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## SOLUBLE SALTS EXTRACTION WITH DIFFERENT THICKENERS: MONITORING OF THE EFFECTS ON PLASTER

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### Abstract

Soluble salts content and their crystallization play an important role in the deterioration of porous substrates; the common approach to solve this conservative problem is focused on the identification of a proper thickener and application protocol able to reach a good level of desalination. Here we report the results of a systematic study on a late Renaissance plaster aimed at reducing the content of gypsum and sodium nitrates comparing five different type of thickeners. The extractive process has been monitored by Evanescent Field Dielectrometry (EFD) by means of the evaluation of salinity index (SI) and humidity content (HC), whereas the quantification of the salinity level, before and after desalination, has been performed with ionic chromatography (IC). Data coming from the field, have been integrated with laboratory measurements aimed at evaluating the water release trend, according to the micro-structural features and the pore size distribution of both the thickeners and the substrate. This step has the purpose to identify an effective correlation among the characteristics of the desalination systems and the porosity in order to estimate a proper trend of effectiveness, suitable for the procedure of conservators.

### 1. Introduction

Scientific literature underlines how soluble salts content and their crystallization are still an open conservation problem<sup>1-5</sup>; they could be considered among the primary causes of irreversible damage in artistic objects, such as sculpture, masonry and mural paintings. The common approach adopted to front this problem and minimize the damage, is aimed at reducing the salts content by means of water-based systems composed by different thickeners. Water has the role to solubilize the salts, while the extraction mechanism is strongly dependent to the typology of the thickener and its microstructure. Both diffusion and capillary suction are involved in the extraction mechanism. As regards diffusion, salts ions are transported from the artwork bulk to the poultice thanks to a concentration gradient; for what concern capillary suction the size of capillaries could be the driving force of the transport phenomena<sup>2</sup>. Pel et Al. report about the physical working principles of ions salt and moisture transport phenomena; starting from the penetration depth of the saline damage, they demonstrate an important dependency in salts extraction efficiency with the time of treatment<sup>6</sup>.

Water evaporation links the migration of soluble salts to crystallization on the outer surface (efflorescence) or in the underneath region (sub-efflorescence), this latter being the most potentially damaging, due to both the lack of ease in visibility and the huge crystallization pressures, which could rapidly act on cohesion forces<sup>7</sup>. The most common soluble salts are composed of chlorides, nitrates, sulfates of sodium, potassium, calcium and magnesium and their mixtures; generally, their chemical composition is strongly dependent by the composition of the host object.



In this paper we report the results of a systematic study on a late renaissance plaster, located in the Sforza Castle in Milan recently object of a conservation work. As a first step the soluble salts were characterized: a mixture of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), magnesium sulphates (both hexahydrate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and epsomite  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ) and nitrate ( $\text{NaNO}_3$ ) were detected by X-Ray Diffraction<sup>8</sup>. In the second step the conservator team choose a set of different thickener in order to identify the most adequate poultice for a proper desalination. Five different systems were compared: agar (applied by brush and as a rigid gel), cellulose pulp (arbocel), cellulose pulp + sepiolite and cellulose pulp + sepiolite + sand; each one was applied to the plaster with different contact time (2 ½ h, 5h and 24h). A multi-analytical approach was applied to study the extractive process: Evanescent Field Dielectrometry (EFD)<sup>9,10</sup>, was used to monitor the desalination in terms of salinity index (SI) and humidity content (HC) and ionic chromatography (IC) was used to quantify the salts content into the plaster, sampled by drilling as powder, but also extracted from the plaster, before and after treatment. The plaster showed both efflorescence, removable by brush, and sub-efflorescence. This latter decay product could be quantified only with the aid of sampling, but the procedure is often not allowed. For this reason, the application of a non-destructive testing as the Evanescent Field Dielectrometry was crucial and proved to be a winning strategy.

This study suggested to explore another important issue related to the efficiency of the thickeners such as the water release. To reach this goal, a set of model samples composed by specimens of different lithotypes characterized by decreasing porosity, has been assessed. Noto calcarenite, Manciano sandstone and Bergamo limestone have been selected and weighted before and after the application of a water based poultice composed by the same thickener used in the field, measuring accurately the water release at a given time (30 min). At each step, before and after the application of the poultice, also the SI and HC measurements were performed by EFD.

