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A pre-restoration minero-petrographic, chemical and microbiological analysis of the sculpture "Real Infante Carlo Tito di Borbone"

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***Abstract* – A minero-petrographic, chemical and microbiological analysis was carried out on the sculpture "Real Infante Carlo Tito di Borbone", recently attributed to Giuseppe Sanmartino. A combination of microscopic, spectroscopic, chromatographic characterization along with the isolation of the microbial population was adopted to evaluate the conservation state of the sculpture. The stone composition was characterized and both biodeterioration and traces of previous restoration were detected.**

KEYWORDS: diagnostics, marble, wax, adhesive, biodeterioration

I. INTRODUCTION

The hidden cultural heritage is a common feature of many Italian museums. The effort of the Superintendencies to dig out the most valuable artworks represents a continuous activity, coped to a full valorization and fruition of our cultural heritage selected for permanent or temporary exhibitions.

The Royal Palace of Caserta, built starting in 1752 at the behest of Charles of Bourbon, is a museum complex consisting of the Royal Palace, the Royal Park, the San Silvestro Wood and the Carolino Aqueduct. The grandiose project is the work of the architect Luigi Vanvitelli.

The Royal Palace covers an area of 47,000 square meters, 5 floors and 2 underground, over 1200 rooms and a vast collection of historical-artistic assets, located in the museum itineraries and in the warehouses.

In the recent work of reorganizing the deposits and in the inventory activity, which is added to that already underway, we can count approximately: 1800 furnishings of which 223 of a sacred nature, 746 paintings on canvas, in addition to the imposing Farnese collection inherited from Carlo di Bourbon from his mother Elisabetta Farnese. There are also 390 furnishings of artistic interest, to which are added 152 vases, 39 clocks, 4 globes, 32 models partly produced by the cabinetmaker Antonio Rosz, 13 musical instruments, 213 lots of fabrics of various types, liturgical vestments, objects of bronze, bone or ivory, candlesticks, chandeliers.

To these are added the numerous sculptures, mostly located in the Royal Park and English garden, but also busts, decorative elements, etc. Of significant interest is the collection of contemporary art, "Terrae Motus", commissioned by the gallerist Lucio Amelio, which has 72 works by world-famous artists.

Indeed, the Royal palace of Caserta has extensive storehouse, where a significant amount of not-exposed artistic material is conserved. Recently, the art historians of the Royal Palace of Caserta have identified a sculpture ("Il Real Infante Carlo Tito di Borbone", dated 1775, size 54x22x23 cm^3), attributed to Giuseppe Sanmartino (Di Fratta 2021; Di Fratta 2022).

At an initial visual analysis, the artwork was in a fairly good state of conservation, as it did not show any obvious degradation factors at both the structural and optical levels. The surface was clouded by widespread deposits of an inconsistent and coherent nature, probably due to alteration of the protective wax applied in the past added to the dust deposited over time. At the drill holes there was a loose brown deposit resulting from biodeterioration product. The major dirt was concentrated in correspondence with the indentations in the modeling, in the nasal cavities, in the mouth, in the feet, in the hands and in all the strands of hair. This condition interrupted the correct reading of the artwork. The cause of evident deterioration was the presence of spherical spots, with a diameter of about 1-2 mm, greater in correspondence with the upper part of the bust and on the abdomen of the child. A white, stringy deposit was also evident in the baby's nasal and oral cavities.

Following an investigation and sampling, the presence of bacteria and fungi, responsible for biodeterioration, was confirmed (see below). There are numerous micro-holes on the surface, termed marble worms in the jargon, attributed to the intrinsic characteristic of the rock. In the lower part of the nape there is a chromatic alteration and several light red spots attributable to old interventions.

There are numerous surface abrasions, structural micro-lesions, of medium-light size and occluded by cohesive dirt, due to the marble which has undergone mechanical stress and expansion/contraction phenomena, typical of the crystalloblastic structure, since the moment of extraction and then processing.

The rough grouting and additions are evident, evidence of a previous restoration work, probably made necessary by an accidental event which must have resulted in the breaking of the middle and ring fingers of the left hand, the partial detachment of the right arm and a portion of the left one, probably around the 80s of the twentieth century, a restoration that has not been confirmed in the archival documentation.

