2023 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Rome, Italy, October 19-21, 2023

Monitoring of protective products on Peperino stone using portable devices

G. Capobianco[1], C. Pelosi[2], L. Lanteri[2], G. Bonifazi[1], O. Trotta[1], S. Serranti[1]

[1] Sapienza University of Rome, Department DICMA, Via Eudossiana 18, 00184 Rome (Italy)
[2] University of Tuscia, Department DEIM, Largo dell'Università, 01100 Viterbo (Italy)

***Abstract* – The aim of the research presented in this paper is to monitor the stability of three protective products applied on samples of Peperino stone, a volcanic tuff widely used for the historic buildings and architectural elements in Viterbo (Italy), using portable devices. More in detail, two different monitoring techniques were applied: VIS-NIR point spectroscopy (400-1000 nm), and colorimetry. In order to characterize the compositional variability and homogeneity of the samples, X-ray micro-fluorescence (micro-XRF) was preliminary used. Data were acquired before and after the application of the different products in order to monitor and detect the efficiency of the considered low-impact products. Peperino samples were also aged in a Solar Box chamber for 1000 h to simulate a solar irradiation and measurements were repeated at the end of the ageing period to evaluate the stability of the protective products.**

I. INTRODUCTION

Building materials exposed to the atmospheric environment for a long period of time, show signs of deterioration appearing in different forms and modalities also depending on the exposure times and orientation of the surfaces. In later stages, this deterioration causes physical and chemical weathering of building materials, dominated by interaction of chemical and mechanical processes which lead to damage of the microstructure and expansion of micro cracks [1].

Deterioration of stone building materials in historical monuments could be reduced by applying protective and/or consolidating products [2].

However, according to the standard (UNI EN 15886 protocol) for restoring stone buildings, protective and consolidating products should not cause chromatic alterations [3-4]. For this reason, considering the high variety of stones used in historic buildings, the selected protective and consolidating products must be preliminarily tested on the specific stones, in order to evaluate their effect on the material surface and, above all, their stability over the time [5].

In this perspective, it is essential to develop technologies able to monitor the variations of protective and consolidating products over time both at laboratory scale and directly in situ [3]. For this reason, technologies have been tested to develop a recovery protocol for degraded surfaces in real conditions and on monuments undergoing restoration. As representative case study, the buildings constructed with Peperino stone were chosen to develop the methodological approach. More in detail, Peperino stone is a pyroclastic-flow deposit characterized by lithified, granular texture and grey colour, with white and black lithic inclusions, as well as abundant feldspar and pyroxene crystals [6].

In this work, developed within the research project COLLINE (a project of the second phase of the Center of Excellence Technological District of Cultural Heritage of Lazio Region) three protective products were applied on different samples of Peperino stone in laboratory conditions, in order to test and evaluate the stability of the products as a consequence of artificial ageing that simulates solar irradiation.

Three different products were chosen after careful research in the literature and, above all, by considering the practical application of the Italian restorers. From this preliminary study, it was found that the most used protective product for stones exposed to outdoor is Rhodorsil H224 [7], that was chosen as reference material. The other two products, Nano Silo W (functionalized nano-silica) and Nano Silo OR (nano-sized fluorosilane) are recently new in the field of protective formulates developed specifically for the stone conservation. So, they were chosen to test their potential application to treat the Peperino stone.

The behaviour of the chosen protective products was evaluated by applying portable and non-invasive methodologies that could be used also on site on the monuments selected for the above-mentioned research project. Specifically micro-X-ray fluorescence (micro-XRF) was applied to characterize the samples, and then colour measurements and reflectance VIS-NIR spectroscopy were chosen as methods for testing the performance of the protective products before and after artificial ageing.

II. MATERIALS

Twenty Peperino stone samples were taken from a Peperino quarry in Viterbo (Italy), were cut to obtain a 5 cm x 5 cm x 2 cm block according to UNI 10859:2000 standard (Figure 1). The commercial protective products selected for the experimental tests were Nano Silo OR (supplied by CTS Europe), Nano Silo W (supplied by CTS Europe) and Rhodorsil H224 (supplied by Siliconi Padova sas).

The characteristics of the products and the application modalities, obtained from the technical datasheets, are reported in the Table 1. Each product was applied to five samples (fifteen samples used); the remaining five samples were used as control.

