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ADVANCED DOCUMENTATION METHODOLOGIES COMBINED WITH MULTI-ANALYTICAL APPROACH FOR THE PRESERVATION AND RESTORATION OF 18TH CENTURY ARCHITECTURAL DECORATIVE ELEMENTS AT PALAZZO NUZZI IN ORTE (CENTRAL ITALY)

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Abstract

This contribution reports the documentation of the conservation status and the pictorial technique of a wall painting and a stucco arch at Palazzo Nuzzi in Orte, central Italy (Viterbo district), achieved using a wide combination of non-invasive and micro-invasive diagnostic techniques. Specifically, a photogrammetric approach has been used for 2D and 3D ultraviolet fluorescence (UVF) acquisitions. Moreover, the conservation status of the wall painting has been also investigated by a non-invasive active infrared thermograghy technique, i.e. Pulse Compression Thermography (PuCT), used here for the first time on a wall painting to map the surface and sub-surface cracks in the first layers.
Pigments, grounds and organic binders were characterised by X-ray fluorescence spectroscopy, micro-stratigraphic analysis, Fourier transform infrared spectroscopy and gas chromatography coupled with mass spectrometry. The results of this unique combination of advanced tools corroborated the historical-artistic attribution to the school of the architect Andrea Pozzo.

Keywords*: Wall painting; Stucco arch; Andrea Pozzo school; UVF photogrammetry; Pulse-compression thermography; Multi-analytical techniques*

Introduction

Monitoring the state of conservation of cultural heritage (CH) items, including architecture decorated surfaces, is of utmost importance for promptly planning any needed restoration activities for preserving such irreplicable items from the inevitable march of time [1-3].

Over the last couple of decades, many efforts have been made by both restorers and researchers in finding a common ground for improving the effectiveness of both the diagnostic and restoration activities. In fact, using advanced diagnostic tools and their results'

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interpretation are complementary steps, thus requiring both restorers and researchers/operators to work jointly, fusing their expertise and know-how for reaching a thorough understanding of the artwork. In this framework, this paper shows the results of different diagnostics and analysis performed over a wall painting and on the stucco arch within a room (Figure 1) in the noble floor of Palazzo Nuzzi in Orte (Viterbo district, central Italy) [4, 5].

Fig. 1. A view of the room in the Palazzo Nuzzi at the beginning of the restoration activity

The architectural decorative pattern of this room was commissioned by Cardinal Ferdinando Nuzzi around 1715 to embellish his bedroom [6]. The wall painting depicts the episode of Muzio Scevola and Porsenna framed by figures in grisaille and floral elements (Figure 2, left). The stucco decoration consists of an arch with the Nuzzi's family heraldic coat of arms on top of it and decorated with imitation marble and gold leaf elements (Figure 2, right).

As a pivot activity within the Master's Degree in Conservation and Restoration of Cultural Heritage at the University of Tuscia, both the wall painting and the arch have recently undergone through restoration performed by two students, which is still in progress and will be concluded in the few next months. Therefore, a thorough historical-artistic research about the mentioned items has been carried out, leading to the hypothesis of attribution of the decorative cycle to the school of Jesuit's Roman baroque style, and in particular to the that of the architect Andrea Pozzo [7].

The study and the first restoration step of both artworks, i.e. wall painting and stucco arch, have been supported by several techniques operating both in situ and in the laboratory on micro-samples, being today essential to perform diagnostics before restoration and maintenance interventions for the assessment of the state of conservation, specifically of historical architectural surfaces, and more in general of cultural heritage items [8-10]. Particularly, ultraviolet fluorescence (UVF) photography through an innovative photogrammetric approach and X-ray fluorescence (XRF) spectroscopy have been used as non-invasive techniques to obtain information on the general conservation status and on painting materials respectively [11]. A limited area of the wall painting has been investigated through Pulse compression thermography (PuCT), which has been here applied for the first time in situ on a wall painting

for detecting possible cracks, defects and detachment in the surface and sub-surfaces layers [10-13].

Fig. 2. Orthophotomosaic of the wall painting (left) and the stucco arch (right) after the first restoration step performed between 2019 and 2020 (Credits: Francesca Groppi and Davide Vigliotti)

The non-invasive documentation and analysis addressed the choice of sampling points for further laboratory investigation via micro-stratigraphic observation, Fourier transform infrared (FTIR) spectroscopy and gas chromatography coupled with mass spectrometry (GC-MS). These techniques have been chosen to gather information about the stratigraphy of the painted surfaces, on the inorganic and organic binders. It is shown that the combined use of such an extensive amount of different techniques confirmed the attribution of the artworks to the school of Andrea Pozzo, as supposed by the historical-artistic research with the minimum possible amount of micro-invasive sampling.

Experimental part

Ultraviolet fluorescence photogrammetric technique

The UVF digital documentation of the artworks has been obtained through image-based systems using two different approaches. In fact, the wall painting's surface can be considered flat, whereas the arch can be assumed as being a 3D object. The acquisition of UVF frames has been performed through a no metric Nikon D5300 digital SLR camera, equipped with a 35 mm focal lens set with the following parameters: f/11, exposure time equal to 25s, ISO-200 sensitivity. A pair of CR230B-HP 10W LED projectors with maximum emission at 365nm has been used for the UVF imaging. As a rule of thumb, the tilting of the optical camera should not exceed 10°/15° with respect to the inspected surface, so as to reduce the effect of perspective deformations. Thus, the camera has been lifted at 4.5 meters from the floor to get the photograms of the upper portions of the wall and arch.

