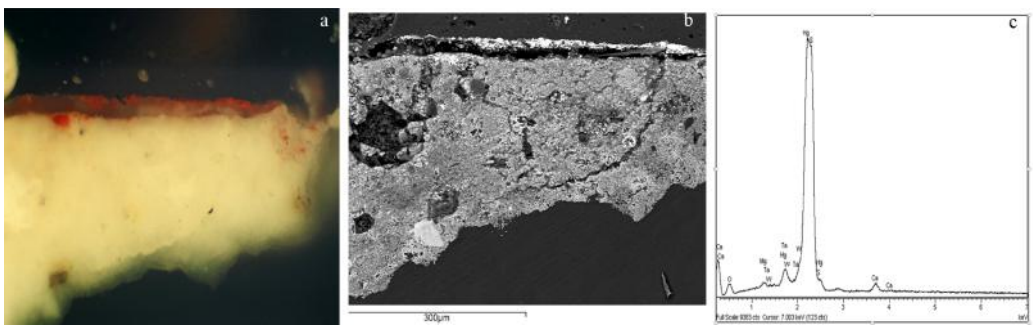

Fig. 6. Red pigment: a - vermilion/cinnabar. Observation by OM (epi - illumination) (500X). Detail picture layer and mortar; b - Observation by SEM (BSE).Detail mortar and painted layer; c - EDX microanalysis on film of paint/analysis of particle: vermilion/cinnabar mixed with calcite and sand.

In its natural form, this pigment is called cinnabar, a bright red pigment obtained by crushing the mineral of the same name (found in the Almadén mines in Spain and at various sites in Monte Amiata in Tuscany, Italy). The synthetic form of the pigment is vermilion, which is obtained by heating mercury with sulphur. Both cinnabar and vermilion have the same chemical formula, and it was thus impossible to distinguish them on EDX analysis. Their only differentiating characteristic is their particle size: the natural pigment has larger, more irregular particles, while in the artificial pigment they are smaller and more homogeneous. The pigment

has considerable hiding power, and despite being a sulphate it is quite stable and compatible when mixed with other pigments.

Nevertheless, it turns black on exposure to light and air, a phenomenon that prompted some scholars to suggest mixing it with red earth to prevent discolouration. Despite this, and the high cost of the pigment, it has been used in wall painting since antiquity (when it was known as minium) to give colour to flesh and articles of clothing, and is found in paintings dating from Roman times. Because of its toxicity, it has now been replaced by cadmium red, although it is still occasionally used as a pigment [9-12].

Flesh: vermilion/cinnabar, red earth, calcite carbonate

The pigment used to colour the flesh of all figures represented has the same technical characteristics: a very pale, flat colour, suggesting that very little pigment has been mixed with the lime [13]. Under OM, the paint layer was observed to be very thin (12µm), with the pink colouration being achieved by combining two different types of red pigment with the lime binding agent, both of which are present as isolated particles, in very small quantities. Under SEM analysis, these isolated red particles presented high electron density. The EDX elemental map (sulphur, mercury, iron, aluminium and silica) revealed these pigments to be vermilion/cinnabar (HgS) and an iron-rich red earth (aluminosilicates with iron oxide, Fe_2O_3). The characteristics of vermilion/cinnabar have been described in the foregoing paragraphs. (Fig. 7)

Red earth is a natural mineral pigment formed by the natural decomposition of feldspar and iron. These pigments contain aluminium silicates (clay and kaolin), silica (quartz), silicic acid, calcium sales, etc., and are obtained by simply washing, grinding and heating the mineral (limonite hematite, etc.) which will take on a different colour depending on the heat used [9]. They have good hiding power and are very stable.

These pigments were also mixed with calcium and magnesium to bind them to the fresco. Iron oxides, with their wide range of colours (from yellow to dark brown), have been used since prehistoric times (in cave paintings), and are widely used in frescoes due to their physical and chemical stability [14].

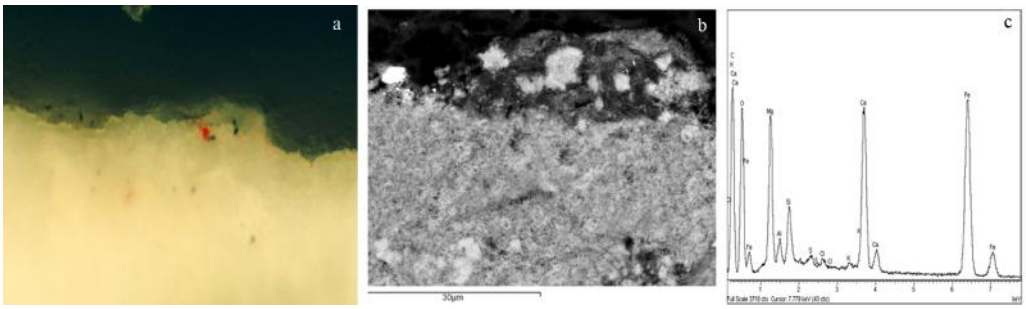

Fig. 7. Flesh: vermilion/cinnabar, red earth, calcite carbonate. a - Observation by OM (epi-illumination) (500X). Details of picture layer and mortar; b - Observation by MEB (BSE). Details of picture layer and mortar; c - EDX microanalysis on film of paint/analysis of particle: vermilion/cinnabar and red earth, mixed with calcite and sand.