## 2. Materials and Methods

### 2.1 Poultices and their formulations

Five different formulations of water based poultices were prepared:

1. agar at 4% in liquid form and rigid (AgarArt, CTS srl)
2. cellulose pulp (Arbocel BC 200)
3. cellulose pulp + sepiolite (Bresciani S.r.l. Milan)
4. cellulose pulp + sepiolite + quartz sand (quarried in Ticino river deposits)

Each system was applied to the plaster with different contact time (2 ½ h, 5h and 24h). The proportions used are reported in table 1. The amount of water in poultices mixes C, D and E, was accurately defined via preliminary tests in order to apply them on a vertical surface.

Table 1 - Formulations of poultices.

System code	Materials	Proportions
A	agar gel	4 % in water
B	agar gel applied by brush	4 % in water
C	arbocel	/
D	arbocel + sepiolite	3:1
E	arbocel + sepiolite + sand	3:1:1

### 2.2 Evanescent Field Dielectrometry (EFD)

The EFD system used here (called SUSI<sup>®</sup>) consists of a resonant probe operating in the microwave frequency range (1-1.5 GHz), of a Vector Network Analyser (VNA) for measuring the probe response

and of a PC portable that driven the previous device by a dedicated software and elaborate achieving the diagnostics results (HC and SI) (Figure 1a).

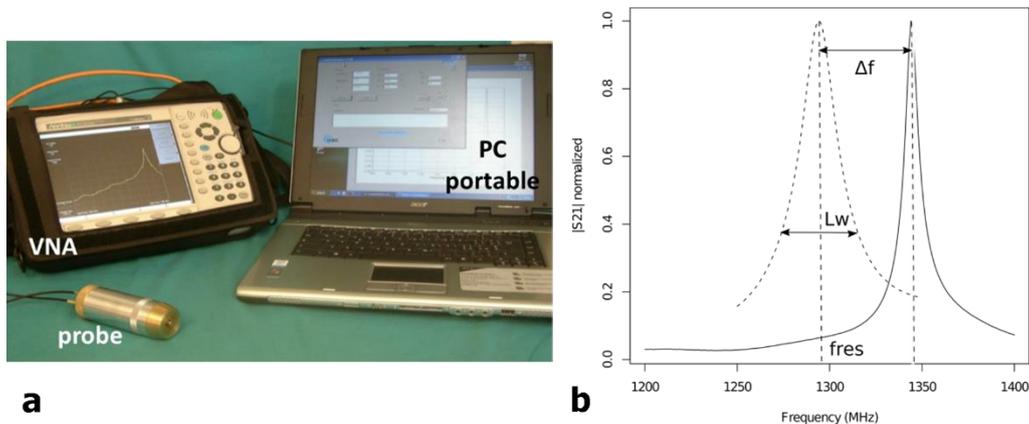


Figure 1 - SUSI<sup>®</sup> setup (a) and frequency response of resonant probe (b).

The electrical parameters of interest of the resonant probe response are the resonance frequency  $f_r$  and the quality factor  $Q$  (or resonance bandwidth  $Lw$ ) shown in Figure 1b.  $\Delta f_r$  corresponds to the resonant frequency shift of the probe between the loaded behaviour, which is in contact with the material under test ( $f_r$ ), and for unloaded behaviour, addressed on air ( $f_o$ ).

These resonant parameters are related to the diagnostics parameters HC and SI<sup>9,10</sup>. In first instance, the frequency shift is related to the HC while the spreading in bandwidth is due to the combination of the dielectric losses in the operation microwave region of the system and conductivity losses, both related to the presence of salts, or better related to electrolytes in solution. The HC of the examined material can be related to  $\Delta f_r$ , according to the simplified equation shown in reference 10 and 11, where a preliminary calibration, performed by of several measurements at the dry state and wet state, is necessary for the determination of the correlation constants.