In the case of wall painting, the UVF ortho-photomosaic was created starting from eighteen photograms orthorectified and mosaiced according to the analytical procedure of the monoscopic simplified photogrammetry. The chosen methodology assumes that the imaged object is flat, thus reducing the unknowns from the three spatial coordinates, to two ones (X and Y). The unknowns can be found by using the two collinearity equations (direct relationship

between object point and image point), so as to obtain a corrected photographic image through the homographic transformations, i.e. a perspective generated by a central conical projection. Homographic transformations have eight degrees of freedom (except the scale factor), which depend on the orientation of the image plane with respect to the object plane, as well as on the internal orientation parameters of the camera. The projective equation can be solved if the coordinates of at least four object points are known, expressed in the object reference system, and identifiable in the image reference system, plus one point to determine the scale factor. For this reason, at least five ground control points (GCPs) with known Cartesian coordinates must be recognized for each frame. In compliance with the non-invasive approach, the GCPs have been selected among easily-recognizable and unequivocally collimable decorative elements of the wall painting. Specifically, the coordinates of the GCPs have been obtained through topographic measurements using a total station Topcon model GPT 7500 equipped with an infrared distance-meter.

In the case of stucco arch, the photographic documentation aimed at creating a 3D model. For this reason, an image based system developed with the Structure from Motion (SfM) technique has been used which integrates digital photogrammetry and the computer vision facilities, as previously detailed [14, 15]. The related software uses the SIFT algorithm (Scale Invariant Feature Transform) to calculate and detecting the positions of the homologous points (pixels) for establishing the spatial relationships within a relative XYZ coordinate system throughout the image set arranging the pictures according to the calculated parameters. Subsequently, the bundle adjustment algorithm controls and limits errors during the transformation of the coordinates of the 3D points taken in a cloud of points more or less dense depending on the amount of key points detected. The subsequent phase involves the generation of a dense cloud points through the dense image matching algorithms. These are divided into two types: area based matching (AMB) algorithms that perform statistical comparison of the intensity of grey tones detected on the images, but do not provide for the extraction of the features; and feature based matching (FBM) algorithms that first look for common features and then extract them. At the end of the image processing, a photorealistic 3D digital model is obtained, with the possibility of extracting Triangulated Irregular Networks (TIN), Digital Elevation Models (DEM) and producing Digital Orthophoto Maps (DOM).

Pulse-compression thermography (PuCT)

Pulse-compression thermography (PuCT) is an active infrared thermography scheme - also known as Thermal Wave Radar Imaging - wherein the use of coded waveforms for modulating the heat source emission and the so-called pulse-compression procedure are combined together for obtaining unique advantages. In fact, in PuCT the bandwidth and the duration of the coded signal are uncorrelated, meaning that the heat can be spread over long time to avoid any thermal shock/thermochromism, while choosing a range of suitable penetration depths tuning the signal bandwidth. Note that this is not possible with other common active thermography schemes, such as Pulsed thermography or Lock-in thermography, as the signal bandwidth/duration is univocally linked to each other. For the PuCT imaging, the signal generation/acquisition has been managed by LabVIEW software, and thermograms have been collected via a Xenics Onca-MWIR (3.6–4.9μm)-InSb infrared camera placed in reflection mode, having a resolution of 320×240 pixels, connected to a National Instrument NI-1433 Camera Link Frame Grabber. The distance between the painted surface and the camera was of about 50cm, and eight LED chips emitting in the visible spectrum have been used as heat source with an operating total power of about 110W. The coded excitation driving the LEDs was provided by a TDK Lambda GEN 750W power supply. The experimental setup used is the same detailed in previous published papers to which the reader is referred for an in-depth theoretical insight of the PuCT technique [12, 16-18].

X-ray fluorescence spectroscopy (XRF)

XRF analysis was performed through a Surface Monitor II (Assing™) spectrometer operating at the following conditions: Ag tube operating at 40kV, current 76μA, acquisition time equal to 60s, distance of 94mm from the analysed surface, spot of 2mm. The XRF spectrometer was equipped with Amptek X-123 Si-PIN detector, resolution 145 to 260eV at 5.9keV, optimum energy range 1–40keV. Spectra have been collected by Gonio software by Assing, which has been used also for gathering the counts per second (cps) of each detected element. Points of analysis have been highlighted with an alphanumeric abbreviation, i.e. the letter X followed by a progressive number.

Microscope observation and Fourier transform infrared spectroscopy (FTIR)

Micro-samples from the wall painting and from the arch have been collected after a careful on-site observation via magnifying lenses and portable videomicroscope.

Sample powders and micro-fragments have been observed with a stereo Olympus SZ and Zeiss polarizing microscope. The latter was equipped with a digital camera Zeiss AxioCam directly connected to a computer for capturing and saving the observed images.

After microscope observation, the samples have been analysed by Fourier transform infrared (FTIR) spectroscopy by using a Nicolet Avatar 360 instrument equipped with a DTGS (Deuterated TriGlycine Sulphate) detector. The FTIR spectrometer operates in the 400-4000cm^{-1} spectral range with a resolution of 4 cm^{-1}. Sample powders were grounded in agate mortar with potassium bromide (KBr) used also as background material. For each sample, 128 scans have been acquired in diffuse reflectance modality (DRIFT).

Gas chromatography coupled with mass spectrometry (GC-MS)

In order to characterize the binder and the superimposed materials of the painted surfaces, an Agilent Technologies 7820A gas chromatograph coupled to an Agilent Technologies 5977B mass spectrometer with single quadrupole has been used. The mass spectrometer operated in the EI positive mode (70eV). Separation of components has been done by means of a fused-silica capillary column (SLB-5) with a 0.25μm (30m x 0.25mm x 0.25μm) methyl-silicone (5% phenyl) film.

