CMA4CH 2014, Mediterraneum Meeting
Employ the Multivariate Analysis and Chemometrics in Cultural Heritage and Environment Fields
5th ed., Rome, Italy, Europe, 14-17 December 2014

Non-Invasive Analysis of Soluble Salts. Preliminary Results on the Case Study of Casa di Diana Mithraeum (Archaeological Site of Ostia Antica - Italy)

C. Scatigno[1], M.P. Sammartino[2], S. Gaudenzi[3]
[1]Department of the Earth Science, Sapienza University of Rome, 00185 Rome, Italy
[2]Department of Chemistry, Sapienza University of Rome, 00185 Rome, Italy
[3] INAF/IAPS, 00133 Rome, Italy

Abstract

The knowledge of materials and microenvironment has a fundamental role on the preservation of Cultural Heritage. Thermohygrometric conditions as well as a direct contact with water are surely a cause of direct or indirect, i.e. as carrier of soluble salts, of degradation.

A new method for a non-invasive analysis of soluble salts (Japanese paper or cellulose pulp) [1], even if already under study, was applied to a wall of the Casa di Diana Mithraeum (Archaeological site of Ostia Antica - Italy) and compared with the method currently in use, invasive and relatively dated (UNI 11087/2003). The proposed method only differs from the above cited UNI in the sampling procedure that, further, is not clearly described there. According to the ruled method, Ionic Chromatography (IC) and conductivity measures were performed on the samples while further pH and redox measures were done together with a characterization of materials (bricks and mortars) by Optical Microscopy in polarized light (MOP) and X-ray diffraction (XRD).

Results coming from a microclimatic campaign are object of a paper ready to be submitted for publication while here we present those regarding the soluble salts analysis together with the material characterization; obviously a correlation between all data will be looked for in a next future.

Introduction

One of the main conservation problems for building materials rises from the practically inevitable presence of salts within their capillary network and from the complexity of the related phenomena. As a fact, such phenomena up today results hard to model because are bound to many factors such as thermo-hygrometric conditions (mainly their variation and variation frequency), characteristics of the materials (mainly its porosity) and of salts (mainly solubility, hygroscopicity, hydration level in the crystalline structure). The determination of the soluble salts content is ruled by the UNI 11087/2003; it is almost dated, the sampling design and procedure lack and, overall, it results invasive so being not so suitable for Cultural Heritage artefacts.

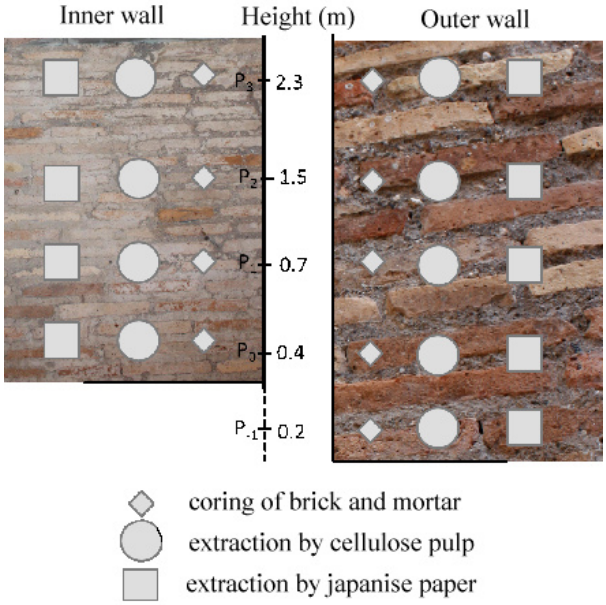

Fig. 1; Sampling design for the analysis of soluble salts

Materials & Methods

Samples: bricks (yellow and red) and mortars were sampled, by drilling (depth of 0-10 mm), on the NE orientated wall placed to the right of the altar of the ancient roman "Casa di Diana Mithraeum" (Ostia Antica); sampling points were chosen, at regular distance, on vertical profiles drawn on both the inner and outer wall (fig. 1). At the same height, salts were extracted by cellulose pulp, contained in plastic Petri capsule (5.5 cm diameter holed on the bottom) and pieces of Japanese paper (5x5 cm^2, 11 g/ m^2) (fig. 1); in both the cases they were opportunely imbibed by deionised water (conductivity $\leq$ 0.5 μS) and then placed and maintained on the sampling points for 24h and 75 or 45 min (inner or outer wall) respectively.

