2023 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Rome, Italy, October 19-21, 2023

Study and restoration of the *Sacra Conversazione* by Lorenzo Berrettini and experimental tests to evaluate the application of diammonium phosphate as consolidant for the wall painting

Antonio Paucecch[1], Luca Lanteri[2*], Francesca Montozzi[1], Paola Pogliani[1], Claudia Pelosi[2]

[1] *University of Tuscia, DIBAF Dept., Via San Camillo de Lellis snc Viterbo, Italy, antonio.paucecch@gmail.com; francesca.montozzi@unitus.it; pogliani@unitus.it*
[2] *University of Tuscia, Dept. DEIM, Via del Paradiso 47, Viterbo, Italy, *llanteri@unitus.it (corresponding author); pelosi@unitus.it*

***Abstract* – This paper reports the study and restoration of a 17th century wall painting attributed to the artist Lorenzo Berrettini and located in a chapel of Palazzo Orsini at Bomarzo, a little town close to Viterbo, in central Italy. The wall painting was recently restored as activity of a master thesis in conservation and restoration of the cultural heritage and on that occasion the artwork was investigated to characterize the materials and techniques with the aim at choosing the best consolidation procedure and products. To reach this goal, multispectral imaging and X-ray fluorescence spectroscopy were applied on-site. After this non-invasive analysis, some laboratory investigation was performed by Fourier transform infrared spectroscopy. The results of the diagnostic campaign were used to plan the experimental tests for consolidation by diammonium phosphate dibasic (DAP) that is a relatively new product in the field of restoration of wall painting. The tests demonstrated the good performance of this consolidant product, with respect to the traditional nano-lime formulate.**

I. INTRODUCTION

The wall painting "The Sacred Conversation", object of the present paper, is located in the Lante Della Rovere Chapel of Palazzo Orsini in Bomarzo (Viterbo, Italy). The wall painting was executed by Lorenzo Berrettini in 1661 and depicts the Sacred Conversation (Fig. 1) between the Madonna enthroned with the Child surrounded by saint [1]. The composition, iconography, drawing, colours, and executive technique of the painting can be clearly referred to the painting of Pietro da Cortona and his workshop [2].

From a conservative point of view, the painting was in a very bad condition, due to the presence of altered fixative and a whitish patina that did not allow a correct reading of the artwork (Fig. 1A).

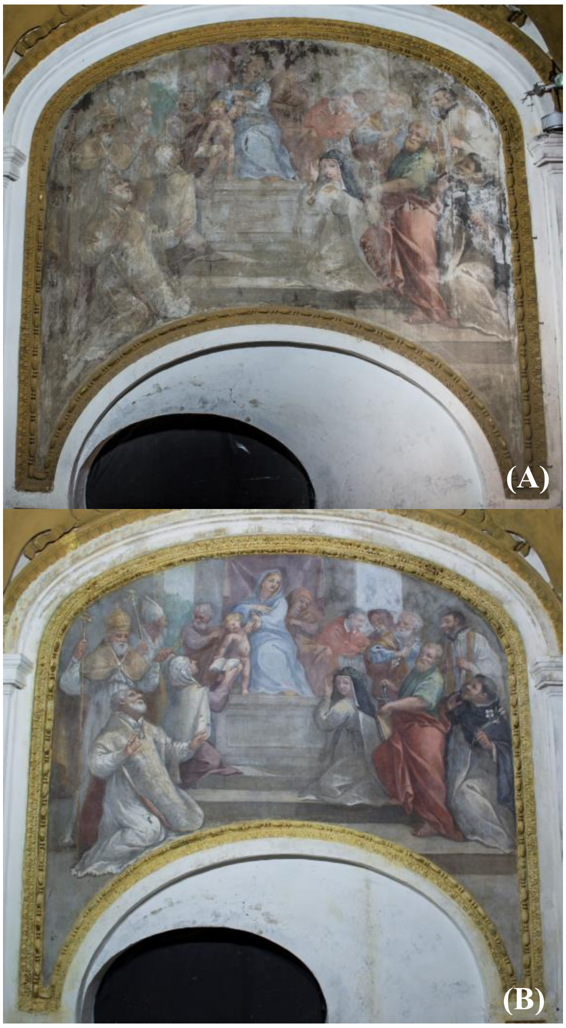

Fig. 1. Photographs of the wall painting before (A) and after (B) the restoration.