Fatty acid and amino acid analytical procedures - The basic methodology relies on the identification of fatty acids and amino acids on the same sample. Two chromatograms have been collected for each sample: the first one from fatty acid derivatives, the second from amino acid oness. The internal standard considered were: tetracosane (100μL, 50ppm) for the analysis of fatty acids; norleucine (100μL, 2.5mM) for the amino acids analysis.

The samples have been treated with CH_3OH/HCl 5% and extracted with n-hexane for 2h at 50°C. The n-hexane phase, which contains fatty acid methyl-esters, has been used for gas chromatographic analysis (1μL). Separation of the methyl ester of fatty acids has been achieved following this temperature program: isothermal conditions at 60°C for 2min, with 20°C/min heating up to 220°C and isothermal conditions at 220°C for 8min, then from 220 to 280°C (20°C/min) and final isotherm at 280°C for 4min. After evaporation to dryness of the methanol phase, the residues were dissolved in 6N hydrochloric acid (0.4mL) and hydrolysed in a screw-capped container for six hours at 90°C under nitrogen atmosphere. Then, 100μL of norleucine 2.5mM has been added, samples have been evaporated to dryness, and 0.4mL of 2N HCl in propan-2-ol at 90°C for one hour. After cooling, the solvent has been evaporated under vacuum and the residue dissolved in 0.3mL of dichloromethane and 0.5 ml of trifluoroacetic anhydride (TFA) at 60°C for 30min. After cooling, the solvent has been evaporated under vacuum and the residue of the sample dissolved in 1mL of CH_2Cl_2, then the solution was used for gas-chromatographic analysis (1μL). Separation of N-trifluoroacetyl-O-2-propyl esters amino acids derivatives has been achieved following this temperature program: isothermal conditions at 60°C for 3min, with 20°C/min heating up to 280°C and isothermal conditions at 280°C for 12min.

The mass spectra have been collected under the following operative conditions: solvent delay 3.50 min, detector temperature 280°C, source temperature 230°C, scan m/z 41-400.

To identify the proteinaceous binding media, the percentage content of amino acids in each sample has been compared to those from a dataset of 62 reference samples of egg (whole, egg yolk, egg white), casein, animal glue and mixtures of these components belonging to the reference collection of the *Opificio delle Pietre Dure* of Florence, Italy [19].

Principal component analysis (PCA) has been performed on the correlation matrix of the relative percentage contents of eight amino acids (alanine, glycine, leucine, proline, hydroxyproline, aspartic acid, glutamic acid, and phenylalanine) components [20, 21].

Results and discussion

The first step of the diagnostic campaign involved the UVF photography, which is commonly used by restorers as a fundamental step to look at the conservation status of the surfaces, to observe repainting and reintegration, to map cracking and possible defect of the surface etc. [14, 22-24]. The results of photographic acquisition and image processing through photogrammetry are reported in figure 3.

Concerning the wall painting, the UVF photography highlighted three main kinds of fluorescence: (i) light blue fluorescence diffused on the entire surface, being particularly evident in the background and on the floral wreaths. This fluorescence could be associated to the organic binder of the painting, as it is visible on the whole surface; (ii) a yellow fluorescence observed in the white areas, possibly caused from the presence of zinc white [25]; (iii) an orange fluorescence localized in few limited areas of the painting and probably associated with pictorial reintegration due to past restorations, such as in the base of the right caryatid [4].

In the case of the arch, UVF images highlight the presence of a thick varnish layer above the imitation marble. Furthermore, it is possible to appreciate the thickness of this surface varnish. In fact, this material acquires a markedly browner colour in many areas of the arch surface, significantly masking the false marble decoration beneath. It is also possible to recognize the recent pictorial reintegration interventions of the ‘80s, as they are well highlighted by a dark colour under UV radiation [5].

Fig. 3. UVF orthophotomosaic of the entire wall painting and of the stucco arch after recomposition and processing of the acquired images, before restoration (Credits: Francesca Groppi and Davide Vigliotti)

The gold leaf of the decorative elements is characterized by a dark-brown fluorescence, while the ground layer shows a yellow-orange fluorescence. Lastly, the presence of surface dirt deposits, characterized by a dark colour under UV, makes the interpretation of the original gilding even more complicated. Details of the above-mentioned fluorescence typologies are shown in the figure 4.

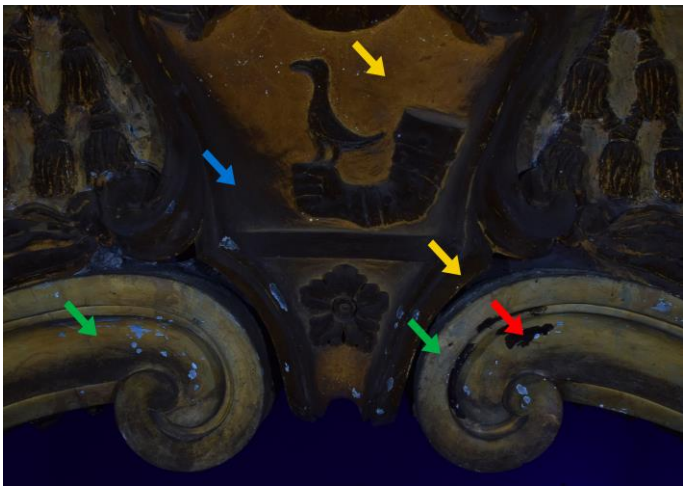

Fig. 4. UVF detail image of the lower portion of the heraldic coat of arms. It is possible to observe: the heterogeneous thickness of the varnish (green arrows); the repainting of the 80s of the last century (red arrow); the different ultraviolet response of the gold leaf and its ground layer (yellow and orange arrow respectively); the fluorescence of the dirt deposit (blue arrow).VF images of the entire wall painting and of the stucco arch after recomposition and processing of the acquired images, before restoration (Credits: Davide Vigliottti)

The conservation status of the wall paintings has been also investigated through Pulse compression thermography (PuCT), which is an active infrared thermography technique applied here for the first time to a wall painting. PuCT has been carried out over a selected area (Fig. 5A) of the wall to detect cracks and defects of the first layers of the wall paintings [4].

