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Two stucco sculptures from the "Salone d'Ercole" in the Racconigi Castle (Cuneo, Italy): a case study

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ABSTRACT

Non-invasive and micro-destructive diagnostic investigations were employed for the study of two stucco statues depicting Putti, from the "Salone d'Ercole" in the Racconigi Castle (Cuneo, Italy). The research made it possible to understand the construction technique, constituent materials, and the state of conservation of the statues. This information was useful for placing the artworks in the correct historical-artistic context and for conservation choices and restoration interventions. Different analytical investigations were applied, specifically: a) the internal metal structure was analyzed by cover meter relief combined with digital radiographic technique; b) the stucco composition and its stratigraphy were characterized by Polarized Optical Microscopy (POM), X-ray diffraction (XRD) and Electron Scanning Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX); c) finally, the presence of organic compounds was observed by UV-Induced Visible Fluorescence (UVL) and then characterized by Fourier Transform Infrared Spectroscopy (FT-IR) analyses. The results show that the stucco Putti were made with the techniques and raw materials widely used by Ticino artists and plasterers' workshops active between the 16th and 17th centuries, in the current Canton Ticino region. As regards the state of conservation, decay phenomena such as exfoliation and loss of material were mainly attributable to the presence of epsomite.

1. Introduction & historical background of the case study

Racconigi Castle (Fig. 1A-B), listed in the UNESCO World Heritage List since 1997, was founded around the 11th century. It shows magnificent rooms, evidence of the changes undergone by the castle between the 17th and the beginning of the 20th century, where stuccos, frescoes, architectural elements, and furniture reflect the aesthetic changes that occurred over time. Among these, the Salone

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d′Ercole (Fig. 1 C), designed in neoclassical style by the architect Giovan Battista Borra, features decorations focused on the heroic virtues of the House of Savoy [1].

A sculptural group featuring six allegorical Putti (Fig. 1D-I) in stucco embellishes the balustrade of the tribune in the Salone d′Ercole, each bearing an attribute representing warrior virtues (Fig. 1D-I). Historically credited to the sculptor Giuseppe Bolina due to his involvement in decorating the Salone d′Ercole, the sculptural style of the modeling could be traced back to the masterful techniques of Francesco Ladatte (Turin, 1706–1787) and therefore datable to the 17th century [2].

Stucco is an ancient artistic technique extensively explored since classical times for crafting architectural embellishments and three-dimensional artworks, often imitating marble sculptures [3].

Three-dimensional stucco statuaries typically comprised: (i) a metal internal structure variously composed of bricks, stones, wood, nails, and metal bars covered by (ii) a coarse mortar layer with a support function; such a layer of coarse mortar is usually made up of a binder (i.e., Ca or Ca/Mg binder, sometimes mixed with gypsum) mixed with coarse aggregates (i.e., siliceous limestone aggregates, brick, etc.); (iii) a second layer of more precise manufacturing, serving a protective and finishing function. The latter consists of the same or a different binder than the underlying unrefined mortar and fine-grained aggregates, such as marble dust or spatic calcite, occasionally with no aggregate at all; (iv) a surface finishing layer, *scialbatura* or polishing, by covering the surface with organic protective products and/or lime-milk [4,5]. To improve the properties of the stucco, organic additives such as sugar, glycerine, and citric acid were added to reduce the solubility of the gypsum [6]. Generally, sugar could be added to the amount of water required for binder hydration and to prolong curing time. Fats and proteins (such as albumen and casein) could be added to impart water-repellent characteristics. Proteins additionally slowed down the hardening process and enhanced adhesion to substrates [7]. Surfactants, like soaps, could be integrated to yield a shiny finish to the stucco after thorough polishing [8].

Between the 16th and 18th centuries, several influential families of artists were active in Italy and highly appreciated throughout Europe [9]. Known as 'Masters of the Lakes' they were expert plasterers from northern Lombardy (Italy) and southern Ticino (Switzerland), particularly skilled in mastering the complex art of stucco [10]. Starting from the basic recipe, the Ticino workshops developed compositional variations and improved the production technique. Felici and Jean [9] documented variations in the use and composition of the raw materials, showing adjustments during the working process. Architectural decorations were often made with gypsum-free mortar, while for the execution of three-dimensional sculptures, the addition of gypsum was essential for the creation of the modeling. The amount of plaster used in the production phases of a sculptural artwork could therefore vary, not only among different artists but also throughout the various phases of creating the same art piece. Typically, the gypsum content around the metal reinforcements was augmented to expedite curing times, minimize mortar shrinkage, and enhance workability in its fresh state [9].

This research aims to conduct a diagnostic investigation on two out of the six Putti located in the Salone d′Ercole in the Castle of Racconigi (Fig. 1), hereafter described respectively as Putto A and Putto B (Fig. 2). They have been chosen as representative examples to illustrate the execution technique and decay phenomena present throughout the entire collection, aiming for a better comprehension of this series of sculptures, currently lacking attributed authorship.

The Putto A (Fig. 1 A) depicts a naked child lifting a robe with the left hand while holding a bow in the right hand. The Putto B (Fig. 1B) instead portrays a child seated on armor looking upwards and an axe in his right hand. Both the full-length sculptures, resting

Fig. 1. (A) Location of Racconigi Castle in Italy and in the Piedmont Region; (B)Front view of the Castle and (C) of the Salone d′Ercole where a collection 6 Putti (D-I) is exhibited; (H-I) Putti as a case study of the present research. Notes: Images taken from https://catalogo.beniculturali.it/detail/HistoricOrArtisticProperty/0100404954.

Fig. 2. Stucco's artworks from the Salone d'Ercole in the Castle of Racconigi selected as cases study: (A): Putto A; (B) Putto B.

on gilded wood bases, have similar sizes, measuring approximately 80 cm×35 cm x 45 cm (height, width, depth respectively) each.

A multi-analytical and integrated approach was undertaken with non-destructive and micro-destructive investigations, in order to (i) identify the construction technique and assembly methods of the internal structure; (ii) characterize the constituent materials of both the mortar layers and the finishing one to guide conservation choices and restoration products as well as to have data for comparison with other contemporary artists and workshops; (iii) document the state of conservation, identify degradation products and retouches attributable to previous interventions.

2. Materials and methods

2.1. State of conservation, materials and sampling

The initial on-site investigations enabled us to assess the conservation state of the Putti and establish the most appropriate sampling strategy. These investigations provided crucial insights into the sculptures' condition (Figs. 2–3), allowing us to determine the best approach for further analysis.

Putto A (Fig. 2A) displays surface flaking and leafing near the nape of the neck, between the shoulder blades, on the buttocks, on the draped back, and, to a lesser extent, on the face. In addition, on the back of the sculpture there are widespread punctate flaking and detachments on the surface suggesting the presence of salt efflorescence. Moreover, incoherent deposits and absorbed dirt were widespread over the surface, especially on the horizontals and overhanging. The autoptic analysis also allowed to observe a thick layer of material on the surface, probably deriving from previous maintenance interventions, which also highlighted some lack and flaking on the drapery and putto's face. Careful observation of the surface highlighted various filling in the drapery, such as some modeling reconstructions made with gypsum plaster, less fine than the original stucco, used for rough structural reconstructions such as in the right foot or the upper part of the bow.