In order to evaluate the effect of the protective product on the ageing of the surfaces, the samples were aged in Solar Box for 1000 hours.

Table 1. Product characteristics and application procedure, according to the technical data sheets from the supplier.

Characteristic and application	Rhodorsil H224	Nano Silo W	Nano Silo OR
Composition	Alkyl poly-siloxane	Functionalized nano-silica	Nano-sized fluorosilanes
Solvent	Aliphatic hydrocarbons	Water	Water
Physical state	Liquid	Liquid	Liquid
Colour	Colorless or slightly yellow	White	Colorless
Viscosity	20 mm^2/s at 25 °C	1 mPa·s at 20 °C	1 mPa·s at 20 °C
Applied mixture	6% v/v in white spirit	1:1 v/v in demineralized water	Without dilution
Method of application	Brush	Brush	Brush
Number of treatments	2 (the 2^{nd} after 3 days)	2 (consecutive)	2 (consecutive)
Number of samples	5	5	5

Fig. 1. Example of a Peperino stone used in this project as a sample.

III. METHODS

A. Micro-X-ray Fluorescence

In order to evaluate the compositional variability of Peperino stone samples were preliminary characterized by micro-XRF acquiring element distribution maps by Bruker Tornado M4 equipped with an Rh tube, operating at 50 kV, 200 µA, with 25 µm spot. Mapping acquisition conditions are 10 ms/pixel and step size 110 µm in vacuum condition at 25 mBar.

B. VIS-NIR spectroscopy

Spectra acquisitions were acquired using the Qmini Wide (AFBR-S20M2XX; Broadcom Inc.) portable spectroradiometer in reflectance mode. This portable instrument, working in UV-VIS–NIR regions (225-1000 nm), had a spectral resolution of 0.8 nm.

The spectroradiometer comprised a detector unit, a fiber optics cable connected to a contact probe controlled by a personal computer and a light source. The detector has a 2500-pixel linear CCD sensor. The illumination is provided by a Tungsten Halogen light source of 6V (BPS101; BWTEK Inc.) and UV Grade Fiber (BWTEK Inc.). The focal length was 50 mm in diameter. Data acquisition and calibration procedures were performed using the WAVE Spectrum Analyzer software (Brodcom Inc.). The calibration was performed by dark and white acquisition reference measurement, acquiring the white with a Micronized PTFE squared reference standard. After this calibration stage, nine spectrums were acquired, and reflectance was computed for each sample. Raw spectra were preliminary cut, from 400 to 850 nm, in order to remove unwanted effects due to lighting/background noise and focus only to the colorimetric variation. Spectral data were analyzed adopting the PLS_Toolbox (Eigenvector Research, Inc.) under Matlab® environment (The Mathworks, Inc.). Different preprocessing algorithms were applied in order to enhance spectral differences between untreated and treated Peperino stone samples: Smoothing, Detrend and Mean Center (MC). Principal Component Analysis (PCA) was carried out to explore data in order to reveal the relationships existing between variables and samples (e.g., clustering), to detect outliers, and to find and quantify patterns [8].

C. Colorimetry

Colour measurements were performed by a digital portable apparatus of EOPTIS CLM 19x colorimeter under the following conditions, according to the CIELAB space: illuminant D65, standard observer 10°, geometry of measurement 45°/0°, measurement diameter 6 mm, white reference supplied with the instrument. The points of colour measurement were 15 for each stone sample (75 for each set of samples).

D. Artificial ageing

Artificial ageing on the samples was performed by a Model 1500E Solar Box (Erichsen Instruments) to simulate the exposure to solar radiation under the following conditions: 550 W/m^2, 55 °C for 1000 hours. The chamber is equipped with a Xenon lamp and a probe for the temperature control.

IV. RESULTS

A. Micro-X-ray Fluorescence results

Micro-XRF maps obtained on a selected sample and the distribution of the different chemical elements are reported in the Figure 2.

