



Preliminary Study to Set Up a Non Destructive *In Situ* Method to Monitor Soluble Salts Content in Stone Materials; The Usefulness of a Multivariate Approach

C. Tropea, M. P. Sammartino, G. Visco

Chemistry Dept, "La Sapienza" University, p.le A. Moro 5 - 00185 - Rome (Italy)

Abstract

A new equipment and procedure to monitor *in situ* soluble salts content in stone materials were set up. They base on the extraction, by flowing deionized water, of soluble salts from stone surfaces and on the continuous registration of the real-time response of a conductivity probe; the resulting solution can be collected and then analyzed by ionic chromatography in the laboratory. A correlation between the signal obtained *in situ* and the chromatographic data was looked for; satisfying results were obtained but further investigation are needed in order to take into account all the involved parameters/variables and to extract the most significative index from the signal curve. Surely a multivariate approach will be of help to optimize both the equipment and the procedure. The engineering of the apparatus must be improved too.

Introduction

There isn't a standard method to monitor soluble salt content in stone materials, which is one of the main cause of their deterioration[1, 2]. The standard UNI 11087 [3] defines the sample's treatment and the laboratory analysis to determinate the soluble salts content in stone materials, but nothing says about sampling. This kind of monitoring is needed in order to decide if a restorer had to intervene; the most common desalinization procedure used by restorers is based on the extraction of salts using cellulose pulp supporting water, but, also in this case, no standard procedure is foreseen. This research not only offers an innovative non invasive analysis of the soluble salt content in stone materials but also aims to contribute to the standardization of the full analytical procedure, e.g. including all the steps from sampling to data evaluation.

Materials & Methods

A scheme of the instrumental apparatus is shown in figure 1. The heart of the apparatus consists of a silicon pad, hosting a sheet of japanese paper that must be put in contact with the stone surface. It was obtained pouring a viscous silicon gum into an aluminium mould suitably designed and finished with the insertion of stainless steel tubes through which water can reach the japanese paper. The pad is connected to a metallic holder consisting of two perpendicular bars; the horizontal one contains a calibrated spring that allows measuring the pressure applied to the pad through the application of a variable weight at the basis of the vertical bar. The apparatus is completed by a container in which

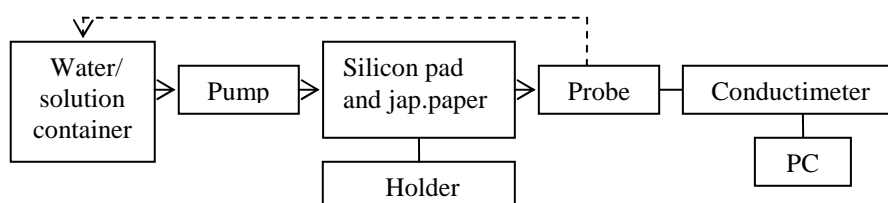


Fig. 1 Scheme of the apparatus. The flux of water is indicated by the arrows.

the initial deionized water continuously enriches in salts content, a peristaltic pump, a flow conductimetric probe, a conductimeter and a PC equipped with a suitable software (fig. 1).

By the described apparatus, a continuous measure of the conductivity of the circulating solution is performed; the signal curve can be correlated to the salt content of the stone surface in contact with the wet japanese paper. The signal can be seen in real time on the PC's screen so allowing to stop the analysis when a plateau is reached if this final condition is chosen. To verify the correlation between the conductivity signal obtained under fixed conditions and the real content of soluble salts, mortar samples with known salt content (chloride, nitrate and sulphate) were prepared and tested. Mortar samples were prepared at the ICCROM Laboratory in Rome with the help of Dr. Ernesto Borrelli. Some real samples were also analyzed; in all the cases results were compared with those obtained by ionic chromatography. More, the conductivity values of the final solutions obtained by the proposed procedure (method a), were correlated with those of a solution obtained following the first part of the UNI 11087 procedure, e.g. by putting 100 mg of drilled sample in 100 ml of deionized water (method b).

Results

As an example, in fig.2 the signals recorded by the equipment for three mortars with different salt content are reported. A satisfying correlation was found between such data and those obtained by IC; an analogous result was obtained from the comparison of conductivity values obtained by methods (a) and (b).

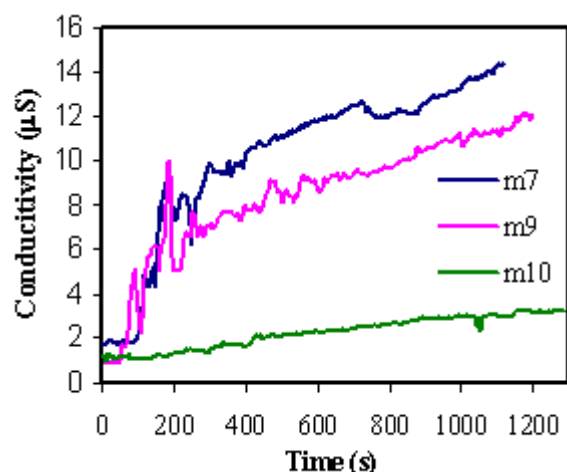


Fig. 2 Trend of conductivity for three mortars with increasing salt content.

Conclusions

The application of the proposed analysis on both simulated and real samples demonstrated its usefulness to obtain a reliable aspecific information on the total salt content; the procedure can be used for a quick non invasive monitoring of the conservation conditions of stone artefacts. This allows limiting the invasive analysis that could be performed only when an "alarm signal" is obtained.

Some problems, rising from the adhesion of the silicon pad on the stone surface, must be solved; really an optimization of the pressure to be applied on the pad is needed to ensure

no loss of solution during the measure and, at the same time, to avoid damages on sensitive materials such as frescoes. Overall, the most significative index must be extracted from the response curve in order to obtain the best index that can represent the real content of salts in the artefact. More, further experiments on simulated samples of different stone materials containing different kind of salts are necessary to better understand the correlation between conductivity signals and salt content as well as to have more data to be compared with *in situ* measurements.

References

- 1) E. Borrelli, Desalination systems: types, applications and efficacy, in: Sais soluveis em argamassas de edificio antigas, Lisboa 14-15 Feb, 2005.
- 2) J. Petkovic, Moisture and ion transport in layered porous buildings materials: a Nuclear Magnetic Resonance study. PhD Thesis, Eindhoven University of Technology, 2005, ISBN 90-386-2151-5.
- 3) UNI NorMal n. 11087, Beni culturali - Materiali lapidei naturali ed artificiali. Determinazione del contenuto di sali solubili, in italian, 1 Nov 2003