Black and grey: carbon black, calcium carbonate

Black was used to outline all the figures in the mural (back panel of the niche, jambs and arch), and grey was used in some of the garments.

As can be seen on the OM and SEM images, the outline penetrates the plaster layer to a depth of 53µm. The colour was obtained from carbon black (C), a pigment with a very low electron density on SEM. EDX analysis (carbon, calcium, magnesium) confirmed that the black pigment is indeed carbon black, surrounded by calcite ($CaCO_3$) mixed with dolomitic calcite [$MgCa(CO_3)_2$] (Fig. 8).

Carbon black (C) is a natural amorphous carbon pigment produced by burning certain woods (mainly vine cuttings) or ram's horns. The particles preserve the cellular structure of the material used, which is why the resulting pigment is a highly stable, very fine blue-ish powder with poor hiding power. Carbon black is an umbrella term for different types of pigment, such as soot, ivory black, vine black, etc. [9].

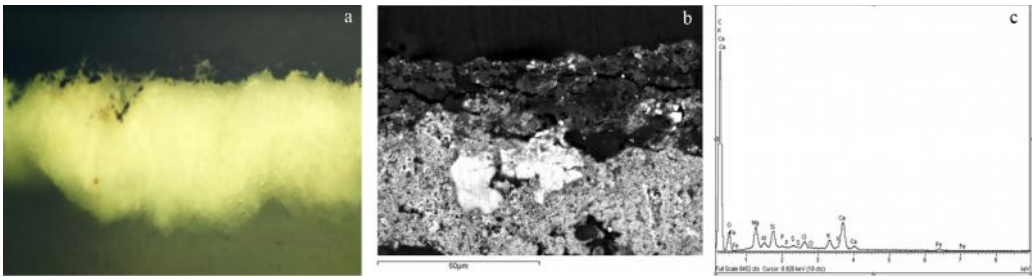

Fig. 8. Black pigment - carbon black: a - Observation by OM (epi-illumination) (100X). General image; b - Observation by MEB (BSE). Details of picture layer and mortar; c - EDX microanalysis on film of paint/analysis of particle: black coal back in dolomitic calcite.

Brown: Vermilion/cinnabar, verdigris, viride salsum, black

Various shades of brown were used to give colour to musical instruments, human hair, and elements of the *Arma Christi*.

Under OM, the brown colour was found to be a mixture of different pigments in a single, very thin layer (26μm.). SEM analysis revealed a generally low electron density, with a few high-density particles. After examination under EDX (aluminium, silica, iron, mercury, sulphur, copper, chloride, etc.), we determined that the brown pigment was obtained by mixing red earth (aluminosilicates with iron oxide, Fe_2O_3), vermilion/cinnabar (HgS), *verdigris* ($Cu(C_2O_2H_3)\cdot H_2O$), in other words, basic copper acetate, more or less hydrated, and a variety of *verdigris* called *viride salsum* ($Cu_xCl_y(OH)_z\cdot nH_2O$), which contains chloride [15, 16]. The pigment is well integrated with the plaster (lime and sand), indicating that the correct fresco technique was used (Fig. 9).

Verdigris is a synthetic pigment, traditionally obtained by applying vinegar or acetic acid to copper to corrode the metal. It is the oldest known green colour. The pigment is highly unstable, and can change rapidly to a dark colour, mainly when it comes into contact with sulphur. It is also known as *cardenillo, verdete o aeruca* [14]. The variety of *verdigris* containing chloride, viride salsum, is obtained by the addition of ammonia salts. It was widely used in Ancient Greece and Rome, and also during the 17th and 18th centuries, until it was replaced by other, more stable, green pigments in the 19th century [9].

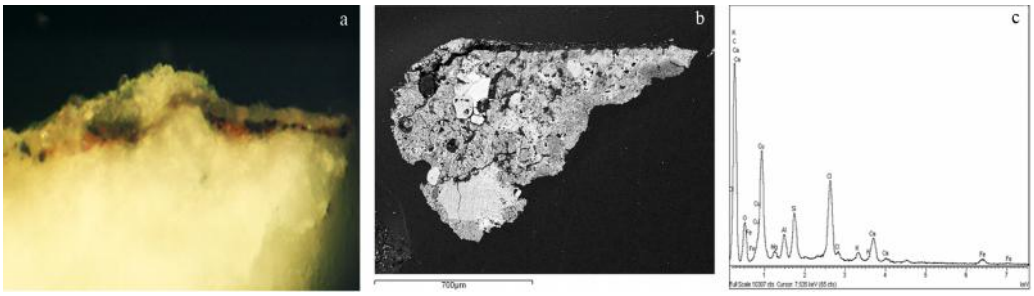

Fig. 9. Brown color, vermilion/cinnabar, verdigris, viride salsum, black: a - Observation by OM (epi-illumination) (200X). Details of picture layer and mortar; b - Observation by MEB (BSE). General image; c - EDX microanalysis: *Verdigrís (viridi salsum).*

The following table summarizes the pigments found in the wall paintings, their chemical composition and elements identified by SEM (EDX).

