1. The fountain and its history
The statue of *Nettuno*, standing in the centre of the fountain located in Piazza della Signoria (Figure 1) (Firenze, Italy), was sculpted by Ammannati from 1560 to 1565. Cosimo I de' Medici planned to build the first public fountain in Firenze locating it at the Palazzo Vecchio corner. The water was taken by means of an ingenious piping system, collecting it from a spring on the opposite side of the Arno river. The fountain includes the statue of *Nettuno* (reminding the Granduke himself), standing on a cart dragged by 4 horses. At the bottom of *Nettuno*, three tritons playing horns are located. The basement of the fountain, made of “breccia medicea”, is decorated with four bronze sculptures representing sea gods with groups of bronze children, satyrs and fauns. In the past the fountain had 70 gushes which were drastically reduced over the time.

From its construction to the present, the fountain underwent many repairs and renovation works. Unfortunately the documentation is often incomplete and scarcely exhaustive. Indeed, the research carried out at the main Florentine archives has shown a very complex conservative history, but the details of
these works (timing, methodologies and materials employed) are not known. Nevertheless the collected information allowed to clarify the following aspects:

a) the fountain and the statue of Nettuno in particular were often damaged by acts of vandalism, the last of which occurred in 2005, when the right hand of Nettuno was broken;
b) the ordinary maintenance of the fountain has been frequently interrupted, making necessary many extraordinary repairs;
c) the most relevant documented renovation works occurred in 1980 and 1991. While the cleaning of the fountain carried out in 1991 through ammonium carbonate poultices applied only on the dirtier parts was very soft, on the contrast the renovation works performed in 1980 were more significant. They included the waterproofing of the basin of the fountain; the removal of calcareous deposits and algae from marble sculptures (the previous cleaning dated back to 1964); the fixing of the detached parts with epoxy resins; the replacement of the plumbing system with a new closed-circuit system with decalcified water; the re-establishment of old blocked gushes and water mains; the complete replacement of the paving around the basin;
d) by 1986 a “yellowing” of the surfaces of the fountain and the statue often occurred. Periodic cleaning did not solve the problem definitively, because the chromatic alteration progressively appeared again. At present the marble shows a pale yellowish colour, particularly evident in some areas.

2. The monitoring project
The present work is part of a wider project, supported by the Municipality of Firenze, which includes the participation of many institutes working in the conservation field. The basic idea of the entire project was to set up and test some techniques suitable to determine the conservation state not only of Nettuno, but also of the surrounding bronze statues. Furthermore, the diagnostic investigations were followed by cleaning and protective treatment tests carried out on both materials to select the more appropriate method of restoration and future preservation. The project is still in progress through a constant monitoring of the previously performed tests.

In this work, only the results concerning Nettuno marble statue are reported. The various institutes’ activities were carried out focusing on non-destructive analyses as follows:
- the micro cracks and their penetration depth into the marble’s bulk were checked by ultrasonic measurements, while pacometric investigations evidenced the position of the anchor bolts and the water pipes inside the statue;
- colorimetric measures and water absorption tests have been performed on several areas of the statue; after that, some areas were monitored to check the variations due to both cleaning and protective tests;
- a portable XRF equipment was used to detect the presence of elements different from marble chemical composition, particularly on some brownish and greenish areas.

In addition to non-invasive tests some micro-fragments have been sampled to characterize the marble and its conservation state by means of optical microscopy, FT-IR and SEM-EDX.

2.a Pacometric and ultrasonic investigations
Pacometric investigations for the detection of the metallic bars and pins inside the statue were performed all over the surface of Nettuno and the tritons. The function of these elements is not clear, even though many of them are supposed to have a structural function and others to be the remains of old water pipes. Ultrasonic measurements, a quick and non-destructive tool for the evaluation of stone’s integrity, showed a generally good preservation state of the marble. This well-known technique detects the reduction of ultrasonic velocity which indicates discontinuities and obstacles for the propagation of the ultrasonic waves. The ultrasonic non-direct methodology was used on Nettuno and the tritons, with the receiver and the transmitter not perfectly placed one in front of the other. To minimize the errors caused by this probe arrangement, ultrasonic tomography was carried out on several cross-sections of the statues and the relative 2D-velocity distributions were computed. In Figure 2 an ultrasonic tomography on Nettuno’ neck section is shown. Blue to green areas are characterized by high wave velocities and some ray paths are marked with the relative values shown in the table. Referring to literature data, velocity values greater than 3000 m/s characterize the sound Carrara marble [Köhler 1999] while velocity values in the 2000-3000 m/s range are indicative of the beginning of the “sugar-like” degradation, typical for exposed marbles. The recorded 2D-distribution maps indicate a general integrity of the stone, while some
criticisms have been pointed out corresponding to marble plugs, attached parts, large cracks, repairs and fillings made by plaster. The wave velocity measured on single paths decreases to values in the 1000 - 1500 m/s range at the left wrist of Netto for the presence of a fracture. A complete stop of the ultrasonic velocity was recorded near the neck of one of the rear tritons, indicating a deep crack into the bulk of the marble, probably caused by the degradation of the inner water pipe.

