A MULTI-ANALYTICAL APPROACH TO ADDRESS A SUSTAINABLE CONSERVATION OF THE MAIN MARBLE PORTAL OF THE MONREALE CATHEDRAL

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Abstract

The Main Portal of the Cathedral of Monreale is one of its magnificent external architectural elements. Recently, a conservation campaign was carried out for increasing its state of conservation, endangered by physical decays phenomena. The previous restorations, occurred over time, and the rising damp have contributed to its worsening. An integrated and multi-analytical diagnostic campaign has been provided to investigate the constitutive materials, the decays and the restorations coverings. Thanks to the analytical results, it was set a sustainable conservation treatment aimed to remove the causes of decays in view of the retractability of the original matter in the future. A difficult and complex cleaning was performed to remove the old coverings and safeguard traces of the original polychromy. An inorganic-mineral consolidating treatment, ammonium phosphate based, was carried out to re-give cohesion to the powdered marble especially in presence of water and salts. Several strategies of application were provided to have an efficient consolidation. A so representative monument, as the main portal, required a sustainable approach, able to interfere with the future conservation.

Keywords: Medieval sculpture; Ammonium phosphate; Polychrome marble; Mosaic tiles.

Introduction

The Cathedral of Monreale (Palermo, Sicily) is one of the most representative monuments of the Arab-Norman period in Sicily. It has been included in the World Heritage List by UNESCO in July 2015, within the serial heritage site “Arab-Norman Palermo”. It was founded by King William II (1166-1184) from 1174 to 1186. The Cathedral is the best example of the magnificent fusion of eastern and western influences taken by Byzantine, Islamic and Romanesque craftsmanship. The Main Portal, known as the “Portal of the Paradise” (Fig. 1), made of marble blocks, is one of the most important external architectural elements of the whole complex. It is articulated in piers, capitals and archivolt. The entire portal is adorned with

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geometric mosaics and figured bas-relief carvings with a symbolic meaning, referring to the path to salvation [1]. A 3D modelling relief has documented this valuable and singular monument, significant of this era [2].

![Image of the main portal of the Cathedral of Monreale before and after conservation treatment.](image)

**Fig. 1.** The main portal of the Cathedral of Monreale before and after conservation treatment. Dimensions: maximum height: 9.8 m; total width: 7.7 m; pier width: 2 m.

In the last years, a conservation campaign was carried out on the Main Portal with the aim of improving the worst state of conservation of lithic matter. The consumption of the marble was so critical and heavy for large areas constituting the gradual losing of mosaics and carving decorations of the portal. The piers (for about 2.20 meters height) and the capitals were the more involved areas by degradation of the portal.

The previous covering treatments, the rising damp and surface condensation have been caused the decays observed, as: browning of the surface, efflorescence, salt crusts, powdering, sugaring, delamination and cracks (Fig. 2).

![Image of piers with various defects](image)

**Fig. 2.** Particular of piers: a) state of conservation of the marble with salts efflorescence, sugaring, powdering, black crust, browning of the surface due to the previous covering; b) losing of the flourishing shape due to the effect of the salts efflorescence with following sugaring and powdering of the marble.

The ageing of synthetic covering, applied in the past for surface protection, created not only an aesthical damage as the brown film that hid the original marble nature mistaken for limestone, but also it produced a barrier effect on the surface that occluded the marble porosity causing the decrease of water permeability. Unfortunately, the considerable amount of internal moisture due to the rising damp was the main origin of physical degradation led by the carrying of soluble salts [3, 4, 5, 6]. The constant presence of water and salts have caused the ever-increasing losing of marble, not only on the surface, but especially below of the hard-brown crust, originated by the protective. This crust has confined the disgregational processes inside the marble causing the following detachment of portions; the originated surface from the
detachment, already degraded, was still more attachable from the physical phenomena as the wind, favouring secondary faster processes of consumption of carvings (Fig. 3).

Fig. 3. Particular of a capital. Losing of the carving due to the action of the ageing of a synthetic adhesive applied in a previous restoration.

Even if the capitals showed the same decays of piers, probably in this case caused by interstitial condensation phenomena, the previous wide use of a synthetic adesive for consolidating cracks and powdering have produced the tear-off of the marble surface because of the contraction of this film.

Thanks to a scientific methodological approach each conservative activity has been set to preserve the original matter. No archive data were found about the past restorations. It is possible to deduce useful information from the scientific analysis of materials added over time on the surface, allowing to reconstruct the history of material culture that begins in the 12th century till our days. On the basis of the diagnostic results, a proper conservation treatment was performed for preserving the monument and its wholeness. The conservation treatment has been articulated in several phases including the two most complex for the preservation of the monument: namely the cleaning and the consolidating treatment. In particular, an inorganic-mineral consolidating treatment, di-ammonium phosphate based was set to re-give cohesion to the marble and in the hard cases of disintegration it helped the following cleaning measure.