Table 1. Original murals. EDX microanalysis: pigments of wall paintings. Chemical composition and elements identified.

Pigment / Load	Chemical composition	Elements detected on SEM (EDX)
Calcite	$CaCO_3$	Ca,
Dolomite	$MgCa(CO_3)_2$	Ca, Mg
Sand	SiO_2	Si
Vermilion/cinnabar	HgS	Hg, S
Earth (red)	Al_2O_3, SiO_2, Fe_2O_3	Si, Al, Fe
Verdigris	$Cu(C_2O_2H_3)\cdot H_2O$	Cu
Viridi salsum	$CuxCly(OH)z\cdot nH_2O$	Cu, Cl
Carbon black	C	C

Later murals

Plaster

The plaster used in the later paintings has the same characteristics as that used in the earlier work, and is composed of calcite ($CaCO_3$), dolomitic calcite [$MgCa(CO_3)_2$] and sand (SiO_2). (See section “Plaster” on p. 4.)

Paint layer

Red: red earth, carbon black

Red is used extensively in the later mural in cloaks, hair, floral decorations, etc.

Under OM, this paint layer was seen to consist of a single stratum of dark red pigment with a mean depth of 25µm. It was obtained by mixing two pigments: red and black, the former in a higher proportion than the latter. On SEM analysis, some particles were found to have high electron density, corresponding to the iron content of red earth. This was later confirmed on EDX analysis, where we found iron oxide (Fe_2O_3) and to a lesser extent carbon black (C) (Fig. 10). As in other samples, calcite and dolomite binding agents were also identified in the red pigment. (See the specific characteristics of the different pigments described above.)

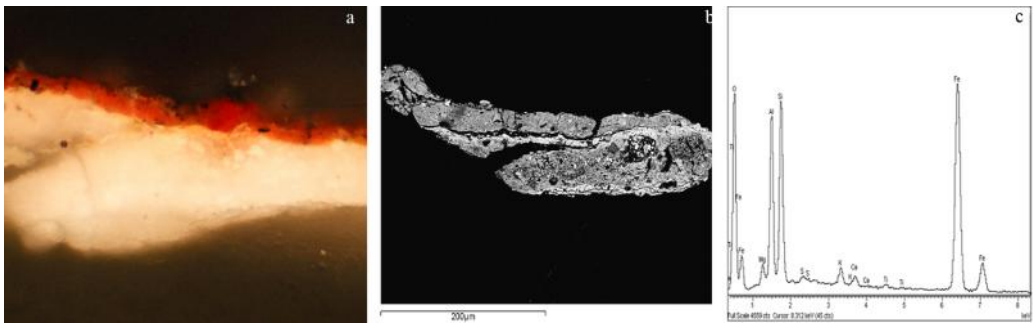

Fig. 10. Red Colour, red earth, carbon black: a - Observation by OM (epi-illumination) (100X). Details of picture layer and mortar; b - Observation by MEB (BSE). General image; c - EDX microanalysis. Film of paint, analysis of particle: red earth, carbon black in dolomitic calcite.

Flesh tones: red earth, calcite carbonate

The flesh tones were monochrome, with only the occasional addition of shadow to give the impression of depth. OM showed very thin strata (20µm), with isolated (barely detectable) particles of red mixed with the lime plaster to give the pink flesh colour. SEM and EDX analysis confirmed that the high-density pigment was red earth, the iron oxide (Fe_2O_3) used in the aforementioned red pigment being bound with calcium carbonate ($CaCO_3$) from the plaster (Fig. 11).

Fig. 11. Flesh tone: Observation by OM (epi-illumination) (100X), general image

Black: carbon black

Black was used in the garments and to outline some elements.

Based on the OM images, it would seem that a layer of black pigment was applied over the plaster layer, penetrating to a depth that varied from 56 to 77µm). The SEM (BSE) analysis showed a pigment with low electron density, consistent with carbon black mixed with a calcite and dolomitic calcite binder. This was later confirmed with EDX analysis (Fig. 12).