Even though the cleaning had not been completed, it was possible to observe the presence of further fillings and additions by modeling. Furthermore, in various areas physical decay phenomena such as micro-cracks were observed, especially in the arms and legs most subjected to mechanical stress, and in areas where the stucco was less thick, as in the case of the bow. A similar state of conservation was observed in Putto B (Fig. 2B) although with different severity. The surface showed flaking and lack of the surface layer, probably due to the aging of the protective compound applied in a previous conservative intervention, visible above all on the robe, inside the armor, and widely on the putto's body. Salt efflorescences, as in the Putto A, were also found in the hair and on the inner part of the armor. Unlike Putto A, Putto B showed many more lacks in the hands, feet, and armor. The lack of the big toe of the left foot allowed us to observe the remains of a plaster used to remodel the foot, which is now missing.

Already from these first observations it would seem evident that the two artworks show similar properties, highlighting an innermost layer of mortar with a coarse aggregate varying in grain sizes, and a finishing layer with different thicknesses (Fig. 3B). Given the similarity, only the fragment coming from the right hand of the Putto A already detached (Fig. 3A-C), was selected to conduct

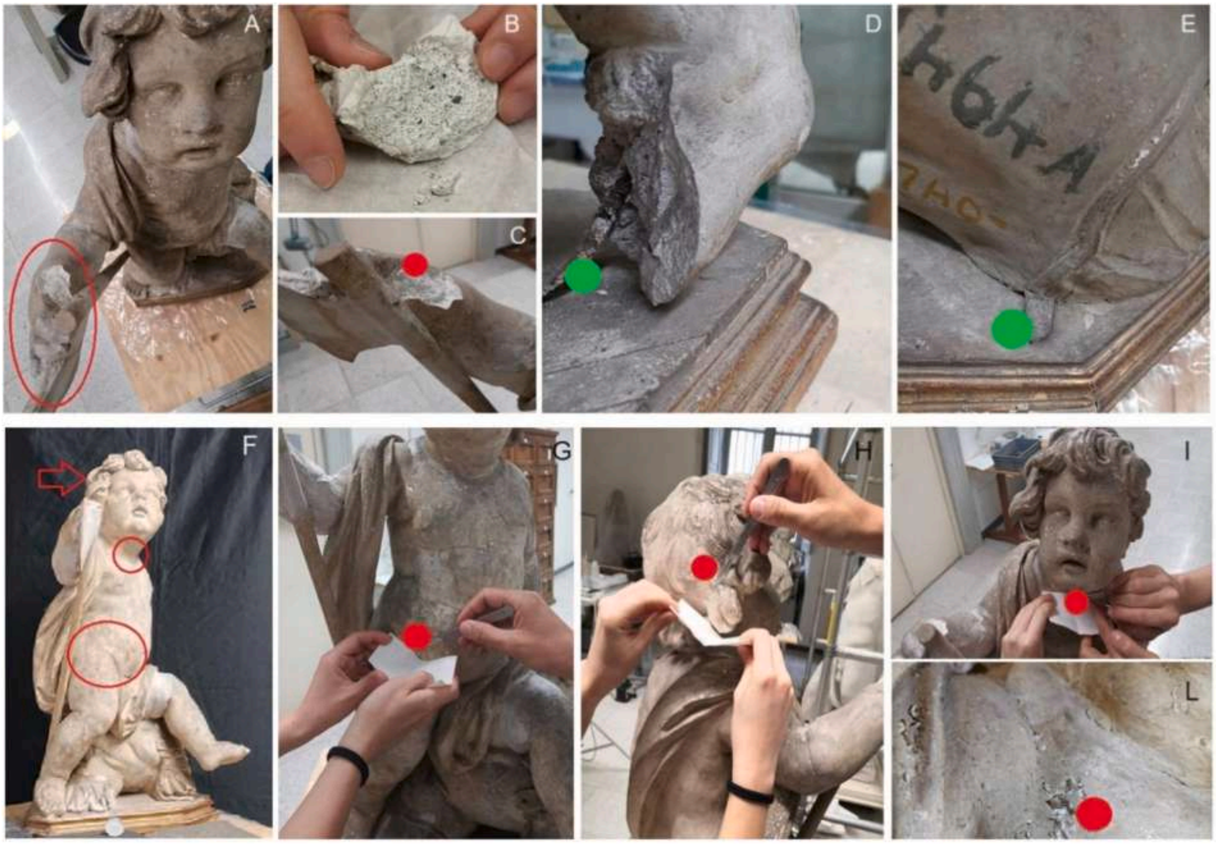

Fig. 3. Macroscopic observation, Sampling points, and Decayed areas. Evidence of the right hand of Putto A (A) with detail of detached fragments subject to investigations (B-C); Evidence of the metal armor in Putto A (D) and Putto B (E); Evidence of the areas (i.e., red circles and arrow) (F) subjected to sampling of powders, surface deposits and thin flaking portions near the belly (G), nape (H) and neck (I-L).

an in-depth study of the raw materials using micro-destructive laboratory methods. Specifically, three micro-samples were taken from the detached fragment (Fig. 3B) for minero-petrographic and geochemical investigations of the constituent materials; while samples in the form of powders, dust, and surface deposits were scraped-off from the surface of the sculpture to study any alteration products (Fig. 3F-L), or compounds from previous restorations. Details on the sampling areas, micro-samples, and powders are summarized in Fig. 3 and Table 1 along with all the analytical techniques employed.

Table 1
Overview of the sampling carried out on Putto A, employed techniques and objectives of the investigations.

Sample ID	Description	Employed techniques	Objective
S1	Fragment from the right hand of the Putto B, approximately 0.5 cm in size, visually consisting of: a) external finishing layer and b) innermost layer of medium-coarse mortar.	POM; SEM-EDX	To know the detailed stratigraphy of the sample through a petrographic and compositional characterization.
S2	Tight micro-fragment from the surface finishing layer of the right hand of the Putto B, approximately 0.3 cm in size with a powdery deposit on the surface.	XRD	To know the mineralogical composition of the finishing layer.
S3	Crumbly and powdery micro-sample from the innermost layer of medium-coarse mortar of the right hand of the Putto B.	XRD	To know the mineralogical composition of the mortar.
S4	Powdery micro-sample from the neck of the Putto B showing yellow-orange fluorescence under UV light.	FT-IR	Identification of the organic and/or inorganic nature of surface deposits resulting from probable alteration.
S5	Powdery micro-sample from the belly of the Putto B showing yellowish fluorescence under UV light.	FT-IR	Identification of the organic and/or inorganic nature of surface deposits resulting from probable alteration.
S6	Powdery micro-sample from the chief of the Putto B showing bluish fluorescence under UV light.	FT-IR	Identification of the organic and/or inorganic nature of surface deposits resulting from probable alteration.