The range of humidity content that can be investigated is between 0% to 20% (on dry basis), and for the salinity index from 1 to 10. The SI is a semi-empirical parameter<sup>11</sup>.

### 2.3 Ionic chromatography (IC)

The soluble salt content of the poultice materials ( $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $C_2O_4^{2-}$ ) was determined by a Dionex DX100 ion chromatography system equipped with Dionex AS4A/CS12 columns.

### 2.4 Stone specimens

Three different stones characterized by different lithology and decreasing porosity have been chosen in order to measure the specific water release using each specific poultice formulations: Noto calcarenite, Manciano sandstone<sup>12</sup> and Bergamo limestone<sup>13</sup>, each one sized 5 cm × 5 cm × 2 cm.

### 2.5 Water release measures

Each specimen was used for the determination of water release from the top to the bottom. The poultices have been shaped on the top of the specimen to cover precisely the upper surface. Each poultice has been sized exactly 1 cm thick, in order to give the same “reservoir effect”, and the measure has been prolonged for 30 minutes. At the end of the test each specimen has been weighed on a precision scale, where the weight of water absorbed has been determined by subtracting the weight of the dry specimen. Each test series has been averaged on the basis of 5 specimens. The tests have

been carried out at room controlled temperature (25°C) avoiding the evaporation during the 30 minutes, by wrapping the system in a polyethylene film.

### 3. Results and Discussion

#### The late Renaissance plaster

The late renaissance plaster has a worrying state of conservation, with an important presence of efflorescence and sub-efflorescence causing a general whitening of the surface<sup>8</sup>. The presence of the soluble salts (gypsum, hexahydrate, epsomite and nitratine) as reported in introduction is possibly due both to the inappropriate use of the room as a stable till the XIX century and to the high level of sulphation involving calcium and magnesium carbonates.

These salts produce a series of whitish rings, some of which visible in Figure 2, together with a general overview of the poultices applied; hence the conservator needed to plan a removal of the soluble salts avoiding as much as possible a large release of water. The conservation problem focused on the correct balance in between desalination effectiveness and low amount of water release.

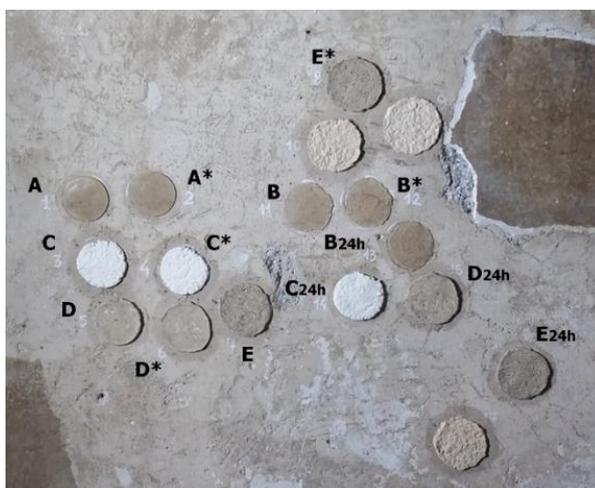


Figure 2 - A general view of different desalination systems applied on plaster. A = Rigid Agar gel; B = Fluid Agar Gel applied by brush; C = Arbocel; D = Arbocel + Sepiolite, E = Arbocel + Sepiolite + sand; \* indicates the poultices kept in contact for 5h. In Figure are showed some other poultices not included in the present study.

#### SUSI

The characteristics of SUSI system, non-destructive measurement and ability to perform the measurement in real-time, are addressed to be the ideal tool for checking the extraction efficacy of poultice of salts. With the aid of SUSI is possible to control the status of the support (HC and SI parameters) before the application of the poultice and immediately after its removal; in this case the monitoring continued up to 48 hours after the removal of the poultice, following the re-equilibrium process of the support with the environment (monitoring of the evaporation process where the efflorescence risk is greater).

The results obtained by SUSI system are presented as to kind of poultice (see Table 1) and time of application: 2½ h, 5h and 24h. The values of HC and SI are plotted in the same graph with a double y-axis; the legend in the graph allows distinguishing the marker for the respective parameter.