Experimental

An integrated and multi-analytical diagnostic approach was provided to investigate the constitutive materials, the original technique of execution, the degradation processes and the covering used in previous undocument treatments.

After a preliminary in situ investigation by using Infrared Thermography and X-Ray fluorescence Spectrometry for a mapping of different tipology of surfaces and its conservation state, 20 significative areas were sampled (Tab. 1) and cross-sections were prepared. Samples were investigated by XRD, Raman and SEM-EDS to discriminate original, degradation and restoration surfaces; ionic chromatography was used to determine the soluble salts; FT-IR (400-6000 cm⁻¹) and Py-GC-MS analyses were applied to characterize organic materials due to previous restoration works.

For the thermographic acquisitions, a FLIR model B335 thermal imaging camera was used which uses an uncooled microbolometric thermal sensor with a resolution of 320x240 pixels (thermal range from -20°C to + 120°C, accuracy +/- 2% of the measured temperature; spectral field 7.5÷13 μm; spatial resolution 1.36 mrad; field embraced 25°×19°). The thermal imaging camera is also equipped with a 3.1 Mpixel photographic sensor that allows the acquisition of the thermal image at the same time as the visible one, therefore with the same shooting conditions.
The thermographic investigation conducted in this case was of an active type. To provide an appropriate thermal gradient to the areas to be investigated, the surfaces were subjected to thermal radiation through the use of 2 halogen red bulb lamps with a color temperature of 3200 K, 800 W/h.

Table 1. Samples and analytical techniques applied to characterize restoration, degradation and original materials found on marble surface

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface</th>
<th>Analytical techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Not cleaned</td>
<td>XRF, FTIR, SEM-EDS, Py-GCMS</td>
</tr>
<tr>
<td>2</td>
<td>Cleaned</td>
<td>XRF, FTIR, SEM-EDS, Py-GCMS</td>
</tr>
<tr>
<td>3</td>
<td>Not cleaned</td>
<td>FTIR, Py-GCMS</td>
</tr>
<tr>
<td>4</td>
<td>Cleaned</td>
<td>FTIR, Py-GCMS</td>
</tr>
<tr>
<td>5</td>
<td>Cleaned</td>
<td>FTIR, Py-GCMS</td>
</tr>
<tr>
<td>6</td>
<td>Not cleaned</td>
<td>FTIR, SEM-EDS, Py-GCMS</td>
</tr>
<tr>
<td>7</td>
<td>Not cleaned</td>
<td>SEM-EDS, Py-GCMS</td>
</tr>
<tr>
<td>8</td>
<td>Not cleaned</td>
<td>SEM-EDS, IC</td>
</tr>
<tr>
<td>9</td>
<td>Not cleaned</td>
<td>IC</td>
</tr>
<tr>
<td>10</td>
<td>Not cleaned</td>
<td>IC</td>
</tr>
<tr>
<td>11</td>
<td>Not cleaned</td>
<td>XRF, IC</td>
</tr>
<tr>
<td>12</td>
<td>Cleaned</td>
<td>FTIR, SEM-EDS, CROSS-SECTION</td>
</tr>
<tr>
<td>13</td>
<td>Cleaned</td>
<td>XRF, SEM-EDS, CROSS-SECTION</td>
</tr>
<tr>
<td>14</td>
<td>Cleaned</td>
<td>XRF, SEM-EDS, CROSS-SECTION</td>
</tr>
<tr>
<td>15</td>
<td>Not cleaned</td>
<td>CROSS-SECTION</td>
</tr>
<tr>
<td>16</td>
<td>Cleaned</td>
<td>CROSS-SECTION</td>
</tr>
<tr>
<td>17</td>
<td>Cleaned</td>
<td>Py-GCMS</td>
</tr>
<tr>
<td>18</td>
<td>Cleaned</td>
<td>XRD</td>
</tr>
<tr>
<td>19</td>
<td>Cleaned</td>
<td>XRD</td>
</tr>
<tr>
<td>20</td>
<td>Cleaned</td>
<td>CROSS-SECTION, SEM-EDS MAPPING, RAMAN</td>
</tr>
</tbody>
</table>