2.2. Analytical methods

2.2.1. In situ investigations by non-destructive methods

Stucco sculptures were investigated using in the first step of study in situ investigations. The selected non-invasive diagnostic techniques enabled a deep understanding of the macroscopic observations, allowing the examination of the internal structure and the acquisition of data on the production technique.

The use of a cover meter made it possible to ascertain the presence of metal armor, already observed with the naked eye (Fig. 3D-E), and how it was distributed internally to the two artworks. The instrument used is a Proceq Profoscope+ cover meter, consisting of an electromagnetic field emission and reading unit, and one or more magnetic field emitter-receiver probes. To locate armor and metallic elements, Profoscope+ uses the pulsed electromagnetic induction method [11]. Specifically, the probe coils are charged at regular time intervals by current pulses thus generating a magnetic field.

The cover meter relief was combined with digital radiographic investigations to thoroughly document the internal structure and assembly technique. A portable X-ray system, Poskom X+, mod.PXP-100 CA, voltage 40 kV to 100 kV was used to acquire radiographic images, by setting the following parameters: maximum voltage 90 kV (50 Mas); X-tube/flat panel distance 120 cm. X-ray images were

Fig. 4. Cover meter relief on Putto A (A-C) and Putto B (D-F).

acquired instantly on a laptop computer equipped with software through which the obtained images can be displayed, stored, and processed by applying image hardening and softening algorithms to highlight the different densities of the artifact components.

UV-Induced Visible Fluorescence was used to differentiate organic and inorganic materials, identify previous restorations and analyse the state of conservation of the artistic surface [12]. In the present study, two 3000 mW LEDs with narrow filter at 365 nm was used like radiation source and UV-induced luminescence images are captured by a digital camera with a CCD photo sensor - MADATEC 28.2 MP multispectral system. Based on the information provided by the UV fluorescence images, further samples (Table 1) were selectively scalpel-primed from the finish surface of the putto under investigation (Putto B) in the areas identified by the different fluorescence. The samples were then analysed by FT-IR spectroscopy.

2.2.2. Laboratory investigations by micro-destructive methods

The second approach to the cases-study examination consisted of analyzing sampled materials (Table 1) through complementary analytical methods.

Polarized optical microscopy (POM) observations were performed using a Zeiss Axioskop 40 microscope coupled with a digital camera, to examine the minero-petrographic composition, characterize the textural properties, and layering of the selected representative sample (S1).

Microchemical and morphological analyses, supporting the POM investigation, were obtained employing a FEI QUANTA 600 FE-SEM equipped with an energy-dispersive X-ray system (EDAX spectrometer with a SUTW-Sapphire detector). The SEM images were acquired in SE mode - Sensitive to Surface Roughness. The used accelerator voltage was 20 keV and the average counting time was 100 live seconds. The apparatus had a resolution of 132 eV.

X-ray diffractometry (XRD) was performed using a Bruker D8 Advance X-ray diffractometer (Bruker, Karlsruhe, Germany) and Bragg–Brentano geometry, with a copper-sealed tube X-ray source producing Cu k radiation (wavelength of 1.5406 Å) from a generator operating at 40 kV and 40 mA. The diffracted X-rays were recorded on a scintillation counter detector located behind a set of long Soller slits/parallel foils. Scans were collected in the range of 3–65° 2θ, using a step size of 0.014° 2θ and a step counting time of 0.2 s. EVA software (DIFFRACplus EVA version 11.0. rev. 0) was used to identify mineral phases by comparing experimental patterns

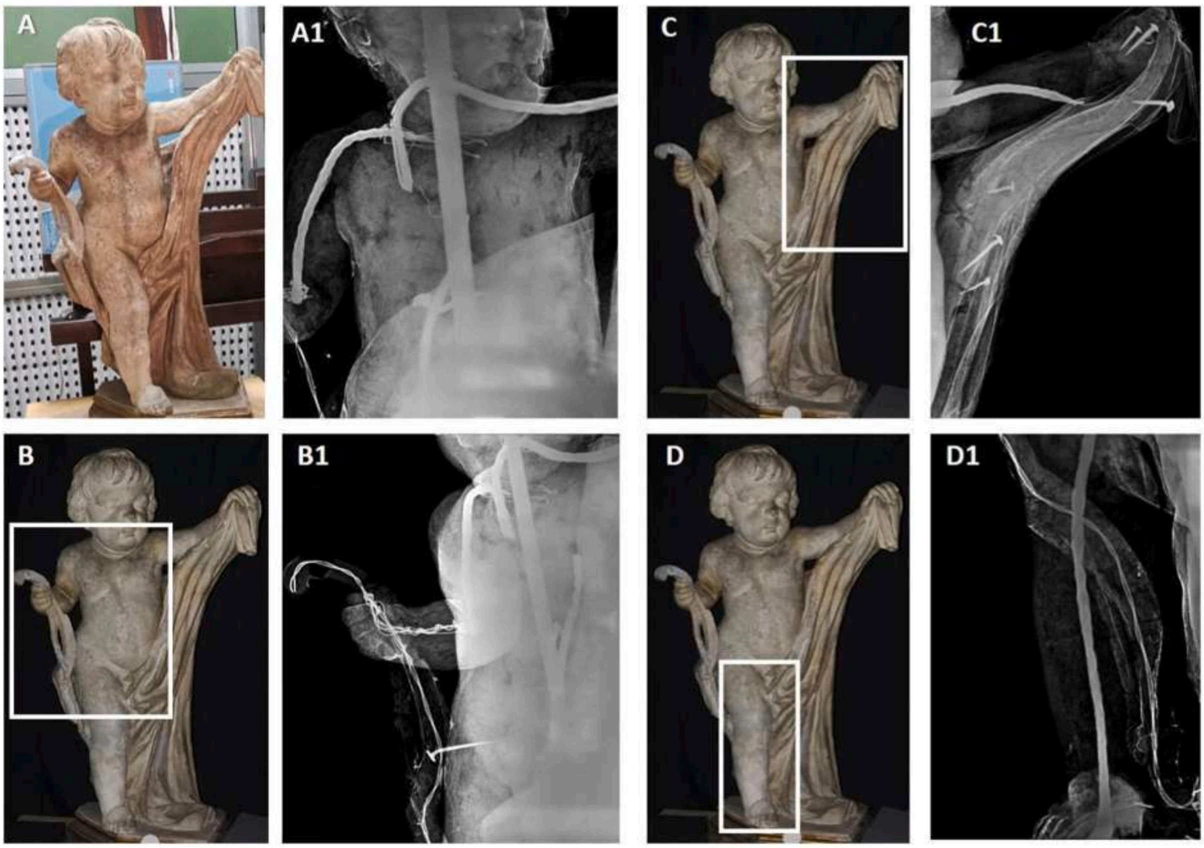

Fig. 5. X-ray Radiography: Putto A. Radiographic images and photographic detail of correspondent X-Rays four exposed area (A-A1, central part of body; B-B1, right arm and part of body; C-C1, part of drapery; D-D1, right leg) in which it is possible to see the use of wire rods employed as support for modelling the mortar and to achieve the desired volumes. A curved nail is also visible in the central part of the bust (A1), inserted from the back for anchoring the drapery and/or constructing the modelling. The portion of the leg up to the ankle shows less radiopacity than the foot (D1).

with 2005 PDF2 reference patterns.