Since the volume of the material investigated by the probe is a hemisphere (2 cm in diameter) inside the support, it is needed to perform several measurements on the area interested by the poultice, in

order to obtain an average information on the salts contamination of the substrates. Hence, at least 3 measurements were performed by SUSI, for each contact area of the poultice.

In Figure 3 the results obtained for each poultice (Table 1) at time contact of 2½ h, have been selected as the most significant. The first measurement series, at wet state, are quite similar both in terms of HC (about 1-2%) and SI (3-4), this confirms the homogeneity of the areas under comparison. After the application of the poultice, we observed an increase in the salinity index SI (contact time 2½h) for each system, probably due to salts moved by water released by poultice. The effect of the increasing in salts amount, is still measurable after 48 h, and it is more relevant for system C, D, E, where the amount of water released in the support is probably greater.

Analogous results were obtained as to the other contact times, without a significant variation, except for a visible trend in increasing the index of salinity SI.

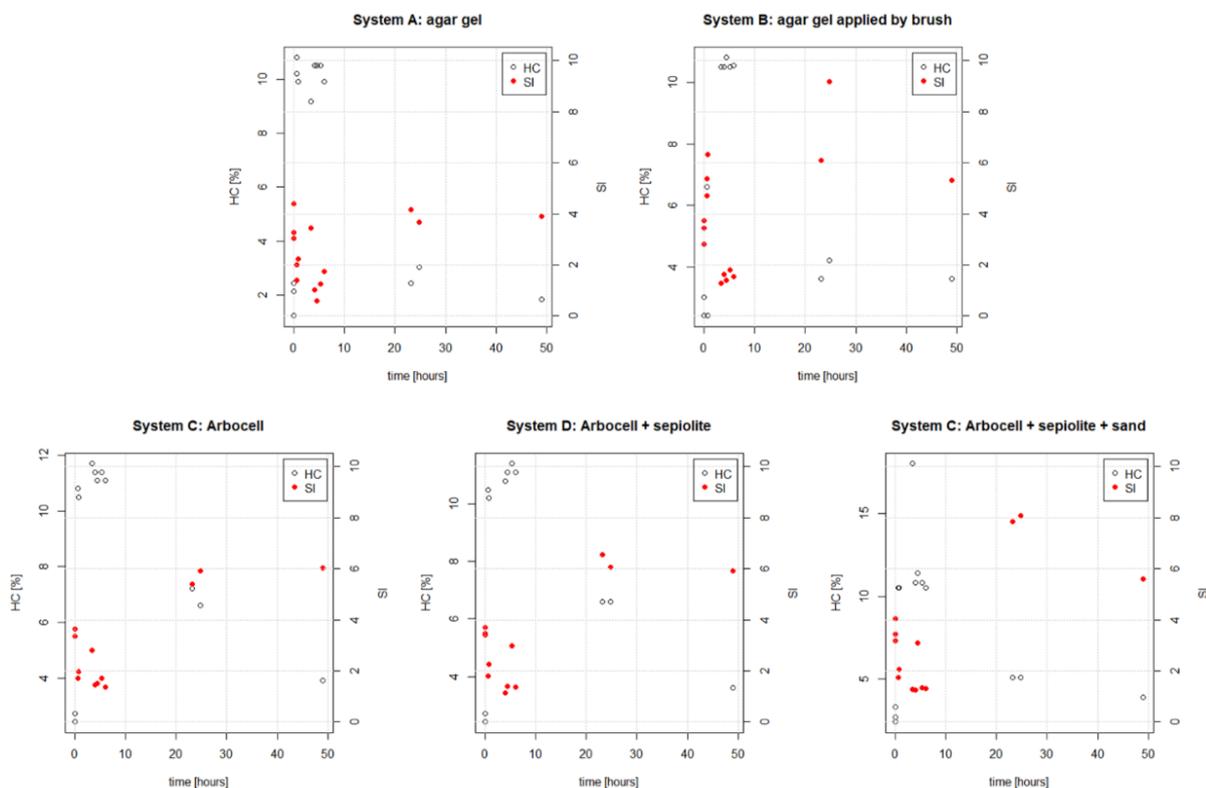


Figure 3 – Plots of HC and SI parameters by SUSI system on the areas where applied the poultices described in Table 1.