The main conservative problems were caused by a previous infiltration of rainwater that produced loss of cohesion and the presence of saline efflorescence. After a preliminary characterisation of the painting materials, by imaging and spectroscopic techniques, a strategy for consolidation was planned and proposed with the idea of choosing an inorganic product that could be respectful of the environment, the health of operators and the constituent materials. The choice therefore fell on diammonium phosphate dibasic (DAP), a product that is increasingly used for the consolidation of stone artefacts, but which is still poorly investigated for the application on polychrome surfaces [3-4].

As described in the technical data sheet: “The treatment is based on the formation of hydroxyapatite (HAP), an extremely insoluble calcium salt, inside the pores of the carbonate matrix of the fresco, which is also unassailable by acids and bases and capable of reforming bonds between the calcite grains having lost cohesion” [5]. Moreover, DAP is able to bind calcium ions eventually present in the mortar and in the painting layer so removing saline efflorescence caused by gypsum [6].

II. MATERIALS AND METHODS

A. Characterization of materials

The wall painting was firstly investigated with ultraviolet fluorescence photography (UVF) and hypercolorimetric multispectral imaging (HMI) in order to obtain preliminary useful information about the state of conservation and the constituent materials.

Imaging was performed by using a Nikon D800 digital camera modified in full range in order to cover the range from 300 nm to 1000 nm, equipped with a 17–35 zoom lens. Hypercolorimetric multispectral imaging (HMI) was obtained by using two filters, named A (UV-Vis) and B (Vis-IR), and two modified flashes (full-range) for lighting [7-8]. To complete the acquisition set-up for HMI, twenty-one white reference patches and a colorchecker were positioned in the scene to have the standards colours to calibrate the acquired images [7-8].

UVF images were obtained by irradiation the wall painting surface with two CR230B-HP 10W UV led projectors, with peak emission at 365 nm. In this case, two filters were used in front of the camera lens: filter A and an UV-IR cut filter to remove undesirable components of the electromagnetic spectrum [9-10].

X-ray fluorescence spectroscopy (XRF) was performed on sixteenth points (X1-X16, Fig. 2) of the wall painting through a portable instrument, Assing Surface II Monitor, equipped with Ag anode operating at 40 kV and 76 µA.

Fourier transform infrared spectroscopy was focused on two micro-samples (S1-S2, Fig. 2) gathered from points that were selected on the base of the preliminary imaging and XRF analysis. FTIR spectra were obtained by a Thermo Nicolet Avatar 360 spectrophotometer operating in the MID-IR with a resolution of 4 cm^{-1}. Samples were ground with spectrophotometric grade KBr, used as reference and background material, and acquired in diffuse reflectance modality (DRIFT).

Fig. 2. Photograph of the wall painting with the points of XRF analysis (X1-X16) and with the sampling points S1 and S2.

B. Test with DAP

After having characterised the constituent materials of the painting, laboratory mock-ups were prepared in order to test the commercial consolidant products.

For the experimental test, six mock-ups (four used for testing the consolidant products and two as control) were prepared as follows: clay bricks (14x25x3.5 cm^3) were used as support, on which a layer of arriccio was applied having as composition an aggregate/binder ratio of 3 to 1 (one part of lime paste, one part of sand, two parts grey pozzolan). A plaster layer made of lime paste (one part) and sand (two parts) was applied on the arriccio. Finally, a thin layer of finishing plaster (the so-called *intonachino*) was superimposed to the previous one. The finishing plaster was made of lime paste (one part) and marble dust (two parts). Four pigments were chosen to be applied by fresco technique on the finishing plaster layer, according to the results obtained by the XRF analysis: smalt, *morellone*, green earth and yellow Sienna. Pigments were supplied by Zecchi (Florence, Italy). Eight frescoes areas (4x4 cm^2, two for each pigment) were made on each mock-up. Before applying the consolidant products, a maturation period of 30 days was elapsed (Fig. 3).

The commercial products tested as consolidant are a traditional nano-lime (NanoRestore®) and diammonium phosphate dibasic (DAP), both supplied by CTS Italy.

They were applied to the mock-ups by following the indications supplied in the technical data sheets.