As far as FT-IR investigation is concerned, the used spectrophotometer was a Bruker Tensor 27, equipped with an attenuated total reflectance (ATR) accessory (diamond crystal). Infrared spectra were recorded in ATR mode, in the 500 ÷ 4000 cm^{-1} wavenumber range, with a resolution of 4 cm^{-1}. Samples' spectra were compared with those of standard minerals from databases and literature for a reliable assignment of the bands [14].

3. Results and discussion

3.1. Construction technique by non-destructive methods

The cover meter relief (Fig. 4) revealed an extensive and complex metallic structure for both stucco statues examined, corroborating initial observations made during the macroscopic inspection (Fig. 3).

The extent of the metal elements required further investigation through radiographic examination to define the distribution and

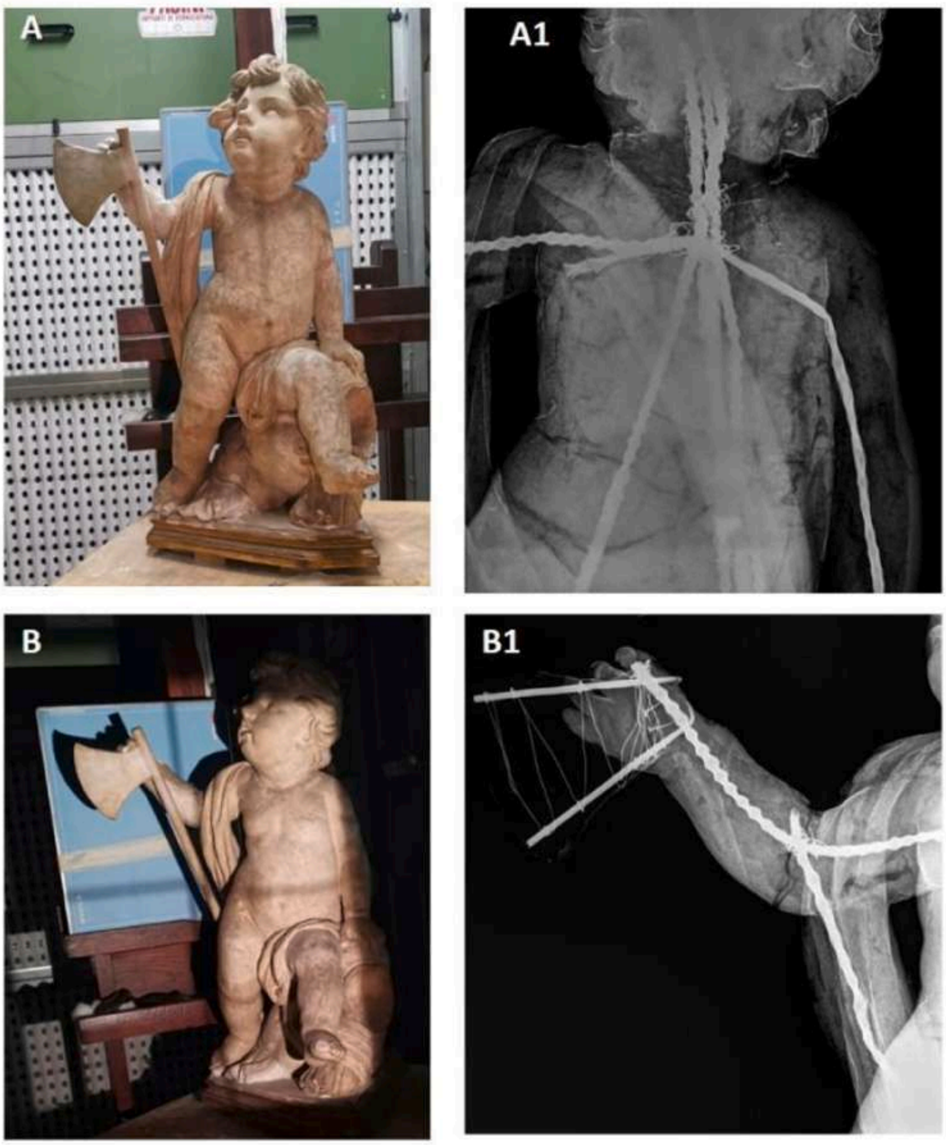

Fig. 6. Putto B. Radiographic images and photographic detail of correspondent X-Rays two exposed area (A-A1, central part of body; B-B1, right arm and axe) in which it is possible to see the use of wire rods employed as support for modelling the mortar and to achieve the desired volumes. The internal structure is assembled by metallic wire and nails of different size e section shape. Areas of mortar affected by fractures or discontinuities in the modelling, missing or thinning can be clearly seen as darker areas due to low radiopacity.

assembly of the components constituting the internal metal armor. Radiographic images highlight the precise positioning of the metallic elements thanks to the contrast between non-metallic (i.e., mortar: low radiopacity) and metallic elements (i.e., rebar: high radiopacity). The use of wire rods, iron wires, and nails for both Putti was ascertained. Individual metallic components appear to be assembled in various ways to create the internal structure, to which modeling was applied for the volumetric construction of the statues. The wire rods are forged iron bars of square section, riveted on the sides in an alternating direction, of different sizes from 6 up to 15 mm. Thanks to this special forging, they have sufficient rigidity and resistance to support protruding loads, guarantee better adhesion of the mortar to the bars, and satisfy the need for malleability during the construction of the structure [10]. The use of bended wire rods to model the arms, legs and drapery, was detected in both Putti (Figs. 5–6). Iron wires were used to tie together the wired rods and to make up the basic skeleton for fine elements [10]. In fact, in both statues, the thinner modeled parts have armor made up of iron wires, single or intertwined. Furthermore, it was possible to identify the use of nails, probably used to realize the perimeter bars of the blade (Fig. 5D-F).

The use of nails and iron wires is associated with the use of string and tow applied to the thinnest portions of the metal reinforcement until there is an almost definitive volume on which to apply the finishing layer [9,13]. It is assumed that this technique was used for the drapery and the rod of the Putto A (Fig. 5), in which only the anchoring nails and woven metal wires of varying thickness can be observed, respectively, due to the lack of radiopacity of the filling materials used. The different material composition was also found in the total radiolucency of the axe stick of the Putto B (Fig. 6) probably made of wood or another organic material.

The radiographic investigation also made it possible to document discontinuities in the internal volume of the stuccoes, mapping out fractures, lesions, and lacunae not directly observable from the surface, or past restoration work. The right leg of Putto A (Fig. 5G-H) shows a lower radiopacity than the foot, probably due to the different constituent materials applied to the leg and ankle during previous restorations.

