EVALUATION OF COLORIMETRIC CHANGES IN THE ITAQUERA GRANITE OF THE RAMOS DE AZEVEDO MONUMENT, SÃO PAULO, BRAZIL

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Abstract

Itaquera Granite, as a building stone material, was widely used in the early 20th century for the construction of buildings and monuments in the centre of the city of São Paulo, Brazil. The color variation of the Itaquera Granite of the Ramos de Azevedo Monument was monitored for two years and these data were compared with those obtained for fresh stone originated from a historic quarry. The oxidation of iron-rich minerals present in this granite, coupled with pollution (high levels of O₃), biological colonization, leaching of bronze, and the dissolution and reprecipitation of mortar, causes colorimetric changes in the stone. Measurements were also performed on zones of the monument with pathologies. Two statistical Canonical Biplot analyses were made on the data of chromatic coordinates monitored (L*, a*, b*, C* and H*): orientation/year and orientation/pathologies. The results obtained for the chromatic variation in the monument are primarily related to yellowing caused by deposition of atmospheric pollutants and weathering of iron-rich minerals.

Keywords: Itaquera Granite; Color; CIE L*a*b*; Spectrophotometer; Biplot analysis.

Introduction

The Ramos de Azevedo Monument, constructed of Itaquera Granite with bronze figures, was inaugurated in 1934 as a tribute to the architect with the same name, a major figure in the development of the city of São Paulo. It has dimensions of 5.60x15.50x13m. In 1967, the monument was removed from its original location for the widening of Tiradentes Avenue and construction of the Metro. After being dismantled and abandoned for 8 years, the monument was reassembled on the campus of the University of São Paulo where it remains today (Fig. 1).

Itaquera Granite was widely used in the construction of the old city centre of São Paulo [1]. It can be found in various monuments and buildings such as the Ladeira da Memória, the Municipal Theatre, Sé Cathedral, São Bento Monastery, Pacaembu Stadium, and many others.

The petrographic analysis of this granite can be found in the literature [2]. This stone (Fig. 2) has a grey color, serial inequigranular granulation, and crystals ranging from 0.2mm to

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2mm. It has a small degree of anisotropy due to its slightly oriented structure. Centimetre-scale micaceous enclaves are common. It is described as a biotite monzogranite and its composition is oligoclase (38%), microcline (33%), quartz (18%) and biotite (9%). Accessory minerals that were found included titanite (1%) with traces of zircon, apatite and opaques, as well as secondary minerals epidote and chlorite.

In this research the Ramos de Azevedo Monument was characterized colorimetrically using a spectrophotometer aiming to detect variations over the years and determine their possible causes. The colors of fresh granite, granite from the monument and soiling standards were compared.

Being a non-destructive technique, it is well suited for the study of monuments. Other advantages of its use are: the lightness of the equipment, its ease of use in the field and the relatively low purchase cost, all without the need to collect samples for testing.

Color analysis is performed on various materials [3–16]. In the case of the stone, it is used to detect changes and evaluate conservation treatments such as applying consolidants, water repellents and biocides [17–20].
When the standard observed is the color, it is necessary to know that changes in stones can be attributed to the degree of oxidation of the chromophore, which is the element responsible for the coloring. One of the most important chromophores is iron (Fe). When iron is oxidized it produces a red–brown color in the stone, whereas when it is reduced it produces a blue–black color. Yellowing can occur due to various processes, such as deposition or oxidation of organic matter and even iron and sulphating [21].

The degradation of stone depends on the combination of environmental factors and constituents of the stone [22-23]. The carbonate stones, for example, readily react with water and SO$_2$ in the atmosphere due to their constitution.

