



## New Analytical Procedure for a Non Invasive Analysis of Soluble Salts in Frescos Using a Statistical Sampling Method

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### Abstract

An extraction of soluble salts from frescos was performed using sheets of Japanese paper embedded of ultrapure water. A mixed sampling method, random sampling and purposive sample design, was adopted in order to obtain significant information about the role of soluble salts in the degradation of a frescoed chapel located in a roman church. Salts were then recovered by the sheets using ultrapure water and the obtained solutions analysed by Ionic Chromatography (IC). Temperature, humidity and drying time were also measured on each sampled zone and all the obtained data were treated by Principal Component Analysis (PCA)

### Introduction

It is well known that soluble salts are responsible of the damage of stones materials, due to their crystallisation inside its pores. Actually, the only analytical procedure able to give full information on the salt content in stone materials foreseen a sampling by coring and a ionic chromatographic (IC) analysis [1]; the procedure is then microinvasive and destructive with all the consequent disadvantages that, mainly in the case of artistic artifacts such as frescoes, often are bound to a not enough statistically significant sampling.

In this communication a new analytical procedure is proposed based on a non invasive systematic random sampling. It was applied to the frescoes of a chapel in a roman church as a part of a diagnostic iter requested to help the restorers work.

### Materials & Methods

Ultrapure water (conduc.  $< 2 \mu\text{S}$ ) was used as extractant, supported on japanise paper ( $12.5 \text{ mg/m}^2$ ). Local humidity and temperature were measured using a contact digital Protimeter Surveymaster SM (GE Sensing, Fairfield, CT, USA) and a K-Type contact digital thermometer (PCE Group, Lucca, Italy) respectively; a Metrohm mod 761 IC (Herisau, Swiss), equipped with the 6.1006.430 column (250mm), was used for the IC analysis. The church to which the chapel belongs is located in an enough traficated zone of Rome and is closed to Tevere river; so, both problems related to humidity (capillary ascent) and pollution (especially sulphate ion) must be considered. More, the window overstanding the altar was not in perfect conservation condition so letting to hypothesise possible infiltrations and related problems.

As shown in fig. 1, three along vertical sampling zones were chosen, for each differently facing wall, starting from a height of 70 cm (L1, just over the marble base) and climbing a meter each step (L2, L3). A second serie of zones (W, see Fig. 2), located at the higher level of the chapel, were chosen around the window overstanding the altar and on the part of vault nearest the window.

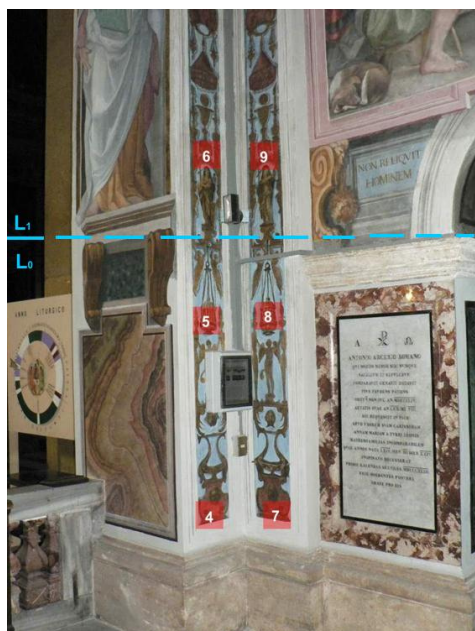


Fig.1; example of systematic sampling

About 50x50 mm japanese paper square were weighted on an analytical balance to obtain the exact area through an apposite calibration curve; each paper square was wetted with 100  $\mu\text{L}$  of ultrapure water, let to adhere to the fresco surface until its complete drying and then accurately stored. The so obtained samples were subjected in laboratory to an extractive procedure by 50 mL ultrapure water and the resulting solutions analysed by IC [2]. The accuracy of the lab procedure was evaluated using squares of japanese paper with different salt content.

## Results

Temperature values ranged from 16.7 to 22  $^{\circ}\text{C}$ , the highest dispersion (about 5 as SD%) was obtained for the W series together with the less variability of humidity (about 23 as SD%) and quickest drying time ( $10 \pm 4$  min). The highest humidity value was found in the L3 serie and results more than twice the danger threshold (20 % moisture content referred to

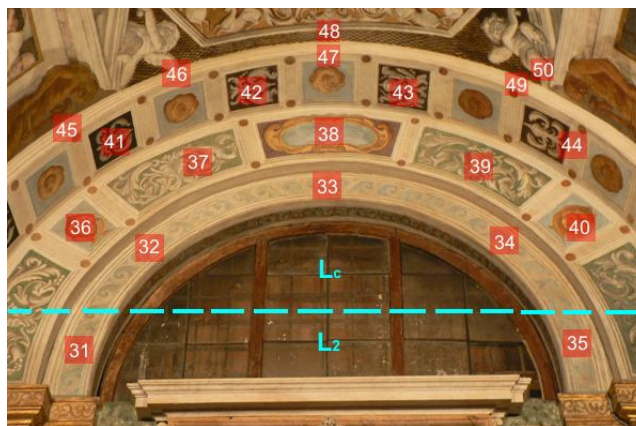


Fig.2; Map of the sampled zones in the series W

Wood Moisture Equivalent). Chloride content, as expected, resulted very low ( $< 200 \text{ ng}/\text{mm}^2$ ) on all the fresco, the most abundant salts resulted to be nitrate with expected maximum values in the series L3 ( $240 \pm 140 \mu\text{g}/\text{cm}^2$ ) and minimum values in the serie W ( $3 \pm 1 \mu\text{g}/\text{mm}^2$ ); finally, the maximum and minimum sulphate content was found in the serie L1 ( $50 \pm 30 \mu\text{g}/\text{mm}^2$ ) and W ( $20 \pm 30 \mu\text{g}/\text{mm}^2$ ) respectively. In all the case a very high dispersion was found in all the data letting to a difficult interpretation. We roughly found some expected trend but this is a classical case to be treated by advanced statistic method; such part of the research is unfortunately yet running.

It must be pointed out that our data are of particular difficult interpretation as other important factors such as the presence of different pigments or eventual finishing layers would be considered. More, the sampling unfortunately and not on our decision, occurs during the restoring works and we suspect that some cleaning intervention occurs on some of the analysed zones.

Anyway the lab method resulted enough accurate, really the % recovery resulted to be 99 – 100, 94-100 and 83-100 for chloride, nitrate and sulphate respectively.

## Conclusions

Even if roughly, the data trend are congruent with the position of the sampling zone and overall the accuracy of the lab procedure is very good. This method, foreseen an indirect non invasive sampling, can be proposed as an alternative to the actual coring sampling.

Further work is requested to find a correlation between the two methods as we have to take into account that our sampling method mainly acts at the surface level; so, just as an example a higher sulphate content could be hypothesised. Anyway the full adopted procedure can give a full view of the conservation state of walls.

It was possible to hypothesise that the salts presence come from both capillary climbing and pollution the last being mainly aged; really sulphate presence must be probably ascribed to both outside and inside pollution caused by no low sulphur fuels (actually forbidden by law), as traffic contribute and by the use of old lighting and warming methods as internal contribute.

## References

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- 2) S.H. Perry, A.P. Duffy, The short-term effects of mortar joints on salt movement in stone, Atmos. Environ., 31(9) (1997) 1297-1305