The acquisition and processing of PuCT data returned a series of infrared images as time elapses (thermograms) recorded during the cooling period of the wall following the thermal coded pulse. The intensity of the pixels in each of these frames corresponds to the response that the material has in relation to the thermal impulse. The initial heat emission returned images relating to the most superficial layers of the painting, while the deeper layers are recorded at longer cooling times.

Since the materials of the painting are heterogeneous and their resistivity coefficients are not known, the analysis carried is not aimed at quantifying the actual depth reached by the thermal impulse, but to perform a purely qualitative analysis that discriminates the temperature differences within the materials and layers. The different temperatures can be observed on the thermograms through a grey scale, in which the light areas refer to low temperature while the dark areas would correspond to those characterized by higher temperatures, therefore warmer.

From the results of the thermographic campaign before consolidation, a series of significant information regarding the state of conservation have been obtained. In the first series of images, relating to the initial cooling phase of the surface (T = 1.5s), dark areas appear near to the fractures and correspond to lacunae and lifting of the first painting layer (Figure 5B, yellow ellipses). White lacunae appear in some points of the thermogram suggesting the flaking of the pictorial film (Fig. 5B, red circles) [4].

In the thermograms related to longer cooling times (T = 3.5 and 12.5s, Fig. 5C-D), it can be seen that some of the forms of alteration initially recorded (T = 1.5s) are no longer visible

here, while others seem to be accentuated. The defects which in the T = 1.5s thermogram are more marked and appear as black, are thought to belong to deeper preparatory layers (see yellow ellipses in the figures 5C-D and red arrows in the figure 5C).

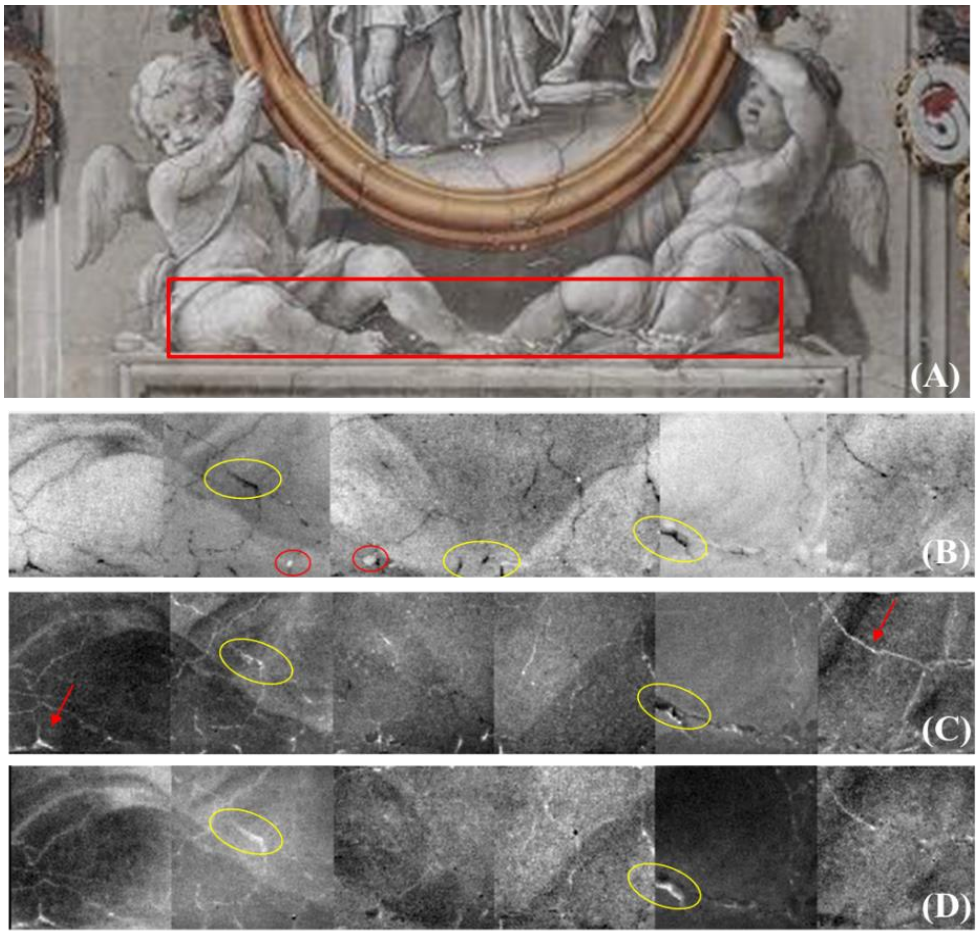

Fig. 5. Results of PuCT analysis before restoration. (A) The investigated area in the red frame; (B) thermogram at time 1.5s; (C) thermogram at time 3.5s; and (D) thermogram at time 12.5s

The results of UVF photogrammetric documentation and PuCT analysis have been highly useful to address further investigation and, above all, to choose and limit the sampling points for laboratory analysis.

Constitutive materials (pigments, binders and possible restoration compounds) have been investigated through XRF and FTIR spectroscopy, micro-stratigraphic observation and GC-MS analysis.