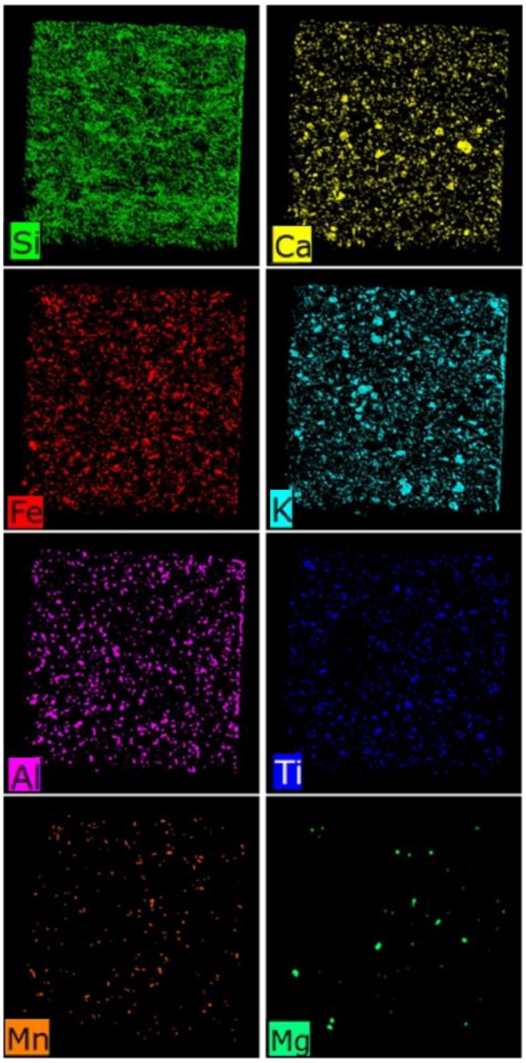

Fig. 2. Micro-XRF maps of Peperino stone showing the distribution of main elements: Si, Ca, Fe, K, Al, Ti, Mn and Mg.

In particular, the Si map shows homogeneous distribution, while the other elements are heterogeneously distributed, due to the various minerals from which the Peperino stone is composed.

B. VIS-NIR spectroscopy results

The average raw and pre-processed reflectance spectra of untreated, treated and aged samples with the 3 different protective products are shown in Figures 3, 4 and 5, respectively. As shown in Figures 3a, 4a and 5a, the main spectral variation between untreated and treated samples are focused on the region 500-750 nm.

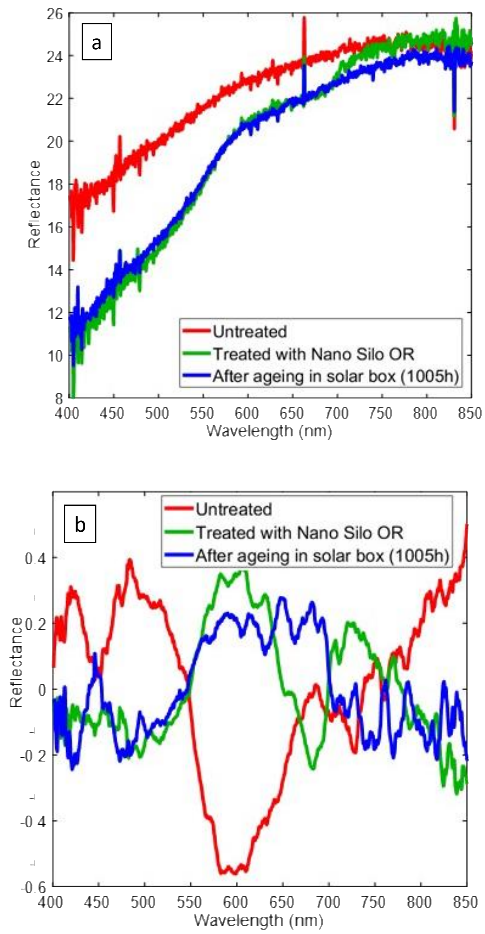

Fig. 3. Average raw (a) and pre-processed (b) reflectance spectra of a Peperino sample: untreated, treated with Nano Silo OR, and after ageing.