When exposed to weathering, stone structures are subject to the appearance of soiling, which modifies their colors. This process is enhanced when this environment contains atmospheric contamination (acid rain and particulate matter), as is the case in major cities and industrial areas. One of the components of acid rain is sulphur dioxide (SO$_2$), which comes from the burning of fossil fuels. This is rapidly oxidized to sulphur trioxide (SO$_3$), which readily reacts with water vapour in the atmosphere to form sulphuric acid (H$_2$SO$_4$). The deposition of particulate matter causes a darkening of the surface, known as soiling. This darkening is due to carbon particles that are expelled in the exhausts of vehicles powered by fossil fuels. This deposition is critical on stone due to the porosity and roughness of the surface [21].

P. Brimblecombe [23] points out that the yellowing of the stone can be originated from reactions with atmospheric sulfur dioxide or organic deposition such as ozone.

The color change can also occur due to other causes, including the growth of microorganisms, animal droppings, bonfires and the appearance of efflorescence. It is worth noting that maintaining the original color during restoration processes is a problem, because the color can be altered due to the use of mortars, consolidants, water repellents and biocides. When it is
necessary to replace blocks of stone, chromatic homogeneity is a factor that requires due consideration.

**Experimental**

The color of Itaquera Granite was evaluated using spectrophotometric and statistical methods.

**Spectrophotometric method**

The spectrophotometer is a device that measures the light reflected by a surface at each wavelength of visible light and produces the reflectance spectrum regardless of the ambient light where the measurement is being taken.

The light acquired by the spectrophotometer was divided according to the CIE L*a*b* diagram, which characterizes the color numerically according to the intensity of the wavelengths [4]. This system, which consists of a three-dimensional space, divides light into colorimetric parameters: luminosity, which is represented by the letter L*, for which the value 100 identifies white and 0 black, a* represents the colors green (negative values) and red (positive values) and b* represents blue (negative values) and yellow (positive values). A fourth parameter, C*, represents saturation. The parameter H* indicates the metric hue angle, which is similar to the chromatic hue [4, 6, 9, 10, 17].

The spectrophotometric method determines the chromatic homogeneity of heterogeneous materials such as stones, and can be used to track changes in color due to the processes of physical and/or chemical change (natural or accelerated), to check the aesthetic quality of ornamental stones and to monitor the application of chemical products such as consolidants, waterproofing agents or even for cleaning products [11, 13, 15, 24].

A Konica Minolta CM 2500d spectrophotometer was used with a D65 illuminant (which uses daylight for its calculations, including ultraviolet), specular component included (SCI) and excluded (SCE) modes, the observer at an angle of 10° and an aperture of 8mm. For rough surfaces, as is the case for the stone in the study, the specular light is very weak.

Due to the small size and light weight of the apparatus, spectrophotometry becomes an attractive technique for application *in situ* with cultural heritage, since as a non-destructive analytical method it allows a broad examination of an object for analysis of its statistical data [9].

This technique is also used to determine the degree of soiling of urban buildings and monuments, which are constantly exposed to pollution, and also to determine the effectiveness of cleaning techniques. For this, the parameters L*, a* and b* are measured before and after treatment. It is also interesting to compare these data with the original color of the stone [6, 25].

Many authors have used the spectrophotometer with cultural heritage [4-16, 26–30].

**Statistical method**

Biplot Methods [31, 32] is a simultaneous representation of n rows (elements) and p columns (variables) of the data matrix (nxp). In Canonical Biplot, the n rows of the data matrix are divided into K groups and they are column centered. We represent the group means as markers (stars) and the column markers as vectors through the origin in a scatter diagram. It can be shown that the Euclidean distance between two means markers approximates the Mahalanobis distance between groups. If a marker (star) projection is close to or points in the direction of a variable, this means that the average value is high in that variable, while if it is far away it will take only low values. When projecting the marker of each group onto the variable, the range of values may vary from negative to positive values. The angle between variables can be interpreted as an approximation of its correlation.