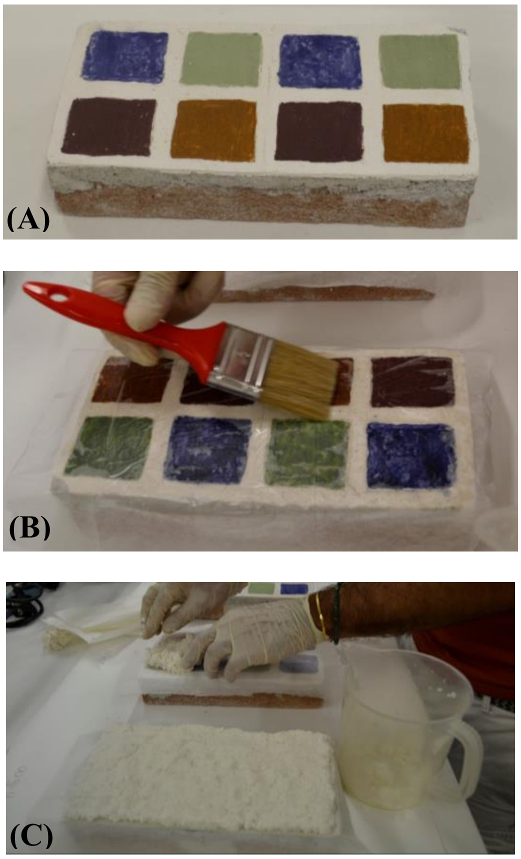

Fig. 3. (A) One of the mock-ups at the end of the preparation; (B) application of NanoRestore®, and (C) application of DAP.

Specifically, the nano-lime, in form of dispersion in isopropyl alcohol, was applied by brush on two mock-ups without dilution and left curing for seven days. DAP was prepared in water solution at 15%(w/v) concentration and applied on other two mock-ups by means of Arbocell BC1000 paper pulp (50 g) compress, interposing a sheet of Japanese paper with a weight of 9g/m^2. The DAP solution (about 150 ml) was applied with a contact time of 48h. After the application, as recommended by the technical data sheet, the mock-ups were covered by a transparent film, useful to reduce the evaporation of the water. To evaluate the performance of the products, colour measurements, peeling test and contact sponge method were applied.

Colour was measured, before and after the treatment, with a digital handheld EOPTIS colorimeter model CLM-194 with a measurement aperture of 6 mm in diameter.

The peeling test was conducted by using an adhesive tape (5 cm white fiber base pressure sensitive tape with a peel strength between 6.34 N/cm and 7.00 N/cm in accordance with the standard ASTM D3330/D3330M called Test Method for Peel Adhesion of Pressure-Sensitive Tape). Rectangles measuring 2x5 cm were used for the test.

The contact sponge method followed the standard UNI 11432:2011. In this method, developed by the CNR-ICVBC of Florence, the water absorption can be calculated directly, using the appropriate formula which is based on the differences between the weights.

III. RESULTS AND DISCUSSION

The first step of the diagnostics approach was to evaluate and discuss the UVF image of the wall painting shown in the Fig. 4.

Fig. 4. UVF image of the painting before the restoration.

The fluorescence induced by ultraviolet radiation highlights a diversified and complex situation of the painted surface, indicative of the non-homogeneous presence of variously fluorescent materials of different nature (such as, for example, animal glue applied during previous restoration, saline efflorescence, and pictorial retouching) combined with various levels of intensity in the responses attributable to the difference in thicknesses and degrees of aging of the materials present.

The photographic images of the UV fluorescence highlight a strong cold tone response variously distributed on the painted surface, due to the application of an organic resin used as a fixative of the pictorial film. Furthermore, it is possible to follow the differential degradation suffered by this material over time as the degree of intensity of the fluorescence is directly proportional to the thickness of the layer and is null where the protective appears completely removed by some previously applied cleaning tests, as well-visible in the right part of the painting. In a little zone, indicated by the white arrow in the Fig. 4, a spot of lemon-yellow fluorescence has been detected that could be hypothesised due to zinc white. XRF analysis confirmed this hypothesis (see Table 1, point X2).

Images acquired with HMI system were processed in order to obtain infrared and ultraviolet false colour (Fig. 5). This kind of processing allows to make hypothesis about pigments' composition on the base of their false colours. The light blue areas, especially in the Virgin dress, exhibit a red colour in the IRFC and a light green one in UVFC suggesting the use of smalt as pigment [11].

Iron-based pigments, such as red and yellow ochre, appears light yellow in the IRFC and violet in the UVFC.