The gluing of the limbs does not show any difference in material level, but the presence of yellowed two-component adhesive, in correspondence with the fingers and highlighted with a UV (ultraviolet) lamp, partially disfigures the correct legibility.

At the base there are two paper inventory labels from 1951-52 and 1977-78, as well as two autographed red inscriptions, probably painted with a wax binder, bearing the wording “C. 1081.” and “286”, indicating the old inventory numbers, respectively from 1879 and 1905.

Thanks to an agreement between the University of Naples Federico II and the Royal Palace of Caserta, an extended minero-petrographic, chemical and microbiological analysis of the sculpture “Real Infante Carlo Tito di Borbone” was carried out in order to provide archaeometric and conservative information on the artifact, showing some localized degradation and apparent traces for previous restoration interventions. The current scientific investigation was then followed by a restoration of the sculpture (Manzone 2022). The infant sculpture is currently exposed in the Royal Palace of Caserta, in the Queen’s room.

This minero-petrographic, chemical and microbiological analysis represents one of the very first scientific studies on the works by Sanmartino (Di Turo etal 2018).

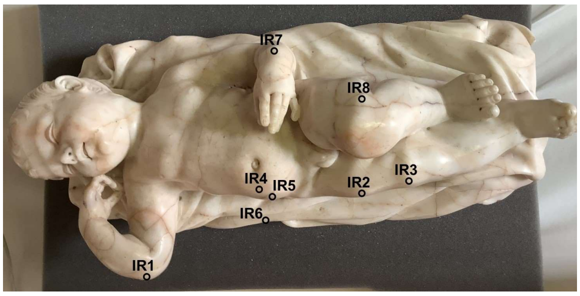

Fig. 1. The statue with locations of ER-FTIR analysis

II. MINEROPETROGRAPHIC ANALYSIS

IIA. Analytical procedure

The surface of the sculpture was preliminary observed in visible light with a MIC-FI portable video-microscope (magnifications 5x-200x). A BRUKER Optics ALPHA-R portable spectrometer were adopted for non-destructive mineralogical analyses in External Reflectance Fourier Transform Infrared spectroscopy (ER-FTIR). The spectra were acquired on selected points (**Fig. 1**) in the range 7500-317 cm^{-1}, with a spectral resolution of 4 cm^{-1}, and then processed and interpreted using the OPUS software ver. 7.8.44. Three selected fragments of the stone were collected below the sculpture for the preparation of thin section (ca. 30 µm) that were observed in transmitted and polarized light microscopy (OPTIKA B-600 POL microscope equipped with a ZEISS Axiocam 105 color camera) for the evaluation of petrographic features. Images were acquired using a ZEN 2.3 Lite software.

IIB. Mineralogical composition and petrographic features

The stone used for the realization of the sculpture displays a whitish, smoothed, and polished surface interested by an intense and irregular network of fractures, filled by reddish to grayish materials, probably consisting in insoluble residues or allochthonous substances. Video-microscope highlighted frequent impurities mainly due to alteration phenomena as well as several discontinuities and integrations attributable to previous restoration activities.

ER-FTIR spectra showed in the fingerprint region (2000-400 cm^{-1}) the typical spectral signals of calcium carbonate (i.e., calcite) affected by *Reststrahlen* and derivative effects normally observed in external reflection sampling procedures (Izzo et al. 2020). Along with the diagnostic bands of calcium carbonate (1500-1400, 1800, 870, 710 cm^{-1}), infrared signals of organic compounds, the nature of which will be discussed in the next sections, were also observed at about 2920, 2948, 1720, 1230, 1140 e 1080 cm^{-1}.

Furthermore, microscope observation of thin-sectioned samples confirmed that calcium carbonate detected in ER-FTIR can be ascribed to calcite. This mineral appears in plane polarized light with a variable relief and euhedral habits. It shows rhombohedral cleavage (75° intersection lines) and high birefringence in crossed polarized light. The granoblastic texture of samples C1 and C2 is medium coarse-grained and well sorted, whereas it is finer and less sorted in the sample C3. At higher magnifications, interlocked crystals intersect at 120° triple junctions and display slightly dissolved boundaries likely due to the presence of aggressive solutions percolating trough the fissures of the stone at relatively high lithostatic pressures.