XRF investigations were preliminary in-situ performed to identify elemental composition on marble or glasses surfaces and to select the sampling area. The used XRF portable spectrometer consisting of a miniature X-ray tube system, which includes the X-ray tube (max voltage of 40 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics and the USB communication for remote control; a Silicon Drift Detector (SDD) with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line Energy Resolution (depends on peaking time and temperature); 1 keV to 40 keV Detection range of energy; max rate of counts to 5.6×10^5 cps; software for acquiring and processing the XRF spectra. Primary beam and detector axis form an angle of 0 and 40 degrees respectively with the perpendicular to the sample surface. Tube voltage 35 kV, current 80 μA, acquisition time of 100 s, no filter was applied between the X-Ray tube and the sample, distance between sample and detector around 1 cm are the measurement parameters adopted for this study. The setup parameters were selected to have a good spectral signal and to optimize the signal to noise ratio (SNR).

Infrared spectra were collected on a FT-IR Perkin Elmer spectrum 100. the spectra were acquired in modality between 400 and 4000 cm⁻¹, with a resolution of 4 cm⁻¹.

The cross-sections were prepared according to the procedures recommended by the UNI 10922: 2001 Standard (Ref. Recommendations CNR - ICR NorMal 10/82, 13/83 and 14/83 - UNI 10924: 2001 - UNI 10922: 2001) and subsequently analyzed by polarized light microscope (observations in transmitted light).

Two Raman micro-spectrometers were needed for Raman measurements; the first is a Labram from Horiba equipped with a 633 nm He-Ne laser source, 18 mW power, the second a Renishaw InVia equipped with a near infrared source (785.5 nm, 300mW power) used inside to distinguish the oxalates present, minimizing the problem of fluorescence.

Py-GC/MS analyzes were performed with an integrated system consisting of a SGE PYROJECTOR II pyrolyser, a Perkin Elmer Clarus 680 gas chromatograph equipped with a Perkin Elmer Elite-5MS column, 30mm×0.25 mm i.d. with 0.25 μm film thickness, and a Perkin Elmer Clarus SQ 8T single quadrupole mass spectrometer. The samples were transferred to a quartz capillary (4 cm×0.53 mm), which was subsequently inserted into the pyrolyser, maintained at a temperature of 500°C and a pressure of 15.0 psi. The pyrolysis chamber is connected directly to the gas chromatograph injector, maintained at a temperature of 280°C.
The temperature of the transfer line was 280°C, while that of the ion source was 250°C. The mass spectrometer operated in the positive ionization mode (70eV) with a mass range of 40-400 m/z. The following temperature program was applied to the chromatographic oven: 40°C for 4 minutes, 10°C per minute up to a temperature of 280°C, which was kept constant for 7 minutes. The carrier gas used is helium with a constant pressure of 13 psi. The solvent delay is 0.5 min. The analyzes were carried out in split mode with split ratios of 30:1.

**Results and discussion**

*Mapping of detached or decoese areas*

Preliminarily, IR thermography provided a mapping of thermal anomalies (detachments, cracks, different construction materials), providing an effective support for the operations aimed at securing and consolidating the surfaces both carved and embellished by mosaic decoration. In the case of mosaic tiles, the thermal anomalies could also be traced back to the deterioration or the total lack of bedding mortar (Fig. 4).

![Fig. 4. IR Thermography: mapping of thermal anomalies (detachments, cracks, integrations) on mosaic decoration and carved marble to provide a support for securing and consolidating the precious surfaces.](image)

*Identification of past degraded treatments and the new conservative approach*

Thanks to the multi-technique analyses carried out on the 20 marble microsamples, consistent information has been obtained, which suggests that conservative events are fairly homogeneous despite the extension of the Portal. SEM-EDS analyses, combined with the elemental analysis, Raman, XRD and FTIR spectra, have made it possible to identify in almost all the samples a top layer of calcium oxalate which insists on a marble matrix predominantly consisting of calcium carbonate, including magnesium compounds (Fig. 5) [7-8]. Two different Raman bands have been systematically identified in most of the acquired spectra, respectively at 1476 and 1479 cm\(^{-1}\), a region linked to the symmetrical stretching of the C-O bond. The 1476 cm\(^{-1}\) band could be assigned to magnesium oxalate [glaubersite, MgC\(_2\)O\(_4\)-2(H\(_2\)O)], while the 1479 cm\(^{-1}\) band to calcium oxalate in the dihydrate form [weddellite, CaC\(_2\)O\(_4\)-2(H\(_2\)O)] [9-10]. Furthermore, the spectra acquired in the substrate area showed the presence of calcite (CaCO\(_3\)) and dolomite [MgCa (CO\(_3\))\(_2\)].
Moreover, on the n.1, n.2, n.3, n.5 and n.6 samples the FT-IR analyses verified the presence of gypsum (CaSO₄), Si-O-Si stretching bands and a signal in the range around 3000-2850 cm⁻¹ attributable to CH₃ stretching. For the same set of samples, the Py-GC-MS analyses provided similar findings, mainly characterized by the presence of siloxane compounds probably due to the use of a polydimethylsiloxane (Fig. 6).