Results of XRF spectroscopy on selected analysis points of the wall painting and stucco arch are provided in table 1 in terms of the main detected elements. In all points of analysis of the wall painting, Ca and Sr elements have been detected, suggesting the presence of gypsum. In fact, Sr is systematically associated to Ca, as occurs when Ca and Sr sulphates are present [26, 27]. This hypothesis was confirmed by the presence of S, and also by FTIR spectroscopy analysis that revealed the use of gypsum in the wall painting (Table 2) and also by the micro-stratigraphic analysis (Fig. 6).

The stratigraphic analysis allows for obtaining information about the the wall painting' layers: (1) is the ground layer (mortar); (2) a white priming characterised by an intense light blue fluorescence: (3) and (4) light yellow painting, probably applied in two different layers and (5) white surface layer with light yellow fluorescence. By combining the results derived by FTIR spectroscopy and cross-section examination, it can be derived that the painting was applied by secco technique on priming made of gypsum and protein binder (light blue fluorescence). This result is highly meaningful as it confirms that the execution technique is in accordance with the indications supplied in the *Trattato* by Andrea Pozzo [7, 28-30].

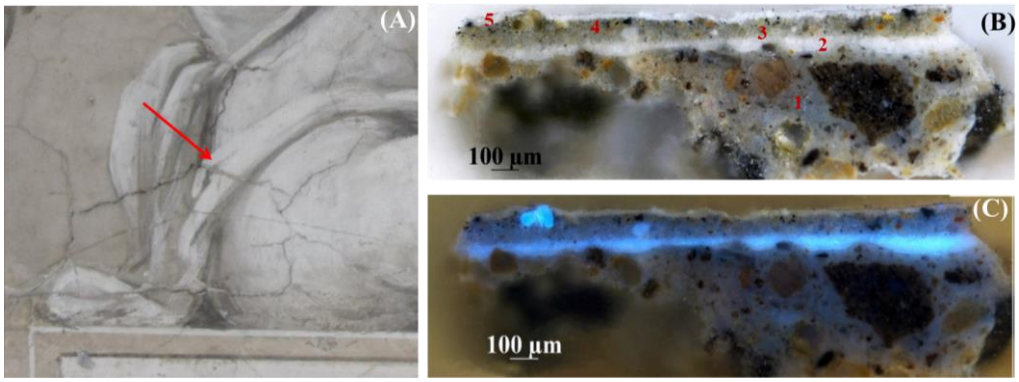

Fig. 6. Microstratigraphic analysis: (A) image of the sampling point; (B) cross-section under reflected light; and (C) the same cross-section under UV fluorescence

Table 1. Synthesis of XRF results on the painted surfaces

Point and colour	Detected elements	Hypothesized pigments on the base of XRF data
WALL PAINTING		
X1 - Thin white frame	Pb (main), Ca, Fe, Sr, S	Lead white. Ca, Sr, Fe and S are elements of the ground layers
X2 - Thick white frame	Pb (main), Ca, Sr, Fe, S, Zn	Lead white. Ca, Sr, Fe and S are elements of the ground layers. Zn is probably due to a repainting
X3 - White area on the knee of the left putto	Pb (main), Ca, Sr, Zn, S, Fe	Lead white. Zn is probably due to a repainting. Ca, Sr, S and Fe are elements of the ground layers
X4 – Yellow of the leaf (left side)	Fe (main), Ca, Pb, Sr, S	Fe-based yellow pigment, lead white
X5 – Light yellow near the left caryatid	Fe (main), Ca, Sr, Pb, K, Mn	Fe-based pigment, lead white
X6 – Brown area near to the left caryatid	Fe (main), Ca, Mn, Pb, Sr	Fe/Mn-based pigment (probably umber), lead white
X7 – Background (beige colour)	Ca (main), Sr, Fe, Pb (tr)	Ca-based white
X8 – Brown shade on the red flower, right side	Hg and Pb (main elements), Ca, Sr, Fe, S	Vermilion, lead white
X9 – Red flower on the right side	Pb and Hg (main elements), Ca, Fe, Sr, S	Vermilion, lead white
X10 – Blue flower on the right side	As (main), Pb, Fe, Co, Ca, Sr, Cu, K	Lead white, cobalt blue, Emerald green (possible repainting)
X11 – Blue flower on the right side (other point)	As (main), Pb, Fe, Co, Ca, Cu, Sr, K	Lead white, cobalt blue, Emerald green (possible repainting)
X12 – Thin white layer on the putto's leg	Pb (main), Ca, Sr, Fe, S	Lead white.
X13 – Blue flower in the central area	As (main), Fe, Co, Cu, Ca, Sr, K	Blue smalt or cobalt blue, Emerald blue (possible repainting)
X14 – Yellow circle in the central area	Fe (main), Pb, Ca, Sr	Fe-based pigment and lead white
X15 – Background (beige colour) in the central area	Ca (main), Fe, Sr, Rb (tr)	Ca-based white

Point and colour	Detected elements	Hypothesized pigments on the base of XRF data
STUCCO ARCH		
X1 – Dark green colour of the false marble decoration	Fe (main), Pb, Ca, Sr, K	Green earth and lead white
X2 – Light green colour of the false marble decoration	Fe (main), Ca, Pb, Sr, K	Green earth, lead white and Ca-based pigment
X3 – White colour of the false marble decoration	Pb (main), Ca, Fe, Sr, S	Lead white
X4 – White ground layer of the false marble decoration	Ca (main), Sr	Ca-based compound
X5 – Dark red colour of the false marble	Fe (main), Ca, Sr, Pb, K, S	Fe-based pigment, Pb-based pigment
X6 – Brown colour of the false marble decoration	Ca (main), Fe, Sr, Pb, S	Fe-based pigment, lead white
X7 – Gold leaf on the stucco surface	Pb (main), Fe, Au, Ca, Sr, S, Mn	Gold applied on a ground based on Pb and Fe pigments
X8 – Orange layer under the gold leaf	Pb (main), Fe, Au, Ca, Sr	Gold leaf, Pb and Fe -based pigments.
X9 – Ground layer under the repainting	Ca (main), Sr, Fe, S	Probably gypsum
X10 – Red colour of the Cardinal's hat	Hg (main), Pb, Ca/S/Fe (tr)	Vermilion, Pb-based pigment

The presence of lead white was confirmed by FTIR spectroscopy, showing the main signatures of the basic lead carbonate constituting this pigment, partially overlapped with those of gypsum and calcium carbonate (Table 2).