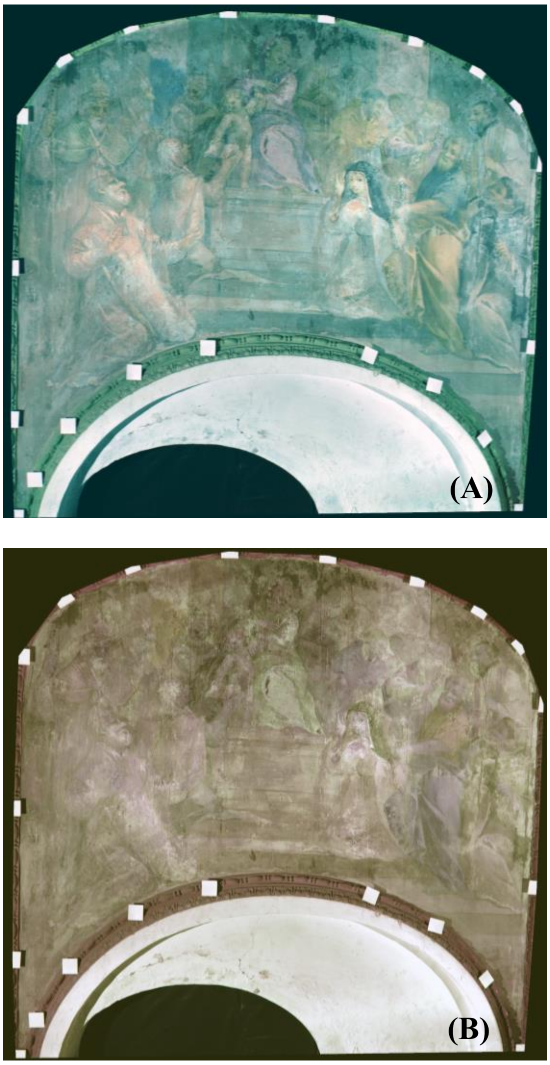

Fig. 5. IRFC (A) and UVFC (B) images of the painting before the restoration.

The pigment composition was defined by using X-ray fluorescence spectroscopy with a portable instrument that gave the results shown in the Table 1. The points examined by XRF spectroscopy always contain elements that can be associated to the mortar, i.e. Ca, Sr, Fe, Zr, Rb and other ones attributable to the pigments. The detected chemical elements suggest the use of pigments typical of fresco techniques: ochre, earth, smalt, and calcium carbonate white. The presence of zinc in a white spot is due to an accidental event and not to a repainting, due to the limited occurrence of this element.

FTIR analysis was performed on two micro-samples from areas appearing dark in the visible: one in the upper part (S1) and the other in the lower part (S2) of the painting. The results showed the presence of gypsum as main component of the sample S1 indicating a surface salt deposit. Gypsum is characterised by the signatures at cm^{-1}: 3545, 3406, 2238, 2112, 1683, 1621, 1145, 672, 603 and 467 [13-14]. In the spectrum of sample S1 the other bands can be attributed to calcium carbonate (at cm^{-1}: 2981, 2877, 2519, 1795, 1449, 875, and 712). In the sample S2 the main constituent is calcium carbonate, with silicates (broad band at 1051 cm^{-1}) and traces of gypsum (Fig. 6).

Table 1. XRF results expressed as main elements in order of measured counts per second.

Measured point	**Elements**	**Hypothesised pigments**
X1, green	Fe, Ca, Sr, K, Zr, Rb	Green earth
X2, white spot	Ca, Fe, Zn, Sr, Zr, K, Rb	Zinc white
X3, yellow	Ca, Fe, Sr, Zr, Rb	Yellow ochre
X4, white	Ca, Fe, Sr, Zr, Rb	$CaCO_3$ white
X5, light blue	Ca, Fe, Co, As, Ni, Sr, Zr, Rb, K	Blue smalt
X6, dark zone	Ca, Fe, Co, As, Sr, Ni, Zr, Rb, K	Blue smalt
X7, red	Ca, Fe, Sr, Zr, Rb	Hematite
X8, red-brown	Ca, Fe, Sr, Zr, Rb	Hematite
X9, flesh tone	Ca, Fe, Sr, Zr	Hematite and $CaCO_3$ white
X10, green	Ca, Fe, Sr, K, Zr, Rb	Green earth
X11, light blue	Ca, Fe, Co, As, Ni, K, Zr, Rb	Blue smalt
X12, white-light blue zone	Ca, Fe, Co, Sr, As, Ni, S	
X13, yellow	Ca, Fe, Sr, S, Zr, K	Yellow ochre
X14, red	Ca, Fe, Sr, Zr, Rb, S	Hematite
X15, dark zone in the upper part	Ca, Fe, Sr, S, Zr, Rb	Hematite
X16, gilding	Pb, Ca, Fe, Cu, Au, Zn	Original gold and over-painting