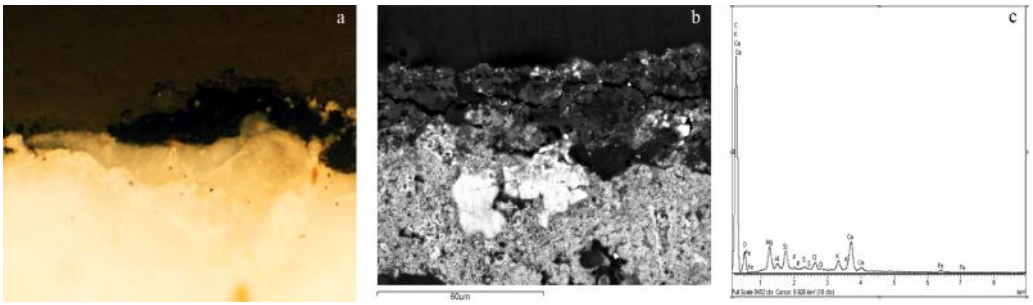

Fig. 12. Black pigment: a - Observation by OM (epi-illumination) (200X). Details of picture layer and mortar; b - Observation by MEB (BSE). Details of picture layer and mortar; c - EDX microanalysis on film of paint/ analysis of particle: carbon black in dolomitic calcite

Brown: ochre, raw sienna, carbon black

The dark brown shades used on the tree trunk and in some floral motifs on the jambs and arch were achieved using a different technique from that used to obtain dark red. In the latter case, the colour was obtained by mixing two pigments (red earth and black), while in the case of the brown shades, OM examination showed that these consisted of two layers of paint. The first layer, which penetrated to a depth of 20µm, is reddish in colour, while the second layer is black, with a depth of 10µm. The combination of these two layers gave the brown shades seen in the murals. Under SEM, the red pigment was seen to have a high electron density, while that of the black was low, with isolated high-density particles. EDX analysis (potassium, iron, sulphur, magnesium, silica) of the paint layer showed the presence of iron, specifically jarosite [$KFe_3(SO_4)_2(OH)_6$, potassium sulphate and basic hydrated iron] mixed with raw sienna (Fe_2O_3, iron oxide with silicic acid and manganese oxide) [9]. The binding agent used is dolomitic calcite (Fig. 13).

Ochre, obtained from jarosite, is a natural mineral pigment formed by the oxidation of iron sulphides. In antiquity, it was used as a yellow pigment, and can be seen in some Egyptian paintings.

Raw sienna is a natural mineral pigment obtained by simply washing, drying and crushing the earth. This pigment has been used from pre-history to the modern day due to its stability and its affinity to any kind of binding agent.

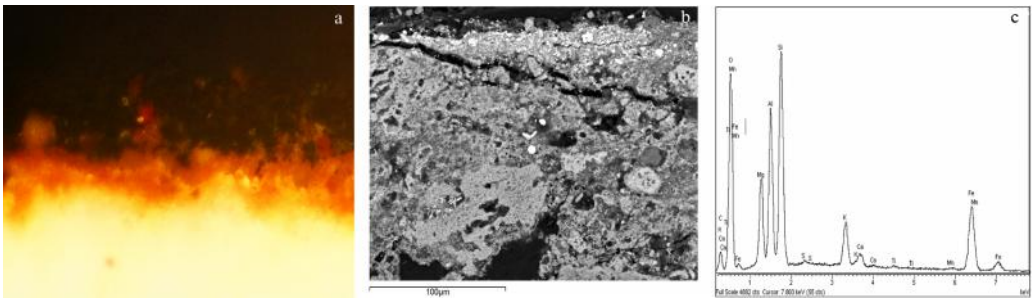

Fig. 13. Brown shades: ochre, raw sienna, carbon black: a - Observation by OM (epi-illumination) (500X). Details of picture layer and mortar; b - Observation by MEB (BSE). Details of picture layer; c - EDX microanalysis on film of paint/analysis of particle: ochre, raw sienna, carbon black.

Green

Green is only used in the central figure of the brightly painted dragon, which contrasts significantly with the colour scheme of the rest of the painting.

Under OM analysis, we observed that a layer of green, obtained by mixing green and white, had been applied to the plaster layer, penetrating to a depth of 35-40µm. This green pigment showed high electron density on SEM (BSE). EDX analysis showed the presence of copper and lead, amongst other compounds. This allowed us to identify both a copper and a lead pigment: malachite (copper hydroxy carbonate [$Cu_2(CO_3)(OH)_2$]), and lead white or basic lead carbonate [$Pb_3(CO_3)_2(OH)_2$] (Fig. 14).

Malachite is a natural mineral pigment, generally found together with azurite. The difference between these two minerals is that azurite holds less water that malachite. Malachite is easily identifiable by the moderate to large size of its particles [15, 17]. It is obtained by precipitation of a solution of copper nitrate or copper sulphate to which sodium carbonate has been added. The pigment is highly stable under normal conditions. Evidence of the pigment has been found in Egyptian tombs, and it was in use up until 1880, when it was replaced by artificial green pigments. It is also knows as green *verditer*, green bice, or mountain green [9].