Drilled samples were treated according to the UNI 11087/2003 while salts contained in the cellulose pulp and Japanise paper were re-estracted by deionised water (conductivity $\leq$ 0.5 μS). On all the solutions, coming from the three methods, salts content was determined by IC (Cromatograph 761 Compact IC, Metrohm); conductivity (Amel conductivimeter mod. 160 equipped with cell AMEL mod. 192/R2 and T probe AMEL TC-100), pH (Amel pH-meter mod. 338 equipped with electrode CRISON mod. 52-02), and Redox Potential (Crison MicropH 2002 equipped with Deltaohm ORP electrode) were also measured.

An Olympus BX60 Optic Microscope and a D5000 Siemens X-ray diffractometer were used for the mineralogical characterization of the bricks and mortars.

Results

Data coming from the application of the ruled method evidence a total content of soluble salts (Cl^-, NO_3^- and SO_4^{2-}) more than double on the inner wall with respect to the outer one, sulphate and chloride are more abundant in the inner wall while for nitrate a slightly higher concentration results on the outer one. On both the side of the wall their concentration follows the order sulphate>chloride>nitrate while a clear trend along the profile lacks. Organic salts were also found but not identified; their presence could be correlated to sacrificial rite performed in the site: the roman "podia" were used like a "butti" during the meal bull. No correlation was found between the ruled method and the other two; this can be imputed to the different depth of the sampling that is known (10 mm) for the UNI one while is unknown in the other two cases even if it is reasonable to assert that the lower corresponds to the extraction by Japanise paper [1]. Conductivity and pH measures have evidenced higher values for the solutions coming from the UNI method and from the less cohesive zones; this can be imputed to the higher extent of dissolution of the constituting carbonatic materials that depends on the effective surface in contact with the deionised water.

The petrographic analyses are in progress. Preliminary results obtained by MOP (only polarizing and cross-polarizing) on cross sections and by semi-quantitative XRD on powders, have shown that the grain size in the yellow brick are finer than in the red one and the mineralogical composition also shows different percentages in the major and minor phases, probably due to the different firing temperatures: the red brick presents a $CaCO_3$ amount (~ 4%) more lower than the yellow one (~ 30%); the quartz quantity in the yellow bricks ranges from 20% to 50% with a grain size from medium-fine to fine; the presence of relatively high amount of gypsum in some samples of bricks can be reasonably imputed to degradation (sulphatation).

The mortars are characterized by the presence of quartz below 1%, analcime, type "augitico", pyroxene and biotite and black slag typical of Lazio's vulcanite. Sulphate was also found in a sample of "marble" taken from the altar. The pumice (located in the apse to simulate the Mithra's born) presents a blue pigmentation, probably to reproduce the night sky. Finally, an isotopic analysis of oxygen and carbon has been performed on a travertine sample through the mass spectrometer Finnigan Mat252, revealing a probable origin from the Tivoli area.

Conclusions

Basing on some European guidelines concerning risk of damage caused by salt contamination in stone materials, a worrying concentration of sulphate was found on both the side of the considered wall. The two non-invasive analyses of salts result not correlated with the UNI method but it could be due to the different depth of the salts sampling. This evidence leads us to further study in view of a possible modeling of the distribution of salts within the stone material; they definitely needs to take into account the thermohygrometric conditions [1]. Although the analyzed samples are relatively few, they have produced a considerable mole of data that needs a multivariate treatment.

References

1) M.P. Sammartino**,** G. Cau**,** R. Reale**,** S. Ronca, G. Visco, A multidisciplinary diagnostic approach preliminary to the restoration of the country church "San Maurizio" located in Ittiri (SS), Italy, *Heritage Science*, 2(4), (2014). doi:10.1186/2050-7445-2-4