Invasive and Not Invasive Analysis of Soluble Salts in Stones; Look for Correlation in the Case Study of the Todi Cathedral Floor

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Abstract

Two non invasive methods and the UNI 11087/2003 method [1] for the determination of soluble salts content in stones were compared looking for correlation between obtained data. Three different kind of stone, constituting the Todi Cathedral floor, were considered.

Ionic chromatography (IC) and Inductively Coupled Plasma (ICP) were used for the determination of anions and cations respectively; pH, conductivity and redox potential (ORP) measurements were also performed. Samples were characterised by Scanning Electron microscopy coupled with X-ray microanalysis (SEM/EDS) and X-ray diffraction (XRD). Density and porosity were also determined, the second by a new methodological approach (running research).

Interesting results can be drawn by the very big mole of obtained data; surely it would be better evaluated by chemometrics or multivariate analysis.

Introduction

It is well known that the presence of salts in the porous net of stone materials is the main cause of their degradation [1,2]. On the contrary, it is almost difficult to foreseen the minimum salt content that can cause degradation in stones as lot of parameter must be taken into account. Really, different salts behave different mainly due to their different solubility and capability [3] to form crystals of different volume depending on the water molecules present in the structure; so, the thermoigrometric condition and, overall, their cyclic variation must be considered the main cause of both aesthetic (efflorescences) and structural (subefflorescences) degradation.

The UNI salts determination must be performed on solutions coming from the extraction from powdered stones by deionized water [4]; the method must be considered invasive and at least 0.5 g of sample are needed for each point to be analysed; alternative methods are so welcoming.

Materials & Methods

For collect data values was used: Ionic Chromatograph 761 Compact (Metrohm GmbH, Swiss), Spectrometer ICP-AES Vista MXP Rad (Varian, USA) powder XRD patterns were recorded with Cu-Kα radiation on a Seifert MZ-IV diffractometer (General Electric Company, USA), SEM/EDS measures by SEM-LEO1450VP-EDS (Leica, Germany), density and porosity by Gibertini balance mod E50S (Gibertini, Italy) equipped with the apposite kit.

We compared the UNI method with other two that are not invasive. The first (method A) can be only used in particular cases such as our case study as the floor of the Todi cathedral was completely removed during restoration works.

Method A: Big blocks of the different stones were put in distilled water, samples of the resulting solution were taken at two different time and the anions content determined by IC.

Method B: about 6 g of cellulose pulp were soaked with 50 deionized water, put on the floor covering a surface of about 65x65 mm and left for 24 h; the extraction was repeated on the same zone for three consecutive days. Salt were then extracted from the compresses by 500 mL deionized water and two consecutive washing by 100 mL deionized water. Anions were determined by IC and cations by ICP; pH, conductivity and ORP were also measured.

XRD were performed on both the powdered stones and their residue after acetic acid attack.

Density and porosity were measured for cubic (about 20x20x20 mm) samples using the same balance and kit. The weight increase when suspended in distilled water was monitored for about 24 h to obtain the trend of water adsorption.

Results

XRD and EDS analyses revealed an enough similar composition for the three stones, calcite is the main component, quartz, muscovite and chlorites constitute the siliceous part and red colour must be imputed to hematite (see table 1).

Even if the marbles density differs very little, porosity of the dark red is about a third with respect to the red and white ones.

Nitrate and calcium resulted the most abundant ions using all the methods. As expected the anions and cations balance was not obtained revealing a significant content of carbonate and bicarbonate that cannot be determined by the used IC method (see table 1).

Anyway, it must be pointed out that at least part of them (may be the bigger) come from the solubilisation of the marble itself due to the well known solvent power of deionised water. This effect, obviously greater for the powders, is evidenced in fig. 1; really the total cations-anions balance (as %) is about ten times higher using the UNI method with respect to the method B (see table 1) and can be attributed to the calcium. More, as expected, pH values resulted always higher for the solutions coming from the UNI method.

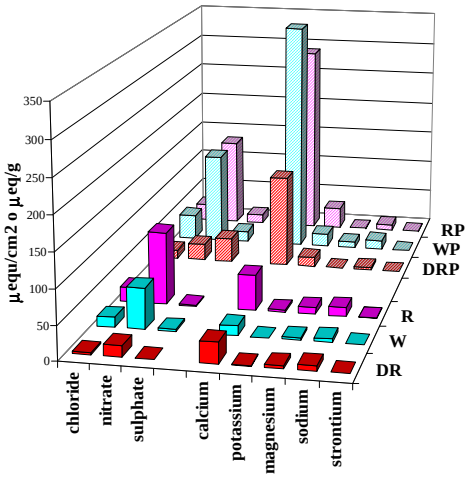

Fig. 1; ions content obtained by UNI method (DRP, WP, RP) and method B (DR, W, R)

marble	Composition [a]	Density (mg/g)	Porosity (%)	(C-A)/A [b] (%) UNI	(C-A)/A (%) [b] method B
B	Ca, Qz, Mu, Cl	2.6561 ± 0.0010	0.64±0.03	117	8.0
R	Ca, Qz, Mu, Cl, He	2.6530 ± 0.0031	0.61±0.05	94	8.4
RS	Ca, Qz, Mu, Cl, He, KF	2.6561 ± 0.0062	0.27±0.01	115	14.1

Tab. 1; Main data obtained for the three marbles. [a] Ca: calcite, Qz: quartz, Mu: muscovite, Cl: Chlorite, He: hematite, KF: K-feldspate. [b] C: cations, A: anions

Even if few data are available, density and porosity show a continuous increase that, if confirmed, demonstrate both a surface and inner pore surface consumption

Conclusions

The non invasive proposed methods could be a valid alternative to the UNI 11087/2003. The error in the total salts content, due to the solubilisation of calcite constituting the marbles, results greater for the official method as a consequence of the huge specific surface of powders. A help from chemometry is needed to treat the big mole of data as well as to find the best correlation index between methods.

References

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