There is no evidence of organic binders in the examined samples apart from a very weak signature at 2935 cm^{-1} (stretching of organic C-H bond) in the spectrum of sample S1 probably due to impurities of previous treatments.This result, combined with the pigments' typology derived from XRF analysis and with the careful close observation performed during the documentation and restoration phases, confirms that the wall painting is made by fresco technique. For this reason, it was decided to use basic di-ammonium phosphate (DAP) as consolidant for the painting instead of more classical nano-lime that could produce surface whitening. Before applying the consolidant product on the artwork, some laboratory tests were performed on mock-ups created with the same pigments of the wall painting, previously characterised.

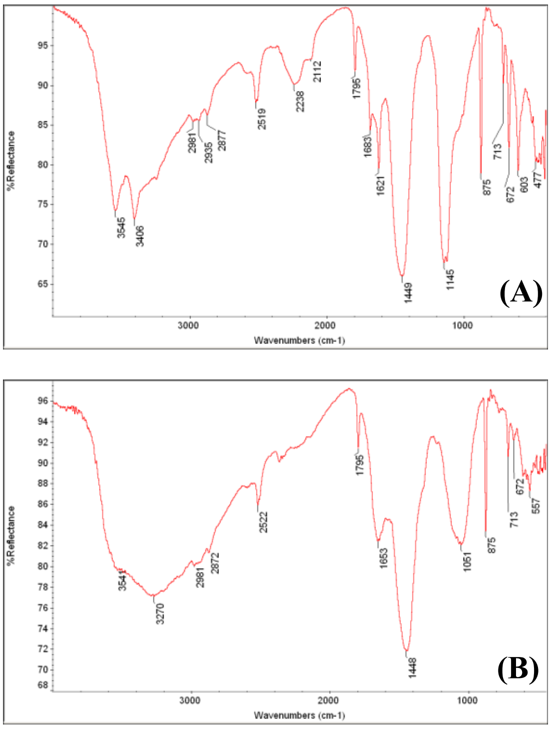

Fig. 6. FTIR spectra in diffuse reflectance modality of sample S1 (A) and sample S2 (B).

Colour measurements before and after the application of consolidant products showed little changes for DAP treated mock-ups with values of ΔE* ranging from a minimum of 2.56 (calculated on the *morellone* areas) to a maximum of 9.03 (calculated on Sienna areas). On the other hand, in the case of nano-lime treated mock-ups, colour changes were extremely high due to the excessive whitening of the surface: ΔE* values ranged from 15.4 in the case of green earth to 31.3 in that of Sienna.

Concerning the contact sponge method, the results for the samples treated with NanoRestore® show a greater quantity of water absorbed by the surface, between 1.00 and 0.55 (g/cm^2) while the samples treated with DAP show a lower water absorption, between 0.30 and 0.34 (g/cm^2). The greater the amount of water absorbed by the surface, the lower the water repellence characteristics or in any case the ability of the product used to create cohesion between the particles of the product.

Lastly, the peeling test was applied to evaluate the effectiveness of surface consolidation of the fresco samples. The difference between the initial weight and the final weight of tape allows to estimate the material removed. The verification of the surface cohesion after the treatment made it possible to measure whether and how much the treated areas had maintained the degree of cohesion achieved with the treatments. On all treated areas, the peeling removed a much smaller amount of pigment than on the untreated area. In particular, the samples treated with DAP showed a greater surface cohesion force, with a quantity of material removed ranging from 0.0118 to 0.0045 g. As far as samples with NanoRestore® are concerned, the amount of material removed is slightly higher, from 0.0434 g and 0.0501 g.

The results of the experimental tests performed on the laboratory mock-ups, allowed to address the choice of the consolidating material toward dibasic diammonium phosphate dibasic. For the purposes of research and experimentation, DAP represents a valid alternative to traditional consolidants, due to its perfect compatibility with the substrate, its effectiveness with minimal quantities of product, ease of application and an almost zero level of toxicity.

IV. CONCLUSIONS

The work presented in this paper demonstrated the synergy between diagnostics and restoration and how the use of scientific investigation can help the restorer in the choice of the best treatment as possible in case of consolidation products.