Regarding the stucco arch, the ground layer of the false marble decoration has the appearance of white mortar based on slaked lime and limestone powder in equal parts, in accordance with the stucco technique described in documentary and literary sources [31, 32].

This visual observation has been further confirmed by FTIR spectroscopy that showed the main signatures of calcium carbonate (Table 2), and by micro-stratigraphic analysis that allowed distinguishing the limestone powder under UV as it results in less fluorescent areas compared to the mortar matrix (Fig. 7). The other materials detected in the FTIR spectrum are due to partial contribution of the red layer and of the surface restoration materials that were not completely separated from the ground.

Table 2. Results FTIR analysis on the pictorial film of the wall painting and of the ground layer of stucco arch

Sampling point	Wavelength (cm^{-1})	Hypothesized material
White layer of the pictorial film	3546(m), 3401(m-w), 3244(w), 2247(w),1689(w), 1620(m-w), 1124(s), 671(m),605(m),501(w), 449(w)	Gypsum
	2509(w), 1799(w), 1455(s), 876(m), 712(m-w)	Calcium carbonate
	3244(w), 2922(m), 2857(m-w), 1661(w), 1588(w), 1455(s),	Proteins
	3546(m), 1410 (s), 1322(m-w), 1043(w)	Lead white
White ground layer of the false marble decoration in the stucco arch	2982(m), 2875(m), 2513(s), 1793(m), 1457(vs), 875(vs), 718(s)	Calcium carbonate (main)
	3638 (vw), 1166(m), 1086(w), 1016(w), 945(w), 785(m), 516(w)	Silicates and quartz (minor)
	3543(w), 3406(w), 1142 (vw), 669(w), 613(w), 460 (vw)	Gypsum (tr)
	1732 (vw), 1644(vw), 1585(w), 1239 (vw)	Traces of organics

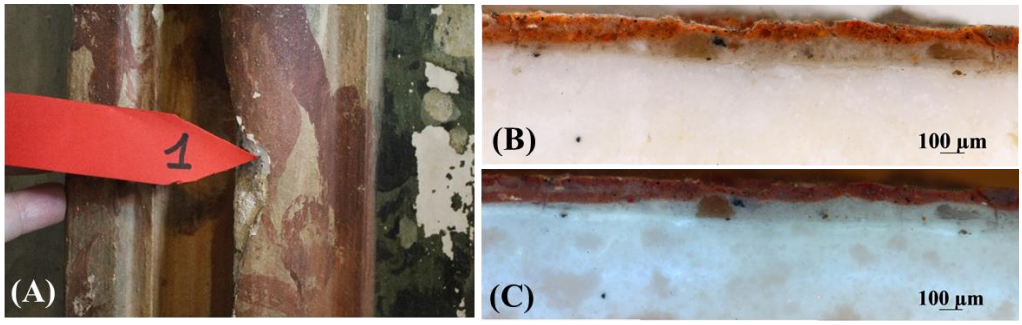

Fig. 7. Microstratigraphic analysis on the false marble decoration in the stucco arch:
(A) image of the sampling point; (B) cross-section under reflected light;
(C) the same cross-section under UV fluorescence

To continue the interpretation of the XRF data, the presence of Fe in all examined points is probably associated to the mortar that acts as support for the painting layers and, when present in higher counts, it may be the chromophore element of red, yellow and green pigments. Pb has been also found in the examined points, both in the painting and in the arch surfaces. It can be associated to lead white but also to other Pb-based pigments such as red lead and lead oxides. Other elements detected by XRF analysis are Mn that, associated to Fe, suggests the use of umber and/or other kinds of earths, Hg that can be associated to vermilion/cinnabar, Au in the gilded areas of the stucco's arch, traces of Zn in the wall painting probably associated to repainting. In the blue flower of the wall painting As, Co, and Cu have been revealed [33]. These elements have been attributed to retouching pigments based on Emerald green and cobalt blue (Table 1).

The proteinaceous and lipidic compounds were further characterised by GC-MS. This last technique has been performed on four selected samples: two from the wall painting (sample D1 and D9) and two from the stucco arch (sample D5 and D6).

The PCA-based evaluation, whose score plot is reported in figure 8, locates all the samples in a new cluster suggesting a mixture of egg and animal glue binders.

The lipid fraction found in the examined samples, mainly palmitic, oleic and stearic acids, is due to the lipid content of egg yolk.