We can determine the groups differences (P < 0.05), checking the no overlapping of two confidence circles over a particular variable. This interpretation is subject to a series of measurements related to the quality of representation of the row or column markers. This
approach can be illustrated by a hypothetical example. For statistical analysis, we have used a MATLAB application specifically made for Biplot. Two Canonical Biplot analyses were made on the data of chromatic coordinates:

a) Orientation/year was applied to a matrix formed by five variables (L*, a*, b*, C* and H*) and 519 rows in eight groups accounting for the different combinations of four faces (F1, F2, F3 and F4) with the two years (2011, 11 and 2012, 12) together with quarry group (Q). The eight groupings were labeled by combining the four faces and two years: FY-Z, where Y = 1, 2, 3 and 4 (type of face), and Z = 11 and 12 (Years).

b) Orientation/pathology was applied to a matrix formed by five variables (L*, a*, b*, C* and H*) and 212 rows in seven groups accounting for the different combinations of four faces (F1, F2, F3 and F4) with the four available pathologies (P1, P2, P3 and P4) together with quarry group (Q). The seven groupings were labeled by combining the four faces and four pathologies: FYPZ, where Y = 1, 2, 3 and 4 (type of face), and Z = 1, 2, 3 and 4 (type of pathology).

Results

The color measurements were carried out using the colorimetric parameters L*, a* and b* of the International Commission on Illumination’s CIELab system. 480 measurements were performed at the monument in two years (2011 and 2012). These data were collected for the four sides of the monument, with 60 measurements on each of the four sides (Fig. 1), totalling 240 measurements per year. The value was established according to the bibliography, which suggests that 14 measurements in an area of 36 cm² are sufficient for the data to be reliable [33], with 25 to 30 measurements for stable mean value [24].

Measurements were collected on the stone part of the monument, with the cleanest parts being chosen, excluding areas with soiling or biological colonization. Enclaves of biotite were also avoided. By obtaining a freshly quarried sample, colorimetric parameters were measured to compare the original color and the color after years of exposure. Areas with different types of soiling were also measured.

The chromatic parameters obtained in this work are presented below. Figure 3 shows the statistical color analysis for the different faces of the monument in the years 2011 and 2012.

Fig. 3. Graphical representation of the color of unaltered granite for the different faces of the monument in the years 2011 and 2012.
The L* parameter increased, so there was a lightening of the granite in the monument compared to the sample from the quarry. The finish of the monument is bush-hammered, whereas the measurements for the fresh sample were performed on a fracture surface. This difference in finish may be the cause of the lightening of the L* parameter for the monument. During the period of analysis, there was a certain constancy in the cleaning of the monument, which would also contribute to a higher L* value. In addition, the sandblasting done in 1999 might also have contributed to the higher L* value for the monument.

No major difference was observed in the measurement of the parameter a* between the monument and the sample from the quarry.

The parameter b* is greater on all faces and for both years, with a notable yellowing of the granite in the monument compared to the fresh sample. Face 3 is the one with the greatest yellowing.

The behaviour of the parameter C* is conditioned by the chromatic coordinate b*, as the parameter a* does not show significant variations. Thus, it is interpreted in a similar way to the parameter b*.

Being a value of an arc-tangent function, the parameter H* follows an inverse direction to that expressed by a*/b*.

There are 4 colorimetric standards for the pathologies observed (Table 1 and Fig. 4). The first one has a bluish-greenish color and is associated with leaching of bronze statues situated above (Fig. 5A). In fact, SEM (scanning electron microscopy) analysis pointed out that the statues are made of brass and not bronze as Cu and Zn were detected.

The second soiling standard is the deposition of leachate from the mortar and is associated with the deposition of soot yielding a brown color (Fig. 5B).

The third standard is due to the presence of biological colonization mainly fungi yielding a green color (Fig. 5C).

The fourth standard is characterized by the yellowing of granite (Fig. 5D) caused by deposition of ozone and/or oxidation of iron-rich minerals. P. Brimblecombe [23] explains the yellowing of the stone by sulfur dioxide attack or deposition of atmospheric urban pollutants (i.e. ozone). There is no high emission of SO2 next to the monument, but the O3 rate is cca. 200µg/m³, which is considered a very bad air quality index [34].

The mapping of the damage patterns in the entire monument has been published by D. Grossi and E.A. Del Lama [35].