Lead white is an artificial synthetic pigment obtained by exposing lead to acetic acid vapour, thus covering the metal in a layer of lead carbonate. Lead white is highly toxic and unstable when exposed to air and light. Because of its excellent hiding power, it was used until the 19th century, when it was replaced by other, less toxic white pigments such as zinc white. Artists sometimes mixed lead white with other pigments to improve their conservation. Lead white is also known as flake white and Cremnitz white [10].

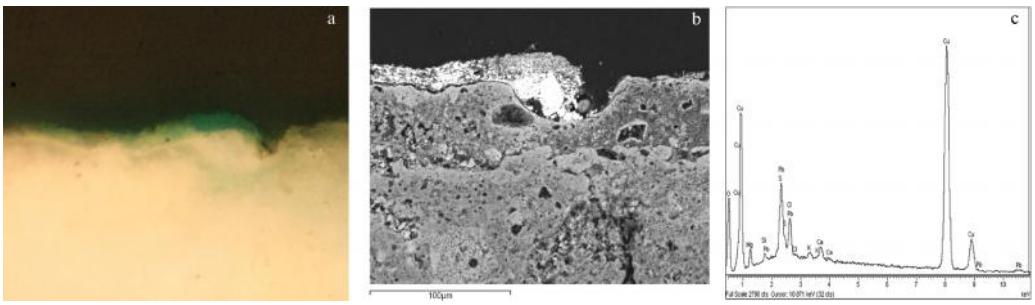

Fig. 14. Green: a - Observation by OM (epi-illumination) (100X). Details of picture layer and mortar; b - Observation by MEB (BSE). Details of picture layer; c - EDX microanalysis on film of paint/analysis of particle: malachite and lead white.

The following table summarizes the pigments found in the wall paintings, their chemical composition and the elements mapped by SEM (EDX).

Table 2. Later murals. EDX microanalysis: pigments of wall paintings. Chemical composition and elements identified.

Pigment / Load	Chemical composition	Elements detected on SEM (EDX)
Calcite	$CaCO_3$	Ca,
Dolomite	$MgCa(CO_3)_2$	Ca, Mg
Sand	SiO_2	Si
Earth (red)	Fe_2O_3	Fe
Jarosite	$KFe_3\ (SO_4)_2(OH)_6$	K, Fe, S
Raw sienna	Iron oxide Fe_2O_3, with silicic acid and manganese oxide	Fe, Si, Mn
Malachite	$Cu_2(CO_3)(OH)_2$	Cu
Lead white	$Pb_3(CO_3)_2(OH)_2$	Pb
Carbon black	C	C

Restoration of the detached murals

The following is a brief summary of the different strategies used in the restoration of the murals discussed in this study.

Consolidation of layers

The plaster on which the murals were applied was disintegrating due to the loss of binder content. In order to strengthen the constituent elements of the fresco, the plaster was consolidated by impregnating and injecting it with organic or inorganic binders, depending on whether the surface was painted or not. Any areas of cleavage on the painted surface were likewise consolidated. The products used in this process included:

- Paraloid B-72 100%: a thermoplastic acrylic resin consisting of an ethyl methacrylate/methyl acrylate copolymer. Characterised by its transparency, resistance to UV radiation and oxidation, and its mechanical strength and reversibility, Paraloid is widely used in the consolidation and protection of stone, metal and wood. Molecular weight: 11.39733 g/mol. Glass transition temperature: 40°C. Softening point: 70ºC. Melting point: 150ºC. Refractive index (RI) = 1.487. Viscosity at 25ºC in solution of 40% acetone = 200, in toluene = 590. Density at 25ºC is 1.15 g/cm^3 Paraloid is soluble in n-butanol, diacetone, acetone, trichloroethylene, ethyl acetate, toluene, xylene, etc. In this case, the resin was used in a 5% acetone solution and applied to painted surfaces. This reduced the viscosity and enabled the resin to penetrate into the treated stratum [18].

- Ethyl Silicate *WACKER TES 40 WN* ($C_8H_{20}O_4Si$): a mixture of monomeric and various oligomeric and cyclic condensates of ethyl silicate. It is generally sold as an ethanol-based solution with an added catalyst. The silicate condenses and precipitates inside the plaster, leaving amorphous silica. This silica binds chemically with the minerals in the plaster to become a binder with the same characteristics as stone mortar, making it very effective in the restoration of stone materials, such as sculptures, mural paintings or architectural details [19, 20]. It is a transparent solution with low viscosity and low surface tension, giving it considerable penetrating and binding power. It has a molecular weight of 208.33 g/mol, a density at 20ºC of 0.93 g/cm^3, and a refractive index of 1.3825 [21]. Its softening point is approximately 400ºC [22].

In this case, this product was used to consolidate areas of plaster with no pigmentation.

Assembly of the back panel

The two sections into which the back panel of the niche was divided were reunited by means of small rectangular wedges made of synthetic material inserted in a dovetail pattern into shallow grooves carved into the plaster surface to form a strong joint. The wedges were made of non-woven fiberglass and epoxy resin (Fig. 15).