A significant reduction (down to about 1200 m/s) of the wave velocity was measured in correspondence of the calcareous accumulations, indicating the presence of voids and the lack of cohesion in the deposits. Pacometric and ultrasonic results have been mapped on a detailed 3D relief of the marble group, together with macroscopically visible structures, in a very enlarged scale.

![Figure 2. 2D-distribution map of ultrasonic velocity on a Netto cross-section, with the values for some specific paths.](image)

**2.b X-ray fluorescence analysis**

X-ray fluorescence analyses [Seccaroni, 2004] had the aim to investigate the presence of elements different from marble chemical composition. The spectra were collected in 16 areas (155 mm² each). For each point a sequence of two measures (70 sec) with different energy was carried out (40 keV - 6,5 μA for heavy elements; 5 keV – 7 μA for light elements).

In all the spectra the predominant signal is that of calcium (Ca, Kα = 3,69 keV) together with a little amount of strontium (Sr, Kα = 14,16 keV). Not considering the obvious presence of calcium, strontium is frequent in marbles as a vicariant element for calcium. In some areas additional signals of heavy elements were also present. On 5 areas, all positioned on the front of the statue, copper (Cu, Kα = 8,04 keV) was detected. In two areas it was associated with zinc (Zn, Kα = 8,64 keV). It might be outlined that the counts for these two heavy elements are lower respect to counts of the same signals in spectra registered on clearly visible green stains which were caused by the leaching of a bronze statue on the base of the fountain. Traces of lead (Pb, Kα = 10,54 keV) were also present in all the spectra.

**2.c Sample analysis**

Patinas and chromatic alterations are uniformly spread all over the surface of Netto, whilst films seem to concentrate where water was flowing slowly. Whitish crusts accumulate along the pathways of rainfalls. Several blackish spots are located on Netto's back and grouts are observed in both front and back sides of the statue. Samples have been taken from differently coloured patinas and films and investigated by means of optical microscopy as cross-sections, SEM-EDX analysis and FTIR spectroscopy and microspectroscopy.

FT-IR results indicate that gypsum, due to the sulphatation of the marble, and silicates associated to the airborne deposit, are widely present. Some samples contain calcium oxalate (wedellite), resulting from
the degradation of organic substances applied on the stone in the past and from the action of microorganisms’ metabolism (Figure 3). Some other weak signals (1020, 1114, 1160, 1380, 1635, 1710, 1730 cm$^{-1}$) detected in some spectra of patinas and films, were attributed to the remains of an acrylic polymer, applied to protect the stone during a past intervention. This hypothesis is supported by the observation in some cross-sections of a very thin layer (less than 30 μm) over the marble surface visible under UV light because of its light yellowish fluorescence (Figure 4). However, these findings are not enough to explain the colour of the patinas, which is rather to be considered as having an inorganic origin. The airborne deposit on the surface could have embedded rare coloured particles, as iron compounds detected by SEM-EDX, which caused the final yellowish appearance of the marble.

![Figure 3. FTIR spectra (KBr micro-pellet) of a sample (red) and its extract in acetone (blue) related to reference spectra.](image1)

![Figure 4. Micrograph (visible and UV light) of a cross-section. The thin fluorescent layer is indicated.](image2)

On the lower part of the statue group, the surface is covered by a thick (240-280 μm), grey and yellowish crust including several superimposed layers. The crust is made mainly of calcium carbonate, with a low
amount of gypsum. Silicon and phosphorus were also revealed by SEM-EDX analysis. Some of the layers contain also copper, iron, lead and zinc, probably coming from the corrosion of the water pipes, consequence of a poor maintenance.