3.2. Characterization of constituent materials by minero-petrographic and geochemical methods

The POM analysis on thin and stratigraphic section (Fig. 7), carried out on sample S1 showed the presence of two layers (Fig. 7A-B), identified as the inner layer (1) and the finishing one (2), clearly differentiated by the presence of a coarse aggregate in the inner layer (Fig. 7C), which is almost completely absent in the finishing one (Fig. 7A-B). The inner layer consists of a lime binder matrix mixed with crystalline gypsum. The petrographic study of the aggregate makes it possible to identify lithic fragments of medium-grade metamorphic rocks (micaschist) with dimensions falling into the medium sand (0.5 mm) and a large limestone lithic fragment covering the thickness of the whole layer.

The presence of small grains of monocrystalline quartz was also recognized. Due to the small size of the inner mortar layer (1), it was not possible to appreciate the distribution of the aggregate nor estimate its thickening. This finishing layer, on the other hand, has a thickness of approximately 1.5 mm and it is made up almost exclusively of a lime binder matrix mixed with crystalline gypsum, like in the inner layer. Very few monocrystalline quartz granules fall into the coarse silt class (0.06 mm). In addition, a very fine surface incrustation is also visible on the outer layer.

The minero-petrographic characterization was completed by X-ray diffractometric analysis (Samples S2-S3, Table 1), performed on both the finishing layer and inner ones (i.e., mortar). The diffraction pattern of the inner layer (Fig. 8B) shows the following mineralogical phases, attributable to the aggregate: clay minerals (illite, montmorillonite, kaolinite), muscovite and quartz. The data are consistent with thin-section observations of S1. Furthermore, the presence of calcite and gypsum may be related to the binder. Finally, epsomite, i.e. magnesium heptahydrate sulfate ($MgSO_4 \cdot 7\ H_2O$), was detected. Epsomite is a salt approximately 300 times more soluble than gypsum and its formation is related to the combined presence of gypsum and Mg-lime in the mortar [5]. The finishing layer consists only of calcite and epsomite (Fig. 8 A). Gypsum was not found, probably due to the smaller quantity added to the finishing layer.

SEM combined with the EDX detector provided a visual representation of the sample supporting the study of the binder elemental composition (Fig. 8). For both layers the binder consists of Mg-lime mixed with gypsum (Fig. 9B-C); while the presence of aluminum and the higher silicon in the mortar layer (Fig. 9C) can be attributed to the composition of the aggregate fraction. Given the absence of

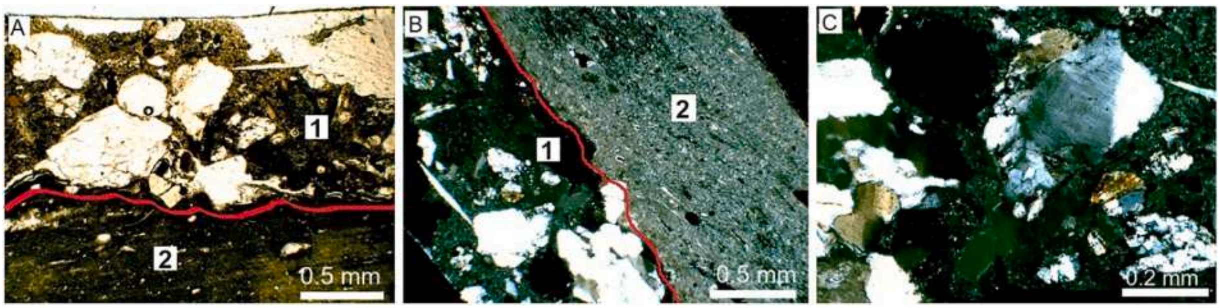

Fig. 7. Thin sections micrograph of the sample S1. (A-B): evidence of innermost layer of medium-coarse mortar (1) and external finishing layer (2) in parallel nicols, magnification 5x, scale bar = 0.5 mm (A) and cross nicols, magnification 10x, scale bar=0.5 mm (B); (C): sandy aggregate of the medium-coarse mortar (layer 2) characterised by a micaschist fragment (cross nicols; magnification 4x; scale bar =0.2 mm).

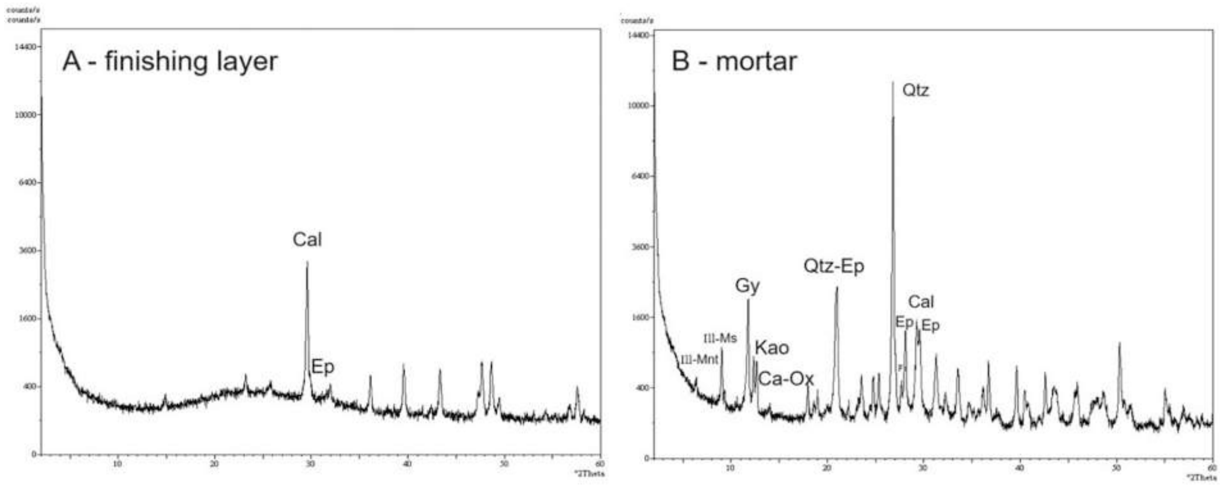

Fig. 8. (A) XRD spectra of mortar layer (sample 3); (B) XRD spectra of finishing layer (sample 2). Notes: Ill= Illite, Mnt= Montmorillonite, Ms= Muscovite, Kao= Kaolinite, Qtz= Quartz, Cal= Calcite, Gy= Gypsum, Ep= Epsomite.

gypsum from mineralogical analysis using XRD, the high sulfur values detected by EDX in the mortar layer (Fig. 9C), could be attributed to the migration of magnesium sulfate salt from the layer of the stucco.

The presence of epsomite detected by XRD has been also verified by the presence of high sulfur content by SEM-EDX analysis (Fig. 9B-C). The evident continuity gap between the two layers (Fig. 7A-B), also confirmed in the SEM image (Fig. 9A), provides information on the execution technique. The finishing layer was probably applied later when the body mortar was already dry since no reaction between the two observed layers is visible.