Fig. 15. Assembly system of the two sections of the back panel.
wedges made of synthetic material: fibreglass and epoxy resin fiberglass.

- Fibreglass threads cut into 6mm lengths (SiO_2): these threads are made by extruding glass to obtain extremely fine filaments that can be used in the manufacture of textiles. Fiberglass is composed of silica, lime and sodium carbonate and was introduced in the first half of the 20th century. When mixed with certain polymers, it is widely used as an insulation material in construction due to its strength and transparency [23].

- Epoxy resin *EPOFER EX 402 + E 430* (ratio 100:30 pbw): a thermal stable polymer that hardens when treated with a catalyst. Glass transition temperature: 90ºC. Density at 25ºC: 1.11g/cm^3 (EX 402) and 0.99g/cm^3 (E 430). Viscosity at 25ºC: 1700 (EX 402) and 80 (E 430). The epoxy resin chosen for this restoration project was a special UV resistant, totally transparent formulation, two characteristics that were essential for the nature of the restoration work carried out [24].

Cleaning

The paint surface was extremely contaminated, having accumulated a variety of particles over time together with fragments of plaster from the construction of the wall covering the niche. It also showed evidence of attempts to retouch some of the painting. The surface was cleaned with a combination of tools, such as micro-aspiration, scalpels, erasers, etc. and chemical solvents with minimum penetration and retention. Gel-based formulations were used to limit the extension and penetration of the solvent.

Stucco work and chromatic reintegration

Areas where the plaster had been chipped or was missing altogether were filled in with a lime and sand plaster consistent with the original material. The oldest fresco on the back panel of the niche had been damaged to such an extent that it was hard to interpret the overall pictorial scene. For this reason, neutral colours were used to fill in the gaps. The damage was caused when the surface of the original fresco was pitted to improve adherence of the second layer of plaster (later fresco). Gaps in the remaining panels were restored using the *rigattino* technique. Only reversible materials that were fully compatible with the original pigments were used.

Installation and assembly

The double-sided fresco panels restored in this project impelled us to seek new, innovative ways of re-assembling the niche for exhibition. For this purpose, the main aim of the rigid framework designed to hold the panels in the form of the niche was to display both sides of the panels. Thus, the viewer can see both the earlier frescos and the impression left by these frescos on the back of the later fresco panels.

The first step involved reinforcing the panels and applying a thin sheet of matte fiberglass blanket on the side bearing the impression of the earlier fresco. The blanket was attached to the frame with epoxy resin. A layer of Beva O.F.® Gel was applied between the two layers (plaster and fiberglass), making it possible to reverse the restoration if required.

Following this, we constructed a frame using alveolar polycarbonate with longitudinal cells measuring 4 x 1cm in cross-section (Fig. 16a), through which hollow, square-section (0.8 cm^2) anodized aluminum bars were inserted (Fig. 16b). The frame was attached to the structure by means of epoxy resin and fiberglass, without touching the painted areas. By this means, the impression left by the earlier painting on the back of the later fresco remained clearly visible. The same system was used to frame the later back panel of the niche (with paintings on both sides), the two jambs, and the arch.

The panels were then assembled on a scaffold made of L-shaped aluminum bars. This support structure was screwed to small plates that had previously been attached to the polycarbonate frame and the enclosed aluminum bars (Fig. 16c). As the reverse of the original back panel of the niche did not contain any artwork, it was attached to a frame made of rectangular-section aluminum bars ($4cm^2$) by means of epoxy resin and fiberglass.

Fig. 16. Frame alveolar polycarbonate: a - Reinforcement frame of alveolar polycarbonate with longitudinal cells measuring 4 x 1cm in cross-section; b - Detail of anodized aluminum bars into the polycarbonate structure; c - System assembly of the main structure: screwed to small plates attached to the polycarbonate frame.

The following materials were used in this structure:

- Beva O.F.® Gel: a water-based acrylic resin spray. Formula developed by Gustav Berger in 1970. The solution contains Elvax (ethylene vinyl acetate copolymer EVA), a ketonic resin (poly-cyclohexanone), an A-C copolymer (EVA), Cellolyn 21 (phthalate ester of hydroabietyl alcohol, later replaced by Cellolyn-121) and paraffin. Density (20ºC): $1g/cm^3$ [25].

- Alveolar polycarbonate: $(OC(OC_6H_4)_2CMe_2)_n$ with ultraviolet filter (a film that is co-extruded and fused with the substrate), with a density of $1.20g/cm^3$. Compression strength: > 80 MPa, and traction strength: 55-75MPa. Refractive index = 1.585 [26].

- Matte reinforcement fibreglass, 200 g: also known as fibreglass blanket. A series of fiberglass threads uniformly and randomly distributed and compressed by means of a polyester or epoxy resin-based emulsion. At 25ºC it has a density of $2.58g/cm^3$, with a softening point of over 100ºC [23].

