SEM/EDS Analysis of Incrustations Coming From the "Fontana delle Tartarughe" (Turtles Fountain) Located in Rome, Italy

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Abstract

In the present study we tested and analysed the incrustations that were covering, before the recent restoration works, the whole surface of the "Fontana delle Tartarughe", located in Piazza Mattei in Rome. Visual observation and "in situ" colorimetric analysis showed that the incrustations, produced by both the fountain and rain water, had a green/grey colour with some grey-brown veins, due to corrosion products generated by the interaction of the fountain bronze statues with the environment. The "in situ" X-ray fluorescence (XRF) analysis revealed the presence of copper but, due to its very low content in the calcite matrix, and the different nature of the copper products in the incrustation samples, it was impossible to obtain further information on its speciation state neither by X-ray diffraction (XRD) nor by simple stoichiometric elaboration of the data coming from Scanning Electron Microscope with X-ray microanalysis (SEM/EDS).

Principal Component Analysis (PCA) of data was tried to cross-check the obtained results.

Introduction

Bronze and copper elements are very frequently present in stone monuments, either as sculptures and decorative elements or as parts added to strengthen the stone (pins, bars, etc.).

Especially in the case of monuments exposed outdoors, stone very frequently shows green/brownish stains produced by the copper corrosion products dissolved by water and adsorbed by the stone. The cleaning of these disfiguring stains is still an open problem, especially in the case of limestone and marble, as the chemical products used, up to now, to dissolve the copper products may have a negative effect on calcite as well.

The "Fontana delle Tartatughe", (designed by Giacomo della Porta with bronze sculptures by Taddeo Landini and located in Piazza Mattei in Rome [1]), is considered one of the most elegant Roman fountain of the Renaissance period.

Its recent restoration gave us the possibility to study incrustation samples, including corrosion products derived from the above said process, that were going to be removed. We were aiming to obtain information on the speciation state of the metals ions, mainly copper, included in the incrustation in order to have an help in the selection of the best cleaning product..

Materials & Methods

Preliminary "in situ" analysis were performed on different zones of the fountain basin, as well as on the bronze statues, by colorimetry and XRF; the first analysis revealed predominant wavelengths corresponding to blue, green and yellow colours and a very low saturation [2, 3] while the second one individuated copper in the stained zones. Samples taken from the same zones, after powdering, have been analysed by XRD while analysis by SEM/EDS was performed on cross-sections obtained starting from chips taken by precision instruments of the same thickness of the fountain incrustation (300-800 micron thick) and then embedded in an epoxy resin. XRD analysis has been negatively affected by the high calcite content of the samples, so high that no other crystal phase could be recognised. On the contrary, SEM/EDS investigations revealed several elements (besides C and O, mainly Ca, Si, Cu). Due to the presence of many elements, it was impossible to

carry out simple stoichiometric calculations for detecting the composition of the incrustation. So we thought to use the PCA technique in order to simplify the dataset through its reduction to a lower dimensions. Our dataset is described by a matrix formed by "m" lines (each one matches a spot of EDS analysis) and by "n" columns (which represent the elements found in the specimens, variables). Even if our variables are expressed by the same measurement unit (the individual element's percentage in the sample), the normalizing procedure was carried out.

Our SEM/EDS instrument, like most of the commercially available, uses the "standardless" EDS analysis; it is a type of semiquantitative analysis, in which EDS reference spectra are collected by the manufacturer and stored in a file that is used during analysis. Algorithms of varying accuracy are used to take into account differences between the experimental conditions during the standard and sample spectra acquisition. The accuracy of such analysis is highly sample dependent and a root mean square of error (RMS) of 10% can be expected [4 - 6].

Results

Different Principal Components methods were used to find correlation in our dataset. PCA allows us to obtain better results with respect to PCoA with its intrinsic Euclidean distance. Loading's graphic shows behaviour and weight analogies for different variables that determine a good scores plot revealing the presence of five homogeneous groups of objects and two isolate objects. The sets analysis revealed the presence of two trends: the first shows that the objects goes from a molar ratio O/C 3:1 and C/Ca 1:1 to a molar ratio O/C 0,7:1 and C/Ca 11:1; the second is related to the behaviour of Si and Mg, even in respect to the Al content. Cu raises towards the PC1 positive and PC2 negative zone of the plot.

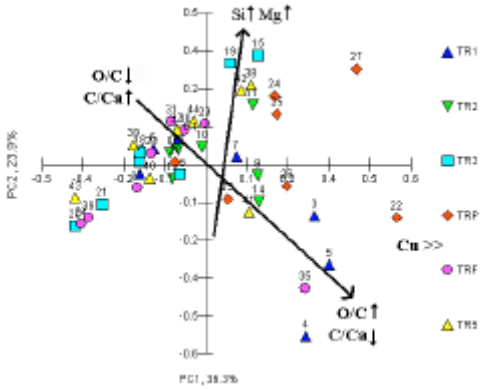

Fig. 1. PCA scores plot after autoscaling of C, O, Mg, Si, Ca and Cu as variables

Conclusions

The application of PCA to our case study improved the interpretation of the experimental results and confirmed the presence of different copper products in the fountain incrustations.

However, the reduced number of samples (which allowed an easy interpretation simply by rough estimate) probably prevented to full exploit the potentiality of the method but, at the same time confirmed the usefulness of PCA for a quick elaboration of data coming from a standardless EDS quantitative analysis.

Our running research foresees the analysis of a larger number of samples coming from different monuments, this finding encourage us to continue to use PCA for the relative data elaboration.

References

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