3.3. Investigations and characterization of surface deposits

An in-depth study was conducted to evaluate the state of conservation of the 2 artifacts and the possible presence of deposits and alteration products, also deriving from previous restorations. The imaging of the two Putti under UV-filtered LED lamps showed for both a different spectral response between the front and the back of the artifacts (Fig. 10A-B, E-F). Specifically, the front surface and part of the sides show a yellow-orange fluorescence, while the back of both statues displays a weak bluish fluorescence. In the black

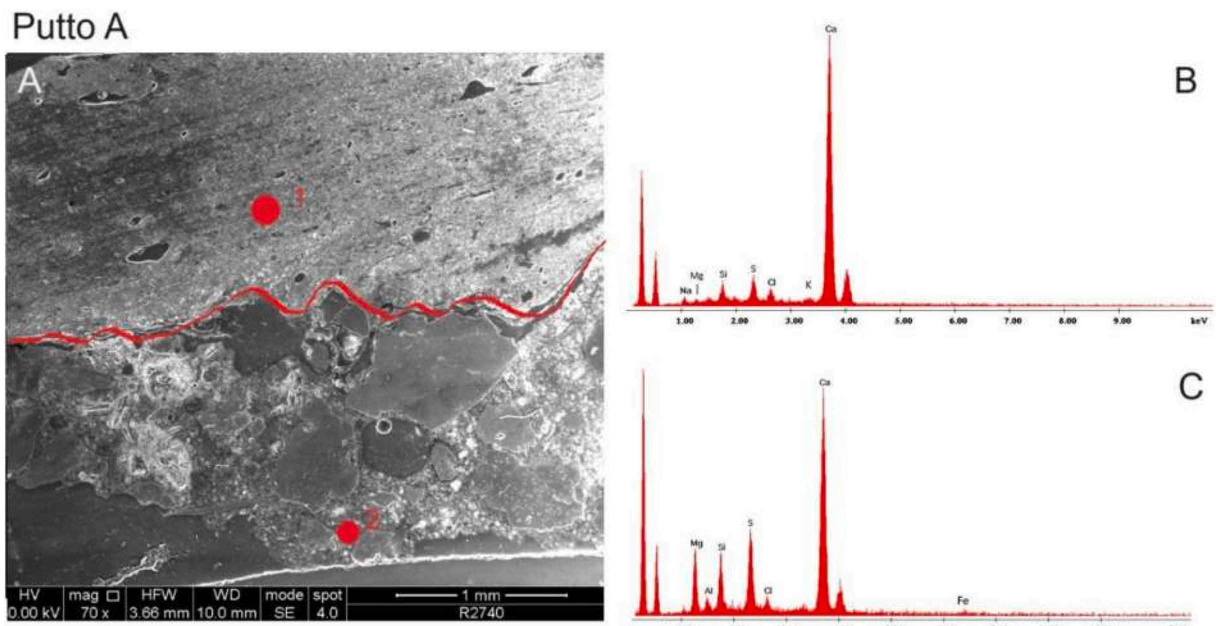

Fig. 9. Morphological investigation with evidence of the two layers highlighted in Putto A (A) and related EDX spectra relating to the finishing layer 1 (B) and the mortar layer 2 (C).

areas, in the absence of total fluorescence, portions of surfaces affected by retouching and reintegration are evident, as in the case of the leg of the Putto A (Fig. 10D) in which the perimeter of the integration is evident.

These adjustments are also confirmed by the radiographic image (Fig. 5) due to the different radiopacity compared to the original stucco. Overall, there is no evidence of any traces of polychromy, or residues of ancient preparation and gilding. UV-induced visible fluorescence does not provide conclusive evidence but requires the use of complementary techniques, especially for material identification [12].

The organic and inorganic materials on the surface were analyzed using infrared spectroscopy (FT-IR). Considering the same spectral response of both Putti, samples were taken from the surfaces identified by the UV-fluorescence analysis and from the surfaces affected by deposits, exfoliations, abrasions, and blistering of Putto B (Table 1).

Samples 4 and 5 were taken respectively from the neck area and the pelvis area of the statue, where a yellow-orange fluorescence was observed. FT-IR analyses of these samples show the presence of bands attributable to a material of a lipidic nature identified by the presence of typical absorption bands (Fig. 11 A, B): methylene bands at 2926–2855 cm^{-1} and olefinic C=C-H stretching band that occurs at 3020 cm^{-1}, oil spectra contain also carbonyl band at 1750–1740 cm^{-1} because of the ester group. Other bands characteristic