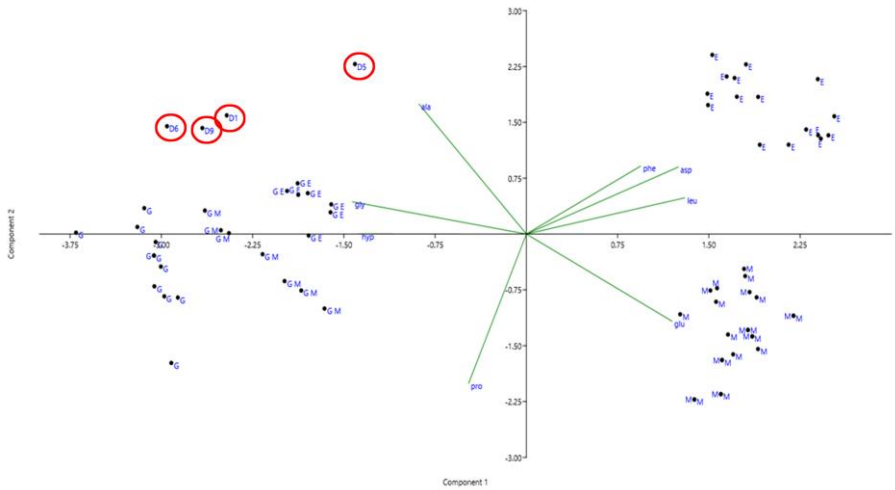

Fig. 7. Score plot of reference materials and artistic samples
(G: animal glue; GE: animal glue and egg, GM: animal glue and milk, M: milk; E: egg)

Conclusions

The non-invasive campaign allowed for obtaining useful and wide information about the conservation status and the possible previous restorations, but above all it addressed the sampling to limit the number of micro-fragments from the painting and stucco arch. In fact, the sampling was aimed at studying the stratigraphy and the organic binder. Micro-samples were investigated by Fourier transform infrared spectroscopy, polarizing microscope observation of cross-sections and gas chromatography coupled with mass spectrometry to completely characterize the organic binder.

The results obtained by the combination of the different techniques, including the Pulse-compression Thermography used here for the first time for the diagnosis of a wall painting, allowed demonstrating that the two decoration pieces are contemporary and have been realized with the same executive procedures. The pictorial technique shows a close correspondence with the indications provided by Andrea Pozzo in the *Breve istruzione per dipingere a fresco*, contained in his famous *Trattato*, both for the modality of painting realization and for the used materials. This is a fundamental result as it allowed for including the artworks in the artistic field of the tempera paintings of the Pozzo's school. The diagnostic approach was also highly relevant for the restoration itself as it aided in preserving and valorising the architectural surfaces of the rooms in the Palazzo Nuzzi, especially in the view of the future recovery and enhancement of the building.

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References

[1] M.R. Escorteganha, A.G. Santiago, H.A. Magosso, F.A. Richter, T.G. Costa, *Conservation State of Mural Paintings from a Historic House in Florianópolis-SC, Brazil. A Multidisciplinary Approach*, **International Journal of Conservation Science**, **4**(1), 2013, pp. 13-24.

[2] S. Sfarra, C. Ibarra-Castanedo, M. Tortora, L. Arrizza, G. Cerichelli, I. Nardia, X. Maldague, *Diagnostics of wall paintings: A smart and reliable approach*, **Journal of Cultural Heritage**, **18**, 2016, pp. 229-241.

[3] M. Alfred, J.A.C. Broekaert, *Mobile depth profiling and subsurface imaging techniques for historical paintings—a review*, **Spectrochimica Acta Part B**, **88**, 2013, pp. 211–230.

[4] F. Groppi, *Muzio Scevola e Porsenna nel palazzo Nuzzi a Orte. Restauro e diagnostica di un dipinto murale*, **Master Degree Thesis,** University of Tuscia, Viterbo (Italy), 2020 p. 309.

[5] D. Vigliotti, *Sinergie per il recupero dell'arco in stucco e finti marmi di Palazzo Nuzzi a Orte. Storia dell'arte, restauro, tecniche diagnostiche e documentazione digitale*, **Master Degree Thesis**, University of Tuscia, Viterbo (Italy), 2020 p. 207.

[6] S.E. Anselmi, **Committenze a Orte in età barocca, cultura gesuita e influenza pozziana. Gli Alberti e i Nuzzi**, Argos, 2006, p. 240.

[7] C. Bigari, A*ndrea Pozzo e Antonio Colli da Trinità dei Monti alle opere toscane. Nuovi contributi sulla tecnica pittorica, in Artifizi della metafora. Saggi su Andrea Pozzo*. In: **Atti del convegno internazionale di studi** (editors: R. Bösel, L. Salviucci Insolera), Artemide, 2011, pp. 127-142.

[8] E. Zendri, L. Falchi, F.C. Izzo, Z.M. Morabito, G. Driussi, *A review of common NDTs in the monitoring and preservation of historical architectural surfaces*, **International Journal of Architectural Heritage**, **11**(7), 2017, pp. 987-1004.

[9] S. Bracci, G. Bartolozzi, *Wall paintings – diagnostic and archaeometric studies*, **Physical Sciences Reviews**, **4**(4), 2019, Article Number: 20180013.

[10] I. Sandu, C.T. Iurcovschi, I.G. Sandu, V. Vasilache, I.C. Negru, M. Brebu, P.S. Ursu, V. Pelin, *Multianalytical Study for Establishing the Historical Contexts of the Church of the Holy Archangels from Cicau, Alba County, Romania, for its Promotion as a World Heritage Good I. Assessing the preservation-restoration works from the 18th century*, **Revista de Chimie, 70**(7), 2019, pp. 2538-2544.

[11] I. Catapano, G. Ludeno, C. Cucci, M. Picollo, L. Stefani, K. Fukunaga, *Noninvasive Analytical and Diagnostic Technologies for Studying Early Renaissance Wall Paintings*, **Surveys in Geophysics, 41**, 2020, pp. 669-693.

[12] S. Laureti, S. Sfarra, H. Malekmohammadi, P. Burrascano, D.A. Hutchins, L. Senni, G. Silipigni, X.P.V. Maldague, M. Ricci, *The use of pulse-compression thermography for detecting defects in paintings*, **NDT&E International**, **98**, 2018, pp. 147–154.