- Epoxy resin EPOFER EX 402 + E 430 (ratio 100:30 pbw). Described in section 2.3.2 above [24].

- Anodised aluminium: abrasion- and corrosion-resistant. The aluminum used in the manufacture of the bars is an extremely strong silicon-magnesium alloy (Mg_2Si). Anodizing is an electrolytic technique used to create an artificial protective film on the aluminum, called alumina. In this case, the protective film measured 10µm.

Conclusions

Based on the analysis of the samples taken from the frescos, we found that the history of the paintings studied can be divided into three clearly differentiated stages:

a. execution of the original frescos, possibly coinciding with construction of the church (16th century);

b. execution of the later frescos (17th century);

c. niche is partially walled-up and the baroque 18th century altarpiece is installed.

In both frescos, the plaster was made from lime derived from dolomitic calcite [($CaMg(CO_3)_2$], mixed with sand (SiO_2). We found the same elements mixed in with the pigments, which indicates that the paintings were executed according to the fresco technique, and retouched when dry using pigments diluted in lime water as a binding agent.

Fiberglass, either in the form of thread, blanket or woven fabric, combined with transparent epoxy resin is ideal for reinforcing rigid panels containing murals, mosaics, tile work, etc., in which it is important to display both sides of the panel. Being transparent, these materials allow the designs on either surface to be seen.

The framework made of transparent alveolar polycarbonate reinforced with aluminum bars provides excellent peripheral support for panels containing paintings, mosaics, tiles, etc. where both the back and front need to be displayed with the least possible encumbrance.

The use of the latest observational technologies gives valuable, in-depth insight into our cultural heritage, and thus contributes to saving historical treasures. The use of 3D photogrammetry is essential to enable such large restoration projects to be adequately viewed and enjoyed (Fig. 17).

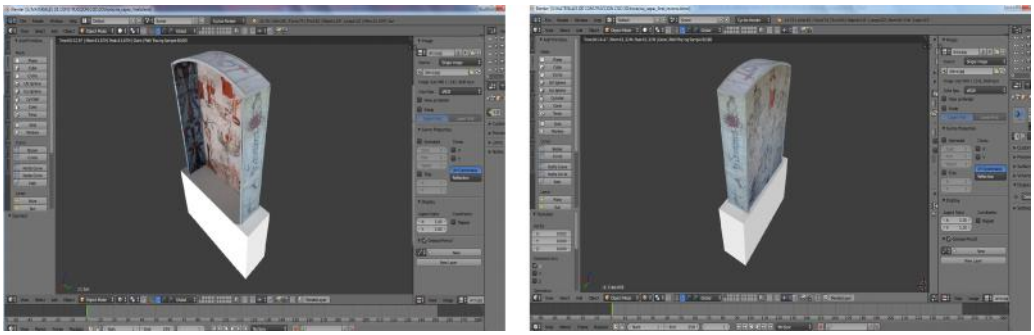

Fig. 17. 3D virtual reconstruction of the whole with Blender program

Acknowledgements

Restoration of the wall paintings was undertaken under 3 research contracts drawn up between the Diocese of Sigüenza-Guadalajara and the Faculty of Fine Arts of Madrid, in compliance with Article 83 of the Spanish Universities Act (ref. 2011/245, 2011/246 and 2011/247). The project was funded by IberCaja, a Spanish bank.

I would like to thank the members of the different teams involved in the restoration and recovery of these frescos: Ángel Balao, Ana Morrás, Cristina Bartolemé and José Álvaro Perdices; Technical directors of the restoration work and research contracts: Marta Plaza Beltrán and Mª José García Molina; Chemical analysis: Margarita San Andrés Moya. Applied Chemistry Laboratory of the Department of Painting and Restoration of the Faculty of Fine Arts of Madrid (Spain); Funding and management: Heritage Department of the Diocese of Sigüenza-Guadalajara and Ibercaja.

References

[1] C.M. Batalla Carchenilla, *El juicio final en el Atance*, **Wad-Al-Hayara, 21**, 1994, pp. 199-203.

[2] M. Munteanu, I. Sandu, *The implications of free 3D scanning in the conservation state assessment of old wood painted icon*, **IOP Conference Series: Materials Science and Engineering, 133**(1), 2016, 012060.

[3] P. Mora, L. Mora, P. Philippot, **Conservation of Wall Paintings**, Butterworth, London, 1984.

[4] M. Merrifield, The Art of Fresco Painting, as Practiced by the Old Italian and Spanish Masters with a Preliminary Inquiry into the Nature of the Colours Used in Fresco Painting, Forgotten Books, United Stated, 2015.

[5] V. Pelin, I. Sandu, S. Gurlui, M. Branzila, V. Vasilache, E. Bors, I.G. Sandu, *Preliminary Investigation of Various Old Geomaterials Treated with Hydrophobic Pellicle*, **Color Research and Application, 41**(3), Special Issue, 2016, pp. 317-320.