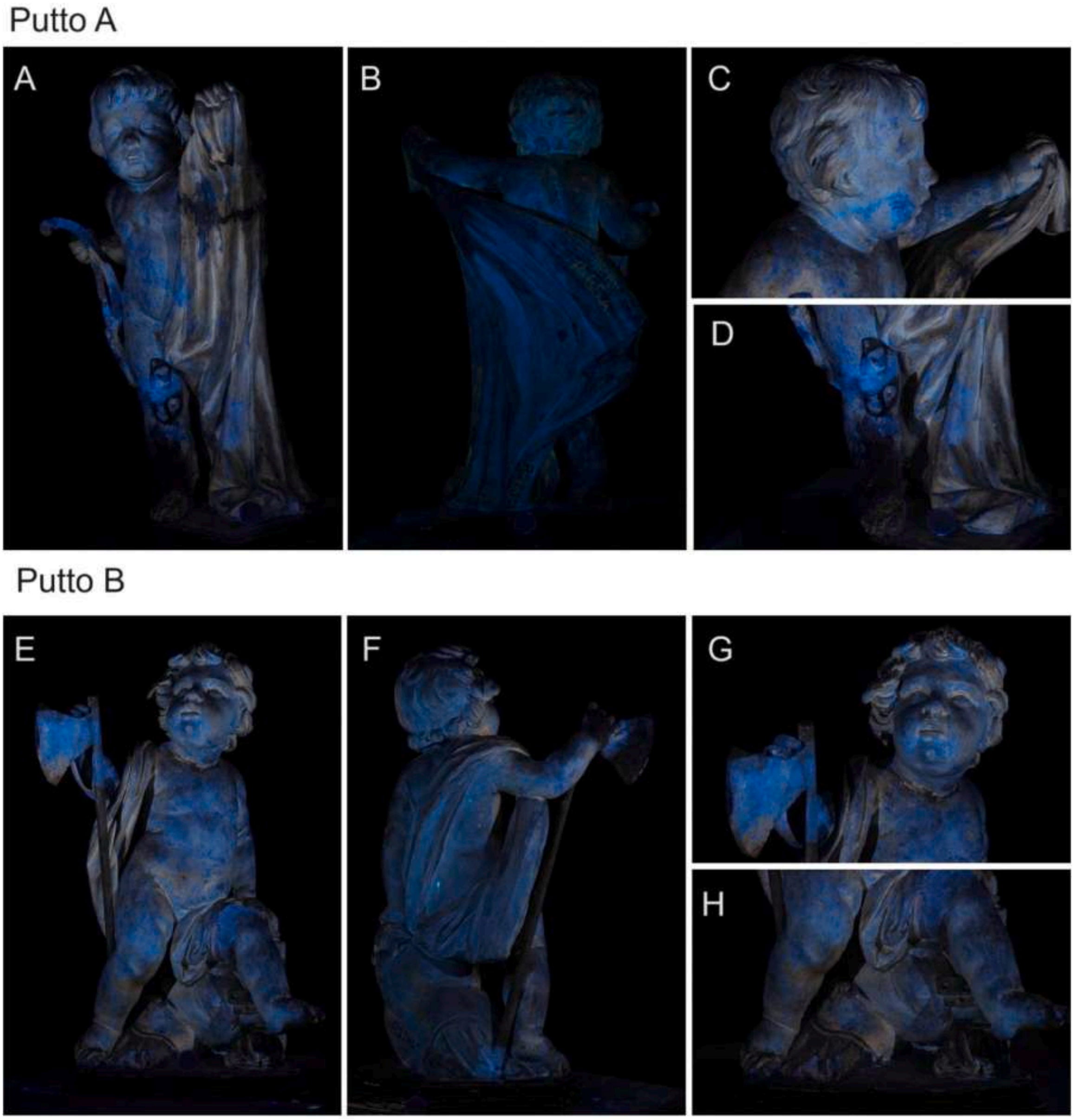

Fig. 10. UV-induced visible fluorescence of Putto A (A-D) and Putto B (E-H). Spectral response of: forehead (A, E); backside (B. F) and details of the faces (C, G) and legs (D, H).

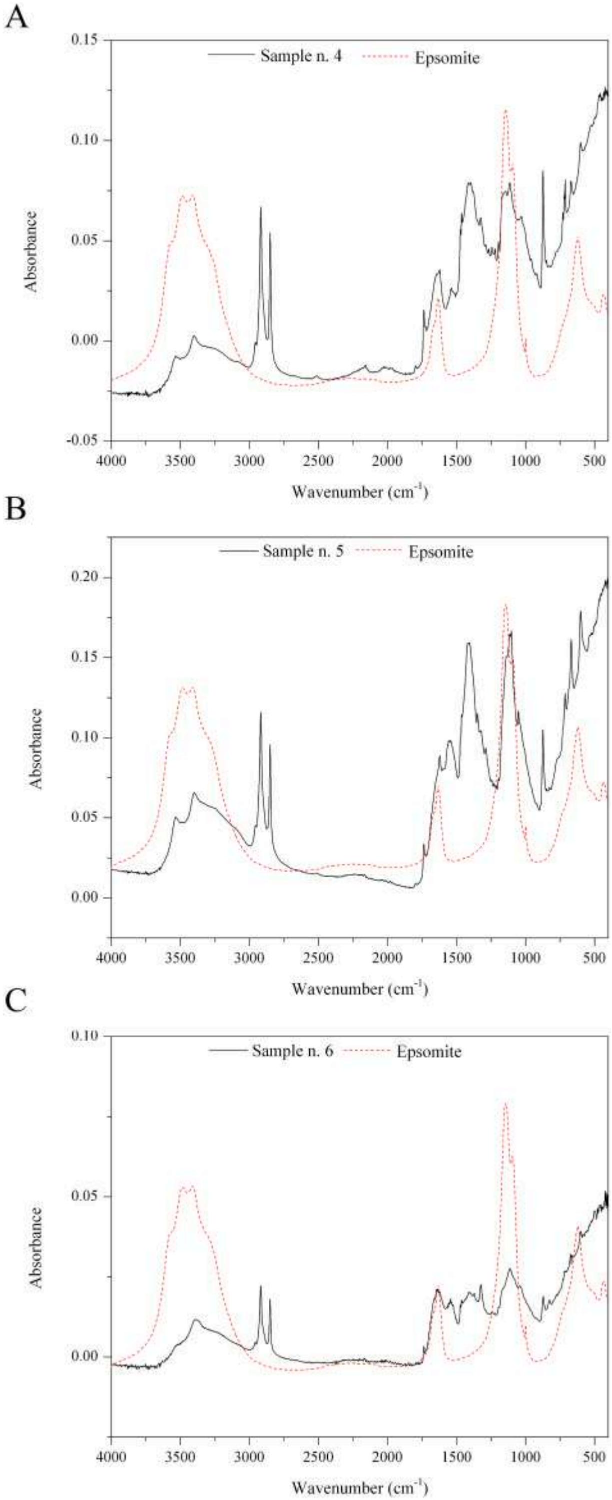

Fig. 11. FT-IR analysis of Putto B: (A) Sample 4: organic component: Lipid, inorganic compounds: Epsomite, Gypsum, Calcite; (B) Sample 5: organic component: Lipid; inorganic compounds: Epsomite, Gypsum, Calcite; (C) Sample 6: organic component: lipid and protein; inorganic compounds: Epsomite, Gypsum, Calcite and trace of Calcium Oxalate.

of the oils are aliphatic C-H bands at 1464–1379–725 cm^{-1} and the C-O bands at 1240–1165–1013 cm^{-1}[15].

Sample 6 taken from the area characterized by a slight bluish fluorescence weakened by a greater presence of surface deposits, shows an organic lipid and protein component (Fig. 11C).

The presence of amide is confirmed by N-H stretching bands near 3335 cm^{-1} and by the presence of bands near 1650 cm^{-1}(Amide I), 1550 cm^{-1} (Amide II), and 1450 cm^{-1} (Amide III) [15]. Moreover, trace of signal at 1323 cm^{-1} attributable to calcium oxalate has been revealed on sample 6 FT-IR spectrum. Concerning inorganic materials, the FT-IR spectra showed for all three samples analyzed the co-presence of calcite with the most typical bands at 2515;1424;875;712 cm^{-1}, gypsum (3612–3556; 1622; 1152; 1116; 1093; 1007; 661; 599; 466 cm^{-1}) and epsomite (3509–3484; 1227; 1082; 1026; 680; 625; 599; 526; 426 cm^{-1}).