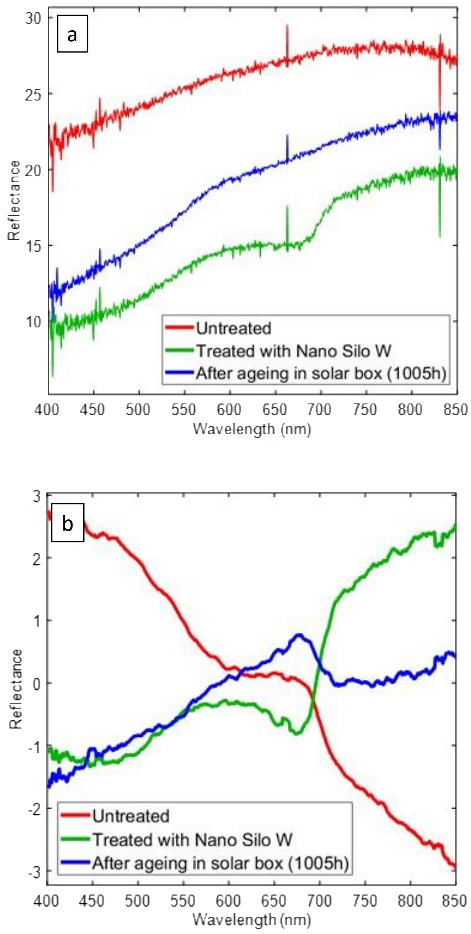

Fig. 4. Average raw (a) and pre-processed (b) reflectance spectra of a Peperino sample: untreated, treated with Nano Silo W, and after ageing.

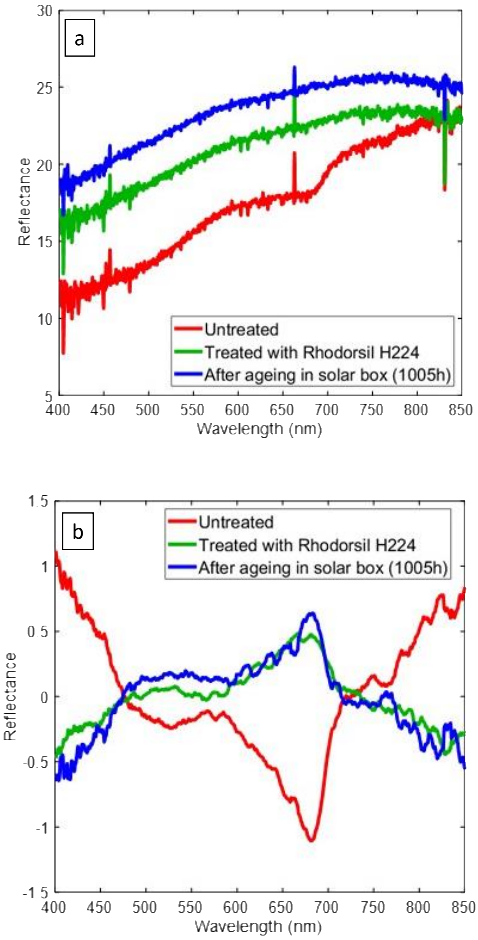

Fig. 5. Average raw (a) and pre-processed (b) reflectance spectra of a Peperino sample: untreated, treated with Rhodorsil H224, and after ageing.

In order to emphasize the spectral differences among samples, data were pre-processed with smoothing, Detrend and mean center. After spectra preprocessing, PCA was applied to the 3 datasets and the obtained PC1-PC2 score plots are shown in Figures 6, 7 and 8, respectively.

Concerning the first dataset (evaluation of treatment with Nano Silo OR), PCA score plot shows that the first two PCs captured most of the variance (Figure 6), explaining 75.79% and 9.12%, respectively. Furthermore, it can be noticed as spectra of untreated sample are clustered in the second quadrant, whereas the spectra of treated and aged ones are clustered in the first and forth quadrants, confirming a low spectral variation between the treated sample and the same sample after 1000 h of ageing in Solar Box chamber.

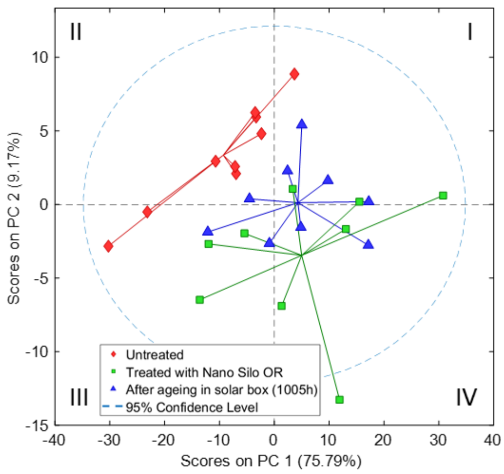

Fig. 6. PCA score plot related to spectra of Peperino sample untreated, treated with Nano Silo OR, and after ageing.

