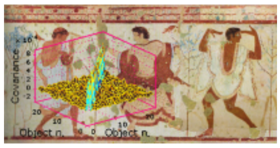

Chromatic 'Alterations' on Stone Surfaces in Contact with Bronze or Copper Monuments: Spectroscopic Characterization and Statistic Analyses

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Abstract

The chromatic alterations visible on surfaces of monuments, induced by coexistence of stone and metallic components, are indicative of damages, which are essentially aesthetic, but also require the cleaning procedures to be carefully studied in order to avoid any further damage to the physical-chemical and structural properties of the surface of monuments themselves.

Within a research programme devoted to optimise analytical procedures for the removal of stains on travertine basements of bronze monuments, it has been shown how the chemical state of copper influences the efficiency of cleaning. Not withstanding the clear evidence of the stains, that were also analysed by colorimetric methods, their analytical characterization has turned to be hard, the low concentration of the compounds responsible of the discoloration being at the limits of detection of the most common diagnostic means. Here the investigation on three different typologies of Roman monuments is reported, using a multi-techniques approach: X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and X-ray Micro Analysis (EDS) combined with PCA-data elaboration, Micro Raman, X-ray Photoelectron Spectroscopy (XPS). The last two resulted the most suitable spectroscopic techniques.

Introduction

Stone materials are often used as basement for bronze monuments, and might either have an intrinsic figurative/artistic importance or simply have dedicatory inscriptions that inform on the monument; in some cases stone and metallic materials have comparable artistic importance (see for example the basement by Michelangelo for the bronze monument of Marcus Aurelius in the Capitolium of Rome) while in other cases the metallic materials are used as a decoration of stone monuments (see for example the memorial to the Unknown Warrior in Rome).

The discoloration of stone materials is favoured by rain, that washes and transports corrosion products of the bronze components (especially if rain is 'acidic' due to atmospheric pollution). It is very difficult to properly clean such patches without provoking further damages to the stone. The cleaning methods used at present are mainly based on ammonium salts (especially ammonium carbonates) [1]. In order to find alternative, better, procedures, it is at first necessary to characterise the components of the stains. The relevant literature is scarce: in some cases the presence of malachite is reported together with minor quantities of azurite and brochantite; in other cases, amorphous copper chlorides are identified as the most abundant compounds; in one of the most interesting articles it is hypothesized that copper forms inclusion compounds with calcium carbonate of the stone substrates [2].

Materials & Methods

The three monuments here investigated are all located in Rome: Turtles' fountain (XVII cent.), the Student's Statue at 'La Sapienza' University (about 1930), the Memorial to the Unknown Warrior, also known as “Vittoriano” (beginning of the XX cent.). XRF analyses have been performed ‘in situ’ using a portable instrument. For what concerns the other techniques listed in the Abstract, the analyses were of the ‘mini-invasive’ type: in case of the Turtles fountain, a large amount of calcareous incrustations was available and could be easily collected, as they were being eliminated during the ongoing cleaning treatment, while for the other two monuments only small surface fragments already detached or powder samples, carefully collected by scalpel, were utilized.

Results

Figure 1 shows the grouping from the Student’s statue basement, as obtained by the statistical process of the EDS data by PCA. By interpreting the graph, it results that sulphur is bonded to copper for samples lying on the negative x-axis and to calcium for the positive one. Chlorine seems to be bonded to zinc and copper.

The samples lying on the upper right quadrant (x- and y- positive axes) correspond to aluminium-silicates containing sodium and potassium, in some cases substituted by magnesium. The majority of the analysed spots show a Ca/C/O ratio typical of calcium carbonate.

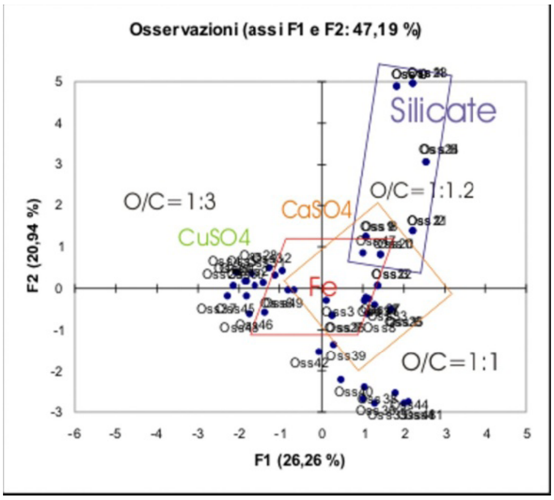

Fig. 1. Scores plot EDS data obtained for the “Student’s statue” samples

In the quadrant defined by x-positive and y-negative axes, the ratio C/O equal to unity and the high content of calcium induce to hypothesize the presence of calcium oxalate. Possible copper-containing organic compounds can be individuated in the area described by negative x-axis.

Tab 1, XPS analysis of “Student’s statue” samples

Grey zone	Green zone
$PbSO_4$: 4.4%	$PbSO_4$: 2.1 %
$Cu_4(OH)_6SO_4$: 7.2%	$Cu_4(OH)_6SO_4$: 23.3%
$CuCaCO_3$: 35.1%	$CuCaCO_3$: 44.4%
$Cu(OH)_2$: 35.2%	$Cu(OH)_2$: 10.6%
ZnO: 3.9%	ZnO: 11.1 %
Carbon: 14.0%	Carbon: 5.6%

Raman analyses performed on two different coloured areas of the basement, grey and green zones, has allowed to ascertain the presence of chalcantite, copper oxalate, lead sulphate, manganese and iron oxides together with sodium carbonate, feldspars, gypsum, talc and carbon-particles. In Table 1 the XPS data obtained for the same samples are reported.

Conclusions

The analytical procedure here adopted for identifying the products responsible for the discoloration observed on the monuments looks efficient. In fact, EDS analysis followed by PCA data treatment allowed to individuate the significant samples to be further investigated with Raman and XPS. The XPS results are the most interesting as they exclude the presence of Cu(I) and reveal the presence of copper and calcium mixed carbonates. This finding can justify the difficulties encountered by the cleaning systems available at present, in removing coloured patches produced by copper salts.

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