Figure 6 shows the data obtained from the statistical analysis. With respect to the parameter L*, we noticed a darkening of all samples with pathologies, with the exception of sample F3P4 (Northwest face and oxidation of iron-rich minerals). In this case, the data for the color parameter L* are at the same level as for the quarry granite (Q), with the conclusion that this sample shows no modification for the parameter L*.

Table 1. Standards for pathologies in the monument by face.

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<tr>
<td>F1</td>
<td>P1</td>
<td>Blue-green with bronze-copper leaching + soiling</td>
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<tr>
<td>F2</td>
<td>P1</td>
<td>Blue-green with bronze-copper leaching + soiling</td>
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<td></td>
<td>P2</td>
<td>Brown with soiling</td>
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<tr>
<td>F3</td>
<td>P3</td>
<td>Green with lichens + biological colonization</td>
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<td></td>
<td>P4</td>
<td>Yellow with oxidation of iron-rich minerals and ozone deposition</td>
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<tr>
<td>F4</td>
<td>P1</td>
<td>Blue-green with bronze-copper leaching + soiling</td>
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<td></td>
<td>P3</td>
<td>Green with lichens + biological colonization</td>
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Fig. 4. Schematic mapping of the pathologies observed in the lower part of the monument. Blue - pathology 1; brown - pathology 2; green - pathology 3; yellow - pathology 4. See Table 1 for the meaning of each pathology.

Fig. 5. Standards for the soiling found on the Monument to Ramos de Azevedo.

Fig. 6. Graphical representation of statistical analysis of the 2013 data for quarry granite (Q) and granites with pathologies on the four faces of the monument.
There was a reddening of F3P4 with respect to Q, since the value of the parameter \( a^* \) is greater for the sample of the monument with pathology P4 than for the sample from the quarry. Samples of the monument with P1 pathology on faces F1, F2 and F4 are more greenish than for that from the quarry, with a decrease in the parameter \( a^* \). Samples of the monument with P2 and P3 pathologies on different faces showed no differences in parameter \( a^* \) relative to the values of the quarry granite.

The parameter \( b^* \) increased for all the altered samples, with a notable yellowing of the samples with respect to the quarry granite, except for the samples presenting pathology P1 on faces F1, F2, and F4, where a reduction in parameter \( b^* \) was seen, indicating the acquisition of a bluish tint.

The behaviour of the parameters \( C^* \) and \( H^* \) is similar to that already described for the unchanged samples. The parameter \( C^* \) is determined by \( b^* \) and is interpreted in the same way. The parameter \( H^* \) has an inverse trend to that of \( a^*/b^* \).

**Conclusions**

After two years of studying the Monument to Ramos de Azevedo, a small change was observed in \( b^* \), while \( L^* \) and \( a^* \) remained very close to the original values, resulting in more yellowish hues in the stone, as we can see in Figures 3 and 6. Considering each face separately, there are no discrepancies in the colorimetric parameters, indicating that solar irradiation, wind and rainfall have homogeneous effects across the monument.

Comparing the stone of the monument to the stone from the quarry, it is seen that the monument is slightly more yellow than the fresh sample, probably due to the ozone deposition and also the oxidation of the iron present in some minerals, such as hematite, pyrite and biotite. The monument is slightly lighter than the fresh stone. However, it should be remembered that the monument has a bush-hammered finish.

The soiling contains various colors, such as blue-green, brown and yellow, which are associated with leaching of copper or biological colonization, deposition of mortar and soot, and oxidation of iron-containing minerals and deposition of atmospheric pollutants (ozone), respectively.

Comparing all the collected data, it is concluded that the monument has a slight yellowing. This yellowing of the stone is also seen in other monuments of the city of São Paulo made of Itaquera Granite. The soiling alters the appearance of the monument and there are major discrepancies between the values of the colorimetric parameters found in them and those of the stone. In general, the monument is in a reasonable state of conservation and sporadic cleaning operations would be helpful for maintenance and a better appreciation of the Monument to Ramos de Azevedo.

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