Concerning the second dataset (evaluation of treatment with Nano Silo W), the PCA score plot is reported in Figure 7, showing that the first two PCs captured most of the variance, explaining 89.01% and 8.62%, respectively. In the plot shown in the Figure 7, three clusters can be observed corresponding to: untreated, treated and aged samples. More in details, spectra of untreated sample are clustered in the second quadrant, those of treated with Nano Silica W are grouped in the first quadrant and, finally, spectra of aged sample are grouped in the fourth quadrant. This result suggests a greater alteration caused by the simulated solar radiation of Nano Silica W compared to Nano Silica OR, as evidenced by a greater spectral variability in the visible range between the treated sample before and after the ageing in the Solar Box chamber.

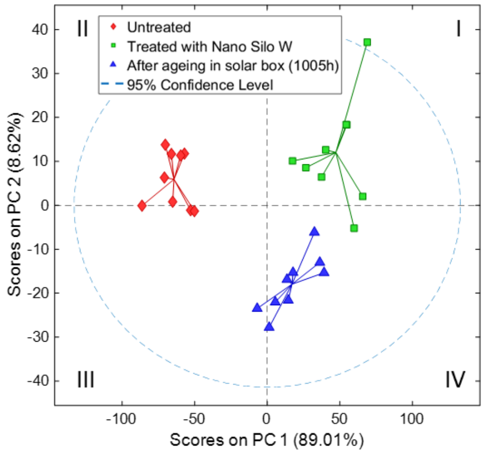

Fig. 7. PCA score plot related to the spectra of Peperino sample untreated, treated with Nano Silo W, and after ageing.

Concerning the third dataset (treatment with Rhodorsil H224), the obtained PC1-PC2 score plot (Figure 8) shows that the first two PCs captured most of the variance, explaining 82.88% and 9.81%, respectively. In the plot shown in the Figure 8, two different clouds can be observed, corresponding to the spectra of untreated sample, in the first and forth quadrants, and to the spectra of samples treated with Rhodorsil H224 and aged, mainly in the second quadrant. The low variability found in the sample treated with Rhodorsil H224 before and after ageing in the Solar Box chamber, suggests some stability of this protective applied on Peperino stone.

C. Colorimetry

Colour measuremnts were performed before and after the application of the protective products in order to evaluate their effect of the surface appearence of the stone. The calculated average variations of the three chormatic coordiated are reported in the Table 2.

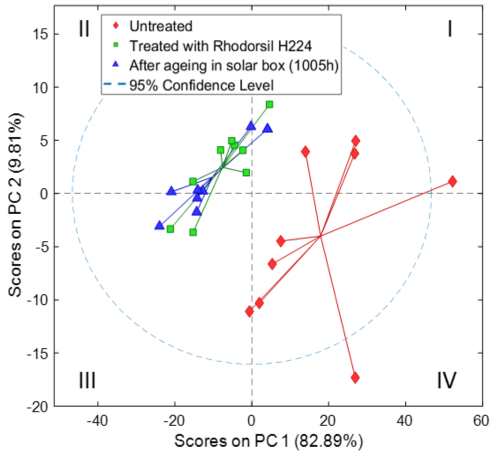

Fig. 8. PCA score plot related to the spectra of Peperino sample untreated, treated with Rhodorsil H224, and after ageing.

Table 2. Chromatic variations due to the protective application.

Product	ΔL*	Δa*	Δb*	ΔE*
Rhodorsil H224	-4.6	0.21	0.30	4.6
Nano Silo W	-5.4	0.18	0.29	5.4
Nano Silo OR	-1.8	-0.19	0.91	2.2

As can be observed from the data of Table 2, the colour variations due to the protective application are low in the case of Nano Silo OR, certainly under the value considered perceptible by human eye, i.e. ΔE*<3-5. In the other two cases the values of ΔE* are higher than 3, so the variations can be observed also by eye. The chromatic variation is due to a decrease of the parameter L*, representing the lightness, that causes the darkening of the surfaces. We can affirm that the commercial product Nano Silo OR gives the better results in terms of chromatic changes of the Peperino surface. Anyway, Nano Silo W and Rhodorsil H224 do not alter the colour, expressed by the two chromatic coordinates a* and b*, but cause a little decrease of lightness. Colour was further measured after the process of artificial ageing in the Solar Box chamber, in this case also considered the untreated samples (control). The results are shown in the Table 3.