[13] G. Agresti, P. Burrascano, G. Calabrò, C. Colantonio, L. Lanteri, S. Laureti, M. Melis, C. Pelosi, M. Ricci, S. Sfarra, *Hypercolorimetric multispectral Imaging and Pulse Compression thermography as innovative combined techniques for painting investigation: the case of a detached wall painting by Pastura*, **IOP Conf. Series: Materials Science and Engineering**, **949**, 2020, Article Number: 012008.

[14] L. Lanteri, G. Agresti, C. Pelosi, C. 2019. *A New Practical Approach for 3D Documentation in Ultraviolet Fluorescence and Infrared Reflectography of Polychromatic Sculptures as Fundamental Step in Restoration*, **Heritage, 2**, 2019, pp. 207-215.

[15] L. Lanteri, G. Agresti, *Ultraviolet fluorescence 3D models for diagnostics of Cultural Heritage*, **European Journal of Science and Theology**, **13**(2), 2017, pp. 35-40.

[16] S. Laureti, C. Colantonio, P. Burrascano, M. Melis, G. Calabrò, H. Malekmohammadi, S. Sfarra, M. Ricci, C. Pelosi, *Development of integrated innovative techniques for the examination of paintings: the case studies of The Resurrection of Christ attributed to Andrea Mantegna and the Crucifixion of Viterbo attributed to Michelangelo's workshop*, **Journal of Cultural Heritage, 40,** 2019, pp. 1-16.

[17] S. Laureti, H. Malekmohammadi, M. Khalid Rizwan, P. Burrascano, S. Sfarra, M. Mostacci, M. Ricci, *Looking Through Paintings by Combining Hyper-Spectral Imaging and Pulse-Compression Thermography*, **Sensors, 19,** 2019, Article Number: 4335.

[18] G. Silipigni, P. Burrascano, D.A. Hutchins, S. Laureti, R. Petrucci, L. Senni, L. Torre, M. Ricci, *Optimization of the pulse-compression technique applied to the infrared thermography nondestructive evaluation*, **NDT&E International, 87**, 2017, pp. 100–110.

[19] G. Lanterna, A. Mairani, M. Matteini, M. Rizzi, A. Vigato, *Characterisation of decay markers on pictorial models simulating ancient polychromies*, **Proceedings of the 2nd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin** (editor: A. Ferrari) A., Elsevier, 2000, pp. 487-489.

[20] A. Casoli, A. Montanari, L. Palla, *Painted models simulating ancient polychromies: a statistical analysis of chemical results*, **Proceedings of 3rd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin** (editor: A. Guarino), Elsevier, 2001, pp. 839-845.

[21] A. Casoli, S. Santoro, *Organic materials in the wall paintings in Pompei: a case study of Insula del Centenario*, **Chemistry Central Journal**, **6**, 2012, Article Number: 107.

[22] S. Abdelaal, I.C.A. Sandu, *Assessment of protease in cleaning of bat blood patches from ancient egyptian wall paintings and surface inscriptions*, **International Journal of Conservation Science, 10**(3), 2019, pp. 459-474.

[23] C. Pelosi, L. Lanteri, G. Agresti, U. Santamaria, *Documentation and Scientific Investigation on the 'Crucifixion' by Balletta in the church of Santa Maria Nova in Viterbo (Italy). Conservation and Religious Requirements*, **European Journal of Science and Theology**, **12**(1), 2016, pp. 271-281.
[24] A. Cosentino, *Practical notes on ultraviolet technical photography for art examination*, **Conservar Património**, **21**, 2015, pp. 53–62.
[25] A. Cosentino, *Effects of different binders on technical photography and infrared reflectography of 54 historical pigments*, **International Journal of Conservation Science, 6**(3), 2015, pp. 287-298.
[26] M. Sbroscia, C. Pelosi, G. Agresti, A. Paolucci, P. Pogliani, L. Ruggiero, A. Sodo, *Spectroscopic investigation of Cappadocia proto-Byzantine paintings*, **Journal of Raman Spectroscopy**, **51**(1), 2021, pp. 95-108.
[27] E. Franceschi, F. Locardi, *Strontium, a new marker of the origin of gypsum in cultural heritage?*, **Journal of Cultural Heritage, 15**, 2014, pp. 522-527.
[28] A. Pozzo, **Perspectiva Pictorum et Architectorum**, Joannis Jacobi Komarek, 1693-1700.
[29] R. Bösel, L.S. Insolera, **Mirabili disinganni. Andrea Pozzo (1642-1707). Architetto e pittore gesuita**, Artemide, 2010, p. 319.
[30] V. De Feo, V. Martinelli, **Andrea Pozzo**, Electa, 1996, p 255.
[31] L. Famiglietti, C. Scioscia Santoro, *La tecnica dello stucco attraverso le fonti: tecnica d'esecuzione e caratterizzazione chimico-fisica dei materiali costituivi*, **Scienza e beni culturali XVII: Lo stucco, cultura, tecnologia, conoscenza** (editors: G. Biscontin, G. Driussi), Arcadia Ricerche, 2001, pp. 19-26.
[32] C. Natali, G. Lorenzini, *Le ricette degli stucchi in Italia settentrionale dal XV al XX secolo. Il rapporto tra le indicazioni contenute nella letteratura architettonica con le indagini di laboratorio*, **Scienza e beni culturali XVII: Lo stucco, cultura, tecnologia, conoscenza** (editors: G. Biscontin, G. Driussi), Arcadia Ricerche, 2001, pp. 219-244.
[33] I.C.A. Sandu, M.H. de Sa, M.C. Pereira, *Ancient 'gilded' art objects from European cultural heritage: a review on different scales of characterization*, **Surface and Interface Analysis, 43**(8), 2011, pp. 134-1151, Special Issue: SI, DOI: 10.1002/sia.3740

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