On the n.3 and n.4 samples phthalates were identified, in particular di-isotyl phthalate added to the resin as plasticizers or present as sample contaminations. Only on the n.6 sample was the presence of sulfur dioxide as a sulfur pyrolysis product, probably due to the presence of a high gypsum content in the stone substrate. All the Py-GCMS analysed samples are also characterized by the presence of short-chain hydrocarbons, which could be due to the presence of a microcrystalline wax previous treatment.

A different composition has the n.7 and n.17 samples, where in the n.7 an alkyd resin modified with styrene [11] has been identified, and di-isobutyl phthalate and poly vinyl phenyl ketone added probably as plasticizers; while in the n.17 sample was found the presence of polystyrene [12] and polydimethylsiloxane found in smaller quantities (Fig. 7).

For these two samples it is possible to hypothesize that the identified chemical composition is attributable to that of an adhesive product. The Py-GC-MS results, in combination with other analytical techniques, allowed to hypothesize the presence of treatments based on polymers and organic substances attributable to undocumented interventions realized in different periods. In particular, a siloxane nature consolidating/protective agent was found.
Fig. 7. Py-GC/MS analysis AF: phthalic anhydride; St: Styrene; K: PVPK: Polyvinyl Phenylketone

Subsequently, the diagnostic investigations were aimed at the characterization of the saline species to understand which could influence the effectiveness of the consolidating treatment over time, and to schedule specific desalination cycles of the surfaces. The ionic chromatography analyses aimed to soluble salts identification revealed the presence of (Tab. 2):

- chlorides, sulphates (anions) and Na, Mg, Ca, K (cations) on n.8 sample taking at a height around of 230 cm;
- chlorides, sulphates, nitrate (anions) and Na, Mg, Ca, K (cations) on n.9 sample taking at a height around of 50 cm, in this case the Mg content is higher than the n.8 sample, taken on the same side of the Portal;
- chlorides, sulphates, nitrate (anions) and Na, Mg, Ca, K, NH4 (cations) on n.10 sample taking at a height around of 50 cm height; in this case the Mg content is higher than the n.11 sample, taken on the same side of the Portal;
- chlorides, sulphates (anions) and Na, Mg, Ca, K (cations) on n.11 sample taking at a height around of 230 cm.

Tab. 2. Results of the ionic chromatography analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H(cm)</th>
<th>Cl(μs)</th>
<th>SO4(μs)</th>
<th>NO3(μs)</th>
<th>Na(μs)</th>
<th>K(μs)</th>
<th>Mg(μs)</th>
<th>Ca(μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>230</td>
<td>0.111</td>
<td>0.073</td>
<td>ND</td>
<td>0.146</td>
<td>0.043</td>
<td>0.188</td>
<td>4.325</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>0.168</td>
<td>29.037</td>
<td>0.225</td>
<td>1.465</td>
<td>1.135</td>
<td>32.074</td>
<td>7.728</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>0.793</td>
<td>4.300</td>
<td>0.673</td>
<td>7.877</td>
<td>2.297</td>
<td>2.890</td>
<td>6.725</td>
</tr>
<tr>
<td>11</td>
<td>230</td>
<td>0.159</td>
<td>0.192</td>
<td>ND</td>
<td>0.306</td>
<td>ND</td>
<td>0.236</td>
<td>4.225</td>
</tr>
</tbody>
</table>

The removal of siloxane aged covering is not usually easy to do, because it forms a hard crust on the top of the marble surface and underneath whole the stone could be disintegrated by the salts crystallization, like in this case. Each conservative trouble (as salts, deposit, black crust, siloxane covering, disintegration) were faced one by one with a proper strategy by ensuring that each of these it was preparatory for the following step. After the cleaning and before the consolidating measure a desalination treatment has been carried out for two times. The aim of the cleaning was the removal of all the extraneous materials from the surface, as the deposits, previous coverings (waxes and poly-siloxane) and salts. Chemical and mechanical systems were chosen methods for the cleaning, taking into account the state of conservation and the kind of surface (mosaics, bas-reliefs, marble slab) (Fig. 8).