In the blackened areas on Nettuno’s back, brown fungi and green algae have been observed by the optical microscope. The blackening of these areas is therefore related to the growth of biofilms containing brown fungi forming thick lumps of hyphae rather than to the deposit of airborne particles. The grouts to fill the cracks and fix the detached parts of the statue were made by a mixture of marble powder and epoxy resin. Different natural and synthetic organic materials such as vinyl and silicone polymers, probably connected to past interventions, were detected by FTIR in some samples.

2.d Tests of conservation treatments

Preliminary cleaning tests were carried out choosing two areas with thick calcareous crusts located in the lower part of the marble group (triton’s chest- area A and Nettuno’s ankle –area B) (Figure 5). Ion exchange resins and disodium and tetrasodium E.D.T.A. solutions were employed. A satisfactory cleaning level was achieved after three treatment cycles by using a cationic resin and a tetrasodium E.D.T.A. 5% solution applied by an Arbocel poultice. Where a thicker and tougher crust was present, the use of a scalpel and an ultrasonic ablator was needed. Finally, the cleaned areas were treated with a dimethylpolysiloxane product (SILIRAIN® 50), as a water repellent agent. The product was applied by brush until 'refusal'.

2.e Colorimetric measurements

A preliminary campaign of colorimetric measurements was carried out [AA.VV. 1998, CIE 2004, UNI EN 15886, 2010]. The measurements did not show considerable differences between the front and the back of the statue despite their different orientation and exposition to atmospheric agents. The lightness values (L*) are lower if compared with colorimetric values of a not aged white marble. L* values undoubtedly depend on the roughness and non homogeneity of the surface. a* (red-green axis) and b* (yellow-blue axis) values resulted spread on a quite large range, with a tendency to yellowish and greenish tones. Further colour tests were carried out to monitor the colour of the areas during and after the cleaning tests and the water repellent treatments. The lightness values L* of area A increased consistently reaching values close to those of sound white marble. A decrease of b* values, the yellow component, was also observed. These values are not similar to white marble’s ones showing a remaining residue of yellow tone. It is useful to mention that area A was positioned on a very yellow strip present on Triton’s chest.
The cleaned area B showed, before cleaning, lower L* values than area A for the presence of a thick greyish crust. After cleaning, L* values increased, showing a good removal of the crust. The total colour variations ∆E were eventually similar in all the cleaned areas (Table 1).

After the water repellent treatment, colour measurements were repeated. L* and b* parameters showed the greater variations. In particular, L* decreases in all the treated areas. In area A, b* parameter slightly raised, whilst decreased a little in B.

∆E values were similar for all the observed areas (Table 1). However the obtained ∆E ~ 7/8 is higher than the limit considered detectable by the human naked eye.

Table 1 – Colour measurements before and after cleaning and after the protective treatment.

<table>
<thead>
<tr>
<th>Area</th>
<th>Description</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>∆E#</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Before cleaning</td>
<td>70.17</td>
<td>0.45</td>
<td>9.60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>After cleaning</td>
<td>83.78</td>
<td>-0.70</td>
<td>6.47</td>
<td>14*</td>
</tr>
<tr>
<td></td>
<td>After protective treatment</td>
<td>76.25</td>
<td>-0.25</td>
<td>7.94</td>
<td>8**</td>
</tr>
<tr>
<td>B</td>
<td>Before cleaning</td>
<td>65.63</td>
<td>0.63</td>
<td>3.18</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>After cleaning</td>
<td>75.61</td>
<td>-0.13</td>
<td>9.46</td>
<td>15*</td>
</tr>
<tr>
<td></td>
<td>After protective treatment</td>
<td>67.68</td>
<td>-0.73</td>
<td>7.55</td>
<td>8**</td>
</tr>
</tbody>
</table>

# \[ \Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \]

*colour difference measured before and after cleaning

**colour difference measured after cleaning and after protective treatment

2.f Sponge contact measurements

The water absorption measures were carried out according to the contact sponge method, after preliminary tests carried out to establish the best contact time which was set at 60 sec [Pardini 2003, Vandervoorde, 2009]. The method uses a cellulose sponge soaked with a known quantity of distilled water. The sponge is kept in contact with the surface for a given time and at a specific and constant pressure. The amount of water absorbed is calculated as the difference of the sponge weight before and after the test, and it is expressed as the weight of water per surface unit per minute of contact (mg/(cm²*min)). Like for the colour tests, a first campaign of measures was performed. Polyacetate masks were used for a correct replacement of the sponge when the measures were repeated. The water absorption measures showed clear differences among the test areas, even if the values’ range is pretty narrow because of typical low absorption of marble.