Table 3. Chromatic variations due to the protective application.

Product	ΔL*	Δa*	Δb*	ΔE*
Untreated samples	1.2	-0.90	-0.35	1.7
Rhodorsil H224	1.8	0.29	-0.57	2.3
Nano Silo W	4.4	-0.01	0.03	4.5
Nano Silo OR	1.8	0.65	-0.94	2.0

The artificial ageing causes negligible changes in untreated samples and in those treated with Nano Silo OR and Rhodorsil H224. On the other hand, the samples treated with Nano Silo W also in this case suffer the higher colour changes. This product not only causes the higher changes in colour on the stones but further is the less stable under simulated solar radiation, confirming the results obtained by VIS-NIR spectroscopy.

V. CONCLUSIONS

A study was carried out to investigate the performance of three protective products applied to Peperino stone, a volcanic tuff used for the historical building in Viterbo (Italy). The chosen products, i.e., Nano Silo OR, Nano Silo W and the traditional Rhodorsil H224, were applied on the Peperino stone samples, and their behaviour was evaluated by measuring colour before and after the coatings application and before and after ageing under controlled conditions. Moreover, VIS-NIR reflectance spectra were acquired with a portable system in order to study the variations between samples with a powerful, fast and non-invasive technique.

The samples were preliminarily characterized by micro-XRF that confirmed the high variability in chemical composition of this kind of stone.

The portable, non-invasive techniques applied to investigate the stability of the samples, both treated and untreated, showed the good performance of both Rhodorsil H224 and Nano Silo OR, whereas Nano Silo W appears less stable.

This result encourages towards the use of Nano Silo OR, being a water-based product that can be applied avoiding the use of solvent necessary for Rhodorsil H224. In the view of a green approach to conservation, this seems the best solution for Peperino treatment.

VI. ACKNOWLEDGEMENTS

The research work presented in this paper was developed in the framework of the project COLLINE founded by Lazio Region – Technological District of Cultural Heritage. Project Nr. 305-2020-35540; CUP: F85F21001090003.

The authors would like to thank Dr. Leonardo Borgioli of CTS Society for having help in the products selection and for the interest in the research.

Finally, the authors wish to express special thanks to the Society Vimet Srl and in particular to Dr. Francesco Chiodo for having supplied the Peperino samples already cut and ready to be used.

VII. REFERENCES

[1] S.M. Patil, A.K. Kasthurba, M.V. Patil, “Damage assessment through petrographic and microscopic studies of stone monuments”, J. Build. Rehabil., vol. 7, No. 1, August 2022, Article Number 81.

[2] K. Elert, C. Rodriguez-Navarro, “Degradation and conservation of clay-containing stone: A review”, Const. Build. Mater., vol. 330, May 2022, 127226.

[3] S. Bracci, B. Sacchi, “In situ Assessment of Conservation Treatments and Monitoring of Their Effectiveness”. In: F. Gherardi, P.N. Maravelaki (eds) Conserving Stone Heritage. Cultural Heritage Science. Springer, Cham, January 2022, pp. 231-274.

[4] UNI EN16581, Conservation of Cultural Heritage – Surface Protection for Porous Inorganic Materials – Laboratory Test Methods for the Evaluation of the Performance of Water Repellent Products (Ente Italiano di Normazione, Milano, 2016).

[5] C. Pelosi, L. Lanteri, G. Agresti, G. Rubino, F. Persia, G. Bonifazi, S. Serranti, G. Capobianco, “Experimental tests for evaluating the stability of a new nano-silica based protective for Sperone stone in comparison to traditional products”, AIP Conference Proceedings 2020, 2257, Article Nomber 020012, pp. 1-13.

[6] J. Farr, F. Marra, N. Terrenato, “Geochemical identification criteria for “peperino” stones employed in ancient Roman buildings: A Lapis Gabinus case study”, J. Archaeol. Sci. Reports, vol. 3, May 2015, pp. 41-51.

[7] F. Antonelli, E. Tesser, Evaluation of silicone-based products used in the past as today for the consolidation of Venetian monumental stone surfaces. Mediterranean Archaeology and Archaeometry, vol. 18, No. 5, 2018, pp. 159-170.

[8] R. Bro, A.K. Smilde, “Principal Component Analysis”, Anal. Methods vol. 6, 2014, pp. 2812–2831.