In general, the cleaning was performed in three steps, but not all of them were carried out over the all surface. The cleaning agents used were described in order of applications: 1) non-ionic surfactant in water solution at 2%; 2) compress of cellulose powder and sepiolite (1:1) with ammonium carbonate in water solution; 3) a o/w emulsion of white spirit and ammonium acetate 5% water solution. All the water solutions were made with demineralized
water. Each of these steps have needed the help of the precision mechanical cleaning using by scalpel and cotton tampons.

The inorganic-mineral consolidating treatment, ammonium phosphate based (di-ammonium-hydrogen phosphate, DAHP), was performed followings different application strategies (compress, slow infusions, mortars) according the seriousness of the disintegration state of the marble (Fig. 9). The ammonium phosphate is a promising consolidant for carbonatic stone [7] useful in the case of presence of water and soluble salts, because the calcium phosphate has a very low solubility [13, 14, 15].

![Fig. 8. a) Particular of the archivolt. Cleaning test of polychrome marble surface for removing deposits, black crust and coverings. b) Particular of a capital. Cleaning treatment carried out with surgical scalpel and magnifying eyeglasses.](image)

![Fig. 9. Particular of capitals. Mineral consolidation treatment with di-ammonium phosphate solution applied by a slow drip. Consolidation treatment of a fissure made by using a lime mortar added with di-ammonium phosphate solution.](image)

**Mosaic glass tesserae: chromophores identification**

The conservative project of the Main Portal of the Cathedral of Monreale also represented an opportunity for a better understanding of the materials that make up the mosaic decorations that have never been studied to date. Indeed, after the cleaning and consolidation treatments of the precious surfaces, XRF in situ analyses were carried out to identify the chromophores of mosaic glass tesserae for red, green, purple and blue glass and top of gold layers (Fig. 10).

![Fig. 10. XRF in situ analyses to identify the chromophores of mosaic glass tesserae.](image)
The identification of the chromophores of both the original portion and those of the subsequent additions have provided the evidence listed below:

**Blue and green tiles**: the chromophore can be identified by copper, detected in association with zinc. The latter allows to hypothesize a derivation of copper from metal processing slag. The intensity of the lead signal is variable: in the green tiles it is present in low counts and also in this case interpretable as the impurity of the metal alloy from which the chromophore is obtained; in the original blue tiles the lead is present with high signal counts, probably added to increase the level of brightness. Finally, the tin identified only in the two blue tesserae probably was added in the form of oxide (cassiterite) with the function of opacifier. The green color is given by the simultaneous presence of Cu$^{2+}$ and Fe$^{3+}$: the yellow due to the presence of iron neutralize the blue component of the copper thus determining a green tone [16].

**Red tiles**: the identified chromophore is copper, attributable to the use of Cuprite (Cu$_2$O) or metallic copper, both verified in the literature to obtain red glass tesserae; it should be noted that for the original red tiles, compared to the red one supporting the gold foil relating to the integration zone, a lower intensity of copper was found and, at the same time, a higher intensity of the iron XRF signal. The latter in the form of oxide was added to the melt in which the copper was already dissolved in a variable quantity according to the shade to be achieved.

**Gold foil tiles with vitreous “cartellina” (a thin top glass layer aimed to preserve the gold foil)**: in addition to the confirmation of gold as the thin leaf, the investigation allowed to verify the presence of manganese also in the composition of the transparent folder added in the form of oxide with bleaching function;

**Purple tiles**: the high manganese levels found in the purple cards are in accordance with what is known in the literature. It has been verified [16] that an excess addition of manganese oxide, compared to the appropriate quantity normally used with a bleaching function, produces this coloring;

**Black tiles**: no unique chemical markers emerged for the identification of the black chromophore, however the evidence obtained can be associated with the hypotheses already exposed in the literature [16] according to which obsidian was not used. In general, the constant presence of potassium was found to be associated with the addition of vegetable ash during the melting of the silica.

No differences were found between the original and the integration cards in terms of the presence of constituent chemical elements, but only in intensity ratios between the characteristic signals, attributable to a different proportion in the mixtures used to obtain the glass pastes.

**Conclusions**

The diagnostic investigations allowed to identify the degraded protectives applied over time on the surfaces, that have contributed to the development of decays phenomena, supporting the methodological approach to clean and consolidate the complex surfaces. About the conservation work, the methodologies applied have been shown a good efficacy. A compromised matter like that, it has required a sustainable approach for the monument in view of its future conservation. The inorganic-mineral consolidating treatment has been chosen precisely because it matches to the retractability criteria, essential a suitable conservation of a monument that it will need future maintenance. Moreover, the investigation analyses allowed to identify the chromophores of glass mosaic tesserae used on piers decoration providing information on production technologies.

**References**


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