4. Discussion

4.1. Characterization of constituent materials

Chemical, mineralogical and petrographic investigations allowed to characterize both the binder phase and the aggregate fraction of the inner and finishing layers. The SEM-EDX analysis shows that the binder phase of the two layers has a similar composition: Mg-lime-based mixed with gypsum. The use of magnesium lime for the production of stuccoes is widely attested in literature both in northern Italy between the 16th and 17th centuries and in Sicily in the 18th century [7,10,13]. Magnesian lime is typical in the Lombardy region and was used not only for its easy availability but also for its good plastic properties and cohesion [4,13]. Concerning the presence of gypsum in the binder, the diffraction pattern of the finishing layer did not detect the presence of gypsum, probably due to the negligible percentage with which it was added in this layer. This evidence is consistent with the recipes of the period that involved the use of gypsum mainly in the inner layer. Gypsum was added to reduce the hardening time of lime, an important aspect in the rough-hawing phase of the sculptures [7], which prevents cracks from shrinkage and influences the workability of the mortar. So, gypsum was used with different percentages and methods depending on the layer, according to the needs of the various workshops [5]. Coming to the aggregate, XRD analysis and petrographic observations identified the presence of clay minerals (illite, montmorillonite, kaolinite), muscovite and quartz, contained only in the inner layer. This evidence is in line with the mineralogical composition of the aggregate of stucco from Lombardy, Piedmont and Veneto cultural sites, studied by Bugini et al. [16] and made up of aggregate coming from the sand of many rivers flowing in the Pianura Padana [16]. This similarity suggests the local origin of the aggregate. In contrast to many case studies analyzed in the literature [10] and carried out by artists and workshops active in northern Italy, the addition of marble crushed fragments or spatic calcite as an aggregate in the finishing mortar was not found in the present case. In fact, the finishing layer consists almost exclusively of a binder matrix mixed with microcrystalline gypsum. Regarding the execution technique, the "*fresco su fresco*" technique [13] was not applied, as no reaction is visible between the two layers. The presence of organic compounds was also detected by distribution maps of under UV LED materials, which may not be otherwise visible to the naked eye [12]. FT-IR analyses carried out in the areas identified by the presence of visible fluorescence emission, detected the presence of lipid and protein material. Lipidic material (yellowish fluorescence) was probably attributable to the use of oil-resin past treatments or traces of original finishes used to polish the stucco over time. Protein material was found in the areas characterized by weak bluish efflorescence, at the surfaces of the back of the statue characterized by more diffuse darkening and greater exfoliation. Trace of oxalate found on sample 6 could be correlate to mineralized original finishing organic compound overlapped to successive treatments. The use of organic additives was common as processing aids for stucco works [17,18] and have been found in various stucco works created between the 16th and 17th centuries, both directly and through the presence of calcium oxalate [7,9]. The presence of epsomite absorption bands in the FT-IR spectra confirms the results of the previous analytical techniques used for the study of samples 1,2 and 3, verifying the identification of neoformation product on surface due to sulphuration of original inorganic compound.

4.2. Construction technique

As the construction techniques concerned, Felici and Jean [9] highlight the potential of the radiographic technique for the study of stucco works. The use of digital radiography, if further developed and applied systematically, could become fundamental both for the observation of internal structures through comparisons of schools and periods, and for identifying the decay phenomena of stucco works. In this instance radiographic investigation has demonstrated the presence of a metal and assembly structure similar to those found in stucco artworks of Ticino artists. Wire rods and wires of the metal armour of the Putti are used in the same way in Agostino Silva's stucco-works in the Oratorio Imbonati di Cavallasca in Como [13]. Another analogy could be made with the works of the statues of the Church of Sant 'Eusebio in Castel San Pietro in which iron wires were used to create a basic skeleton for fine elements such as fingers, dress or wings [10]. The technique of using filling materials such as tow and string inside the armour was also found in Ticino stuccos [13].

4.3. Conservation state

The characterization of the composition of the stucco also helped in the identification of source and mechanism of decay. XRD and FT-IR analysis revealed the presence of epsomite both in the inner and in the finishing layer, due to the combined presence of Mg-limes and gypsum [5]. It is an easily hydrated salt, particularly soluble in conditions of relative humidity above 80 % in the presence of water [19,20]. The epsomite is responsible for visible forms of degradation on the surface characterised by exfoliation, uplift and loss of material as a result of various cycles of recrystallisation of this salt. Identifying the presence of epsomite is particularly relevant for conservation purposes, as it requires the use of non-water-based products. Furthermore, although it is a salt produced by degradation processes, it is at the same time the element that guaranteed a minimum of cohesion to the mortars and therefore its removal would further impair the artworks [13]. From the macroscopic observation of both statues, it was possible to identify detachments, gaps, accumulation of deposits, exfoliations, and lifting, also identified by a different spectral response in UV fluorescence. The presence of a faint bluish fluorescence on the back of the statues could be related to the exhibition conditions of the two statues in the Salone d'Ercole. The location on the balustrade would have made the back of the statues difficult to reach, suggesting that over time the Putti have undergone different maintenance and conservation treatments between the front and back. While on the surface, which was characterized by the absence of fluorescence (black areas), the presence of additions, retouches and deposits was detected. Fractures and discontinuities in the internal volume of the statues have also been found.

5. Conclusion

In this paper, diagnostic investigations were carried out on two Putti stucco statues from the Salone d'Ercole in the Castle of Racconigi (CN) with the aim of identifying the construction techniques, the constituent materials and the state of conservation in order to provide useful information to plan the restoration project and deepen the artistic technique. The study was performed by the portable and non-invasive techniques, such as cover meter relief, digital radiography and UV-Induced Visible Fluorescence imaging in the Restoration Laboratory of Direzione regionale Musei Piemonte in Palazzo Carignano (TO). The data collected from these methodologies were also integrated with those obtained by micro-destructive laboratory analysis, like POM, SEM-EDX, XRD and FT-IR. From the results obtained, it was evident that the stuccoes studied were completely consistent with the peculiarities and developments of artistic stucco technique in northern Italy during the 18th century in terms of construction, raw materials and executional devices. Stucco of Putti statues are made of an internal and external layer made of Mg-lime binder mixed with different percentages of gypsum and aggregate fraction composed by rocks fragments, mainly present in the mortar layer. These are shaped around an internal metal structure. Moreover, the UV-Induced Visible Fluorescence investigation also made it possible to detect the presence of organic materials employed during past surface treatments, recognised by FT-IR analysis as lipid and protein material. Further investigation by means of mass spectrometry analysis (GC-MS) could allow a better characterisation of the organic additives added to the mortars. With regard to the state of conservation, the UV-Induced Visible Fluorescence revealed the presence of areas interested by integrations and retouches and deposit accumulation. This last, present in the back area of the Putti, could be traced back to the exposition environment of the statues in the Salone d'Ercole. Exfoliation, lifting and loss of material due to efflorescence instead can be associated with the migration and solubilisation of magnesium salt heptahydrate. The presence of epsomite salts could therefore guide the choice of conservation methods that did not involve the use of water-based products. The radiographic investigation also made it possible to document the inner metallic structure and discontinuities in the internal volume of the stuccoes, mapping out fractures, lesions and lacunae not directly observable from the surface and past restoration work. The data obtained from these investigations may be useful in the planning and selection of suitable products during the restoration project and to deepen the artistic context of production of the analyzed stucco statues, supporting the belonging to a specific workshop.

CRediT authorship contribution statement

Alessia Pantuso: Writing – original draft, Methodology, Formal analysis. **Michela Ricca:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Giuseppe Milazzo:** Writing – original draft, Formal analysis. **Chiara Cubito:** Writing – original draft, Formal analysis. **Roberta Bianchi:** Writing – original draft, Formal analysis. **Giulia Comello:** Writing – original draft, Formal analysis. **Mauro Francesco La Russa:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Salvatore Schiavone:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Luciana Randazzo:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Maria Francesca Alberghina:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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