The preliminary characterisation of pigments and binders demonstrated the use of a fresco technique by the artist Lorenzo Berrettini and this result addressed to the choice of the consolidant to DAP. The laboratory tests performed on mock-ups consolidated with DAP and with nano-lime in comparison, showed that DAP gave good results in terms of colour changes, resistance to peeling and water absorption, if compared with nano-lime whose main problem is the formation of thick and extensive whitening on the surface of the mock-ups.

This result encouraged us to use DAP for consolidating the entire wall painting with an excellent outcome, as visible in the Figure 1B.

ACKNOWLEDGMENTS

The restoration was carried out as part of the activities of the master's degree course in Conservation and Restoration of the University of Tuscia with the contribution of the Municipality of Bomarzo and the Carivit Foundation.

REFERENCES

[1] A. Paucecch, “Studio e restauro della Sacra Conversazione di Lorenzo Berrettini nella Cappella Lante Della Rovere di Palazzo Orsini a Bomarzo. L'uso di materiali inorganici per il consolidamento delle pitture murali ad affresco”, Master Thesis, University of Tuscia, April, 2023, 245 p.

[2] F.M. D'Agnelli, “Contributi al catalogo di Lorenzo Berrettini. L'affresco del Palazzo Orsini-Lante a Bomarzo”, Bollettino d'arte, vol. 98, October 1996, pp. 81-88.

[3] M. Matteini, S. Rescic, F. Fratini, G. Botticelli, “Ammonium Phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: preliminary research”, Int. J. Archit. Herit. 2011, vol. 5, pp. 717-736.

[4] E. Sassoni, S. Naidu, G.W. Scherer, “The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones”, J. Cult. Herit., vol. 12, Nr. 4, October 2011, pp. 346-355.

[5] CTS technical data sheet of DAP available at the link: https://www.ctseurope.com/gb/246-dibasic-ammonium-phosphate-dap.

[6] I. Natali, P. Tomasin, F. Becherini, A. Bernardi, C. Ciantelli, M. Favero, O. Favoni, V.J. Forrat Pérez, I.D. Olteanu, M.D. Romero Sanchez, A. Vivarelli, A. Bonazza, “Innovative consolidating products for stone materials: field exposure tests as a valid approach for assessing durability”, Herit. Sci, vol. 3, No. 6, March 2015, pp. 1-13.

[7] M. Melis, M. Miccoli, M. Melis, D. Quarta, “Multispectral Hypercolorimetry and automatic guided pigment identification: some masterpieces case studies”, Proc. SPIE 8790, Optics for Arts, Architecture, and Archaeology IV, 2013, Article number 87900W, pp. 1-14.

[8] C. Colantonio, C. Pelosi, L. D’Alessandro, S. Sottile, G. Calabrò, M. Melis, “Hypercolorimetric multispectral imaging system for cultural heritage diagnostics: an innovative study for copper painting examination”, Eur. Phys. J. Plus, vol. 133, No. 526, 2018, pp. 1-12.

[9] L. Lanteri, C. Pelosi, “2D and 3D ultraviolet fluorescence applications on cultural heritage paintings and objects through a low-cost approach for diagnostics and documentation”, Proc. of the SPIE 11784, Optics for Arts, Architecture, and Archaeology VIII, Munich, Germany, 8 July 2021; pp. 1–10.

[10] R. Vettraino, V. Valentini, P. Pogliani, M. Ricci, S. Laureti, S. Calvelli, R. Zito, L. Lanteri, C. Pelosi, “Multi-Technique Approach by Traditional and Innovative Methodologies to Support the Restoration of a Wall Painting from the 16th Century at Palazzo Gallo in Bagnaia, Viterbo, Central Italy”, Buildings, vol. 13, No. 783, March 2023, pp. 1-21.

[11] A. Cosentino, “Effects of different binders on technical photography and infrared reflectography of 54 historical pigments”, Int. J. Conserv. Sci., vol. 6, No. 3, 2015, pp. 287-298.

[12] A. Defus, A. Sansonetti, E. Possenti, C. Tedeschi, S. Vettori, M. Realini, “The effectiveness of di-ammonium hydrogen phosphate (DAP) consolidation treatment on lime-based mortars weathered by freeze-thaw cycles”, J. Cult. Herit., vol. 50, 2021, pp. 1-12.

[13] M.R. Derrick, D. Stulik, J.M. Landry, “Infrared Spectroscopy in Conservation Science”, The Getty Conservation Institute, Los Angeles, USA, 1999.

[14] I. Adrover Gracia, “Applicazion della spettrofotometria IR allo studio dei beni culturali”, Collana I Talenti, Il Prato, Padova, Italy, 2001.