On the front of the statue the areas with a higher amount of water absorbed in 1 minute (4.63 mg/cm², 3.69 mg/cm²) are the ones that appear smooth, whilst the rough areas showed the lower absorption values (2.95 mg/cm², 1.68 mg/cm²). This behaviour is caused by a compact and hard crust present in these areas. On the back, the higher amounts of water absorbed (6.73 mg/cm², 8.42 mg/cm²) correspond to the test areas more exposed to the atmospheric agents.

Cleaning tests and the water repellent treatment were monitored by means of water absorption measures. In area A and area B the sponge method was applied before and after the cleaning, and after the treatment. In both the areas the amount of water absorbed after the protective treatment was considerably lesser than that absorbed after cleaning. This result is related to a good efficacy of the product. In area B the reduction of water absorbed was about 70%, while for area A the reduction reached 85%. The amount of water absorbed in the different areas is reported in Table 2.
### Table 2 – Amount of water absorbed for surface unit measured before and after cleaning, and after protective treatment.

<table>
<thead>
<tr>
<th>Area</th>
<th>Description</th>
<th>Amount of water (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Before cleaning</td>
<td>10.52</td>
</tr>
<tr>
<td></td>
<td>After cleaning</td>
<td>8.84</td>
</tr>
<tr>
<td></td>
<td>After protective treatment</td>
<td>1.26</td>
</tr>
<tr>
<td>B</td>
<td>Before cleaning</td>
<td>19.78*</td>
</tr>
<tr>
<td></td>
<td>After cleaning</td>
<td>5.47</td>
</tr>
<tr>
<td></td>
<td>After protective treatment</td>
<td>1.68</td>
</tr>
</tbody>
</table>

* The values obtained in the area of the ankle before cleaning are not to be considered as water absorbed by the marble, because a phenomenon of dripping from the sponge occurred. It was due to a very low absorption capacity of the area for the homogeneous and hard crust on it.

3. Conclusions

The fountain and *Nettuno*’s statue in particular had a very complex conservative history which is poorly documented. Diagnostic investigations carried out to check the conservation state of the marble group involved micro-invasive tests and, mainly, non-destructive analyses. From a structural point of view, monitoring by pacometer and ultrasonic measurements enabled to locate metallic elements inside the group, belonging to original structures of the fountain or placed by conservative interventions. Moreover the technique allowed to assess fractures or lacks both inside the stone and on the surfaces. The analyses indicated that the marble sculptures are characterized by a quite good conservation state but some critic areas are present. Colorimetric measures demonstrated that the colour of front and back surfaces of the statue is variable. It is generally pale yellow changing to green or orange tones in a few particular areas. Water absorption tests showed low values on average, comparable to the water absorption of non altered marble. However they differ from area to area. The rough surfaces of the front side absorb lesser amounts than the smooth ones because of a thick non-porous crust present on them. The highest values of the back side are detected on the shoulders of *Nettuno*, the most weathered parts of the statue. Cleaning tests enabled to remove the deposit layer at the bottom of the statue, improving the brightness of the surface without eliminating completely its pale yellow tone, and reducing the water absorption. After the application of a water repellent treatment, instead, the brightness of the surface decreases and the water absorption falls down, proving a good efficacy of the treatment. The monitoring of treated areas is in progress.

As for colour and composition modifications of the marble surface, OM, SEM, FT-IR and XRF analyses ascertained that chromatic alterations are mainly due to the presence of iron, copper and lead compounds (sometimes in trace amount) but also to biofilms. Heavy metals probably come from the corrosion of the water pipes as a consequence of scarce ordinary maintenance of the fountain. Other agents, as air pollution or water flow coming both from rainfall and the fountain itself, certainly affected the marble’s conservation state. Finally, acrylic and vinyl polymers detected in some localized areas could support the hypothesis that the chromatic alterations are partially caused by the ageing of protective and/or consolidating products used in previous conservation works.

4. References


Acknowledgements

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