[6] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddal, **The Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments,** Elsevier, Amsterdan, 2004.

[7] D. Juanes, C. Martín de Hijo, *Aplicaciones de la microscopía óptica y electrónica de barrido***, La Ciencia y el Arte, 1**, 2008, pp. 68-73.

[8] M. Matteini, A. Moles, **Ciencia y Restauración**. Nerea, San Sebastián, 2001.

[9] M. Matteini, A. Moles, **La química en la restauración. Los materiales del arte pictórico.** (second edition). Nerea, San Sebastián, 2011.

[10] A. Pedrola, **Materiales, procedimientos y técnicas pictóricas,** Ariel (second edition), Barcelona, 2002.

[11] A. Parrilla Bou, *El arte de los pigmentos. Análisis histórico-artístico de su evolución a partir de los tratados españoles de Francisco Pacheco y Antonio Palomino*, **PhD**. **Thesis ,** Universidad de Valencia, 2009.

[12] R.J. Gettens, R.L. Feller, W. T. Chase, *Vermillion and cinnabar*, **Artists' Pigments: A Handbook of Their History and Characteristics, vol. 2,** Oxford University Press, 1993, pp. 159-182.

[13] R.J. Gettens, E.W. FitzHugh, R.L. Feller, *Calcium carbonate whites*, **Artists' Pigments: A Handbook of Their History and Characteristics, vol. 2,** (Edited by A. Roy), D.C. National Gallery of Art Washington, Oxford University Press, 1993, pp. 203–226.

[14] A. Palomino de Castro y Velasco, **El museo pictórico y la escala óptica**, Aguilar, Madrid, 1947.

[15] R.J. Gettens, E.W. FitzHugh, *Azurite and blue verditer*, **Artists' Pigments: A Handbook of their History and Characteristics, vol. 2** (Edited by A. Roy), D.C. National Gallery of Art Washington, Oxford University Press, 1993, pp. 23–35.

[16] S. Santos, M. San Andrés, N. Sancho, J. M. de la Roja, *Variations in the colorimetric characteristics of verdigris pictorial films depending on the process used to produce the pigment and the type of binding agent used in applying it*, **Colour Research and Application, 32**(5), 2007, pp. 414-423.

[17] R. J. Gettens, E. W. FitzHugh, *Malachite and green verditer*, **Studies Conservation, 19**, 1974, pp. 2-23.

[18] * * *, *Paraloid B-72***, Dow Delivers Solutions at the Intersection of Science and Markets**, http://www.dow.com/assets/attachments/business/pcm/paraloid_b/paraloid_b-72_100_pct/tds/paraloid_b-72_100_pct.pdf, [accessed on 22.07.2015].

[19] M. Loele, U. Santamaría, P. Tiano, *Studio comparativo di silicati d'etile commerciale e sperimentali a confronto con microemulsioni acriliche per il consolidamento di matrici carbonatiche fortemente decoese*, **Congresso Internazionale "I silicati nella conservazione"**, 13- 15 february 2002, Torino, pp. 71-82.

[20] J. Osca Pons, *El empleo de consolidantes inorgánicos y organosilíceos como alternativa a los consolidantes orgánicos*, **Tratamientos y Metodologías de conservación de pinturas murales, Actas del Seminario sobre restauración de pinturas murales,** Fundación Santa María la Real, Aguilar de Campoo (Palencia), 2005, pp. 10-47.

[21] * * *, **Tabla de índices de refracción** (para λ = 589 nm) http://www.vaxasoftware.com/doc_edu/fis/inrefraccion.pdf, [accessed on 22.07.2015].

[22] * * *, **Certificado de calidad,** Productor Chimicos, Manuel Riesgo, S.A. Madrid, http://manuelriesgo.com/docstecnicas/tecnicas/FT_SS984_1000.pdf, [accessed on 22.07.2015].

[23] * * *, *M710B - Manta para laminación manual*, **Customer Acceptance Standard, Owen Corning,** http://www.plastiquimica.cl/wp-content/uploads/2010/07/MAT_225.pdf, [accessed on 22.07.2015].

[24] * * *, *Epoxy Resins - Epofer EX402 + E 442 Epoxy Incoloro-Filtro UV*, **Feroca soluciones para el moldeo,** http://www.feroca.com/es/resinas-epoxi/82-epofer-ex402-e430-epoxi-trasparente-filtro-uv.html, [accessed on 22.07.2015].

[25] * * *, *Beva original formula gel*, **Ficha de seguridad (Dir. 21/58CE),** http://manuelriesgo.com/docstecnicas/tecnicas/FT_AV000183_4.pdf, [accessed on 22.07.2015].

[26] * * *, **Polygal,** The Plastic Sheets Group, http://www.polygalsud.cl/documentacion/POLYGAL%20Manual%20de%20Especificaciones%20tecnicas.pdf, [accessed on 22.07.2015].

Received: February, 26, 2016
Accepted: November, 10, 2016