IIC. Conclusions on the minero-petrographic analyses

According to EN 12670:2001 recommendation and the scientific classification of natural stones, the rock used for the sculpture of "Real Infante Carlo Tito di Borbone" can be classified as marble. From a petrographic point of view this term refers to a metamorphic rock containing more than 50% of carbonates (calcite or dolomite) showing a granoblastic texture and formed by the metamorphic recrystallization of a carbonate rock protolith. Commercially, the term marble indicates a compact and publishable natural stone normally used as building or decorative material, which mineralogical composition (i.e., calcite, dolomite or serpentine) provides a hardness of about 3-4 on the Mohs scale. This category includes also other lithologies such as, for example, limestone, dolomites, serpentinites, calcareous breccias, etc.

The local dissolution and the consequent reprecipitation of carbonate minerals forming the examined sculpture confer, in some parts of the stone, peculiar textural features that resemble those of an alabaster-like marble.

III. CHEMICAL ANALYSIS

IIIA. Sampling for chemical diagnostics

The chemical analysis focused on the nature of the protective films and adhesive materials used in the conservation/restoration, along with incoherent material detached from the sculpture. The diagnostic plan involved a) vibrational (FT-IR and Raman (Vergara et al 2010)) spectroscopy of the adhesive present on the right hand (sample 1), of protective films (sample 2), and of incoherent brown material collected in a cavity/hole behind the right-hand ear (sample 9); b) chromatographic analysis of dark area on the film covering the sculpture (samples 5 e 6).

IIIB. Vibrational spectroscopies

Raman investigation on samples 1 and 2 reveals a mostly organic nature, with sample 1 highly unsaturated. Regarding the adhesive, the Raman band at 1600 cm^{-1} for sample 1, together with several FT-IR bands (1659 cm^{-1} and 827 cm^{-1} in **Fig. 2**), suggest the presence of aromatic rings in the adhesive. The Raman band at 3067 cm^{-1} is compatible with epoxydic groups.

FTIR data in **Fig. 2** show that sample 2 is mostly saturated with traces of $CaCO_3$ (calcite) (Bischoff 1985), likely from the marble statue (see section IIC). No traces of gypsum (Sarma et al. 1998). The FTIR spectrum of sample 2 show a complex band 1710-1750 cm^{-1} suggesting a significant number of carbonyls, including ester (minor), carboxylic and hydroxycarboxylic (Tanner et al 2019; Špaldoňová et al 2020) in mostly saturated alkyl chains. The FTIR spectrum of sample 9 shows calcite dispersed in a mixture of different organic compounds, compatible (see section IV) with an ongoing biodeterioration, possibly responsible for the incoherent detachment from the statue.

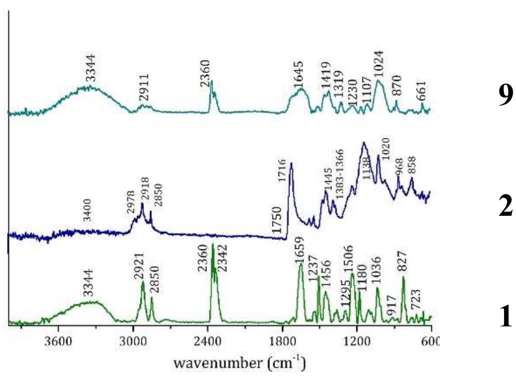

Fig. 2. Representative FTIR spectra of the adhesive (sample 1), the film (sample 2), and the incoherent material (sample 9).

(Asquier etal 2009).

IIIC. GC-MS chromatography

Samples under investigation appeared as dark-colored spots widely distributed over the entire statue. To identify the organic components of this film-forming substance, we used a gas chromatography coupled with mass spectrometry, GC-MS (Bonaduce et al 2017; Mazurek et al 2019) based approach. Sampling was performed after testing the solubility of stains with solvents of different polarity. Hexane (which completely removed stains thus demonstrating their non-polar nature) was mixed with a thickener (Klucel-G) (Melchiorre et al. 2019) and this solution was then used for sampling. The organic component contained in each sample was then subjected to a transesterification protocol and then analyzed by GC-MS. The analysis of the fragmentation patterns and the comparison with the NIST database led to the identification of palmitic and oleic acid. The solubility data indicated the presence of non-polar substances. These data along with the GC-MS characterization allowed us to preliminary hypothesize a wax of natural origin. Indeed, the methyl esters of myristic, palmitic and lignoceric acids are compatible with the presence of beeswax. Moreover, the total absence of variable chain hydrocarbons, excludes the presence of other types of film-forming substances not of natural origin.

IIID. Conclusions on the chemical analyses

The combined spectroscopic (FT-IR e Raman) and chromatographic analysis coupled with mass spectrometry (GC-MS) can be summarized as follow:

a) The protective film is a mixture of carbonyl saturated species (from FTIR), mostly assignable to natural wax, possible bee wax (from GC-MS).

b) Calcite was identified as dispersed into the film (possibly from the sculpture), and no gypsum was detected.

c) The adhesive looks an unsaturated epoxydic resin (from Raman and FTIR).

d) The incoherent fragment is composed of calcite (possibly from the sculpture) and of a variety of organic compounds (from FTIR), indicating a diffuse biodeterioration.

IV. MICROBIOLOICAL ANALYSIS

IVA. Sampling for microbiological diagnostics

The sampling points were chosen based on the visibility of the damage to the surface. Samples were taken by using adhesive tape strips or by gently rubbing the statue with sterile cotton swabs. Samples were deposited into a sterile 1,5 mL tubes containing saline solution 0,8% (w/v), until arrival at the laboratory. Both selected sampling method were chosen due to their non-destructive characteristics (Urzì, C and De Leo F 2001).

IVB. Isolation of microorganisms

Starting from the collected samples, serial dilutions have been prepared and distributed on 9 cm diameter Petri dishes with a different agar medium. Potato Dextrose Agar (PDA), Bacto Yeast Extract (BYE) and Bold's Basal Medium (BBM) were respectively used for growing fungi, heterotrophic bacteria, and phototrophic microorganisms (algae and cyanobacteria). The incubation was carried out at 24–25˚C under a continuous irradiance of 60 µmol photons m^{-2} s^{-1} for phototrophic microorganisms, in darkness for heterotrophic one. Microbial colonies growth was daily checked for 30 days. Afterwards, the obtained colonies from each dish were separately cultivated to obtain monoclonal cultures, useful for DNA isolation.

IVC. DNA-based analyses

Genomic DNA was extracted using the procedure described by Doyle & Doyle 1990 and used for a Polymerase Chain Reaction with primers targeting the universal primers for prokaryotic 16S (primer forward 5'–AGGATGCAAGCGTTATCCG–3'; primer reverse, 5'–GGGGCATGCTGACTTGACG–3') and the internal transcribed spacer region for eukaryotic (primer forward, 5'-TCCGTAGGTGAACCTGCGG-3'; primer reverse, 5' -TTCAAAGATTCGATGATTCAC-3').

The amplification reaction, purification and sequencing of the obtained amplicons were carried out according to the procedure elsewhere describe (De Natale et *al.*2020).

IVC. Conclusions on the microbiological analyses

The samples allowed us to isolate and identify 2 bacterial strains and 10 fungal strains (**Tab.1**), while no cyanobacteria or microalgae were detected. Regarding the fungal isolates, most of them belong to the genera *Fusarium* and *Cladosporium* and have already been observed on marble works of art as responsible for the phenomenon of biodeterioration. On the other hand, the isolate identified as *Sarcoladium subulatum* is reported for the first time as colonizer of marble work of art. Thus, its eventual biodeteriogenic activity should be evaluate. Finally, regarding bacteria isolates, is well known that *Bacillus* genus is a ubiquitous environmental contaminant, whose spores are able to deposit on stone surfaces, apparently without causing damages on them.

Table 1. Identification of microbial isolates based on molecular analyses

Sample	Scientific name	Accession
IR1-2-8	*Fusarium oxysporum*	KJ026701.1
IR2-3-7	*Sarcoladium subulatum*	HG965032.1
IR3-7-9	*Cladosporium cladosporioides*	MN830914.1
IR4-5	*Cladosporium tenuissimum*	HM776419.1
IR5-1	*Fusarium oxysporum*	MN959991.1
IR6-9	*Bacillus megaterium*	KT375323.1
IR7-2-3	*Bacillus kochii*	KC431016.1
IR8-4-5	*Cladosporium limoniforme*	MW450914.1
IR9-1-3-4-7	*Cladosporium sphaerospermum*	MW113292.1

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