### Ionic Chromatography

The desalination level performed by the different systems (see 2.1 and Table 1) were estimated by ionic chromatography, focusing on the fluctuation of nitrate and sulfate content (Table 2a-b). At the first glance, all systems applied for 5h exhibit a good effectiveness compared to the ones applied for 2½; in particular nitrate ion enhance its content in the poultice material doubling and tripling at least in the 5 hours extraction. This result is probably due to the high solubility of the salt, that is around 91.2 g/100 mL at room temperature in the case of sodium nitrate. On the contrary the removal of sulphates does not increase importantly, if the systems are kept in contact for 5 hours, respect to the values obtained for 2½. it is worth noting that the desalination capacity enhances greatly up to the contact time 24h for all the poultices both for nitrate and sulfate groups. Unfortunately, it was not possible to keep in contact the rigid agar gel for 24 hours because of its own weight and its low adhesion to the

vertical surface due to the water evaporation. The same increasing trend with the contact time is observable with chloride, despite its lower values. Agar gel both as a rigid gel and applied by brush seems to be the only system effective in removing phosphates.

Table 2a - Desalination value detected by ionic chromatography on agar gel systems for different contact time

System Code	Time of contact	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>=</sup>	C <sub>2</sub> O <sub>4</sub> <sup>=</sup>
A	2 ½ h	0.000	0.062	0.086	0.049	0.108	0.094	0.000
A	5 h	0.004	0.042	0.069	0.135	0.048	0.090	0.000
A	24 h	-	-	-	-	-	-	-
B	2 ½ h	0.000	0.119	0.000	0.646	0.038	0.144	0.000
B	5 h	0.000	0.215	0.071	1.147	0.085	0.150	0.000
B	24 h	0.000	0.318	0.000	2.756	0.024	0.439	0.000

Table 2b - Desalination value detected by ionic chromatography on traditional systems for different contact time

System Code	Time of contact	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>=</sup>	C <sub>2</sub> O <sub>4</sub> <sup>=</sup>
C	2 ½ h	0.000	0.05	0.000	0.008	0.000	0.007	0.000
C	5 h	0.000	0.006	0.000	0.022	0.000	0.008	0.000
C	24 h	0.000	0.010	0.000	0.076	0.000	0.012	0.000
D	2 ½ h	0.006	0.011	0.000	0.028	0.000	0.030	0.000
D	5 h	0.007	0.020	0.000	0.118	0.000	0.039	0.000
D	24 h	0.000	0.094	0.000	0.899	0.000	0.212	0.000
E	2 ½ h	0.000	0.010	0.000	0.029	0.000	0.021	0.000
E	5 h	0.000	0.017	0.000	0.103	0.040	0.027	0.000
E	24 h	0.000	0.064	0.000	0.725	0.000	0.211	0.000

Indeed, agar gel extract the major amount of nitrates and sulfates compared to the other systems: based on the ionic chromatography results, the desalination systems ordered in terms of effectiveness could be listed as follows: agar gel applied by brush > agar gel in rigid form > arboceel + sepiolite > arboceel + sepiolite + sand > arboceel.

### The water release on model sample

Thickeners and gels could be chosen in function of the control of the liquid released in the surface and near-surface region; as concern agar gel according to the concentration of the polymer, they show a certain degree of flexibility, which helps in modulating some characteristics. The water release is also strongly dependent with the porosity of the substrate on which the poultice is applied. In this work water release was measured by weight comparing all poultices tested on site, on several stones specimen in the lab; stone was chosen with progressive higher porosity (Bergamo Limestone, Manciano sandstone and Noto Calcarenite).

Figure 4a shows the amount of water released by agar gels at 3, 4 and 5% w/v: it decreases proportionally with the increase of the agar concentration on Noto Calcarenite (R2 =0.999) and on Manciano sandstone (R2 =0.928), as well. The case of Bergamo Black Limestone is problematic, due to the compactness of the stone: the series measured at 4% w/v is not linear with the ones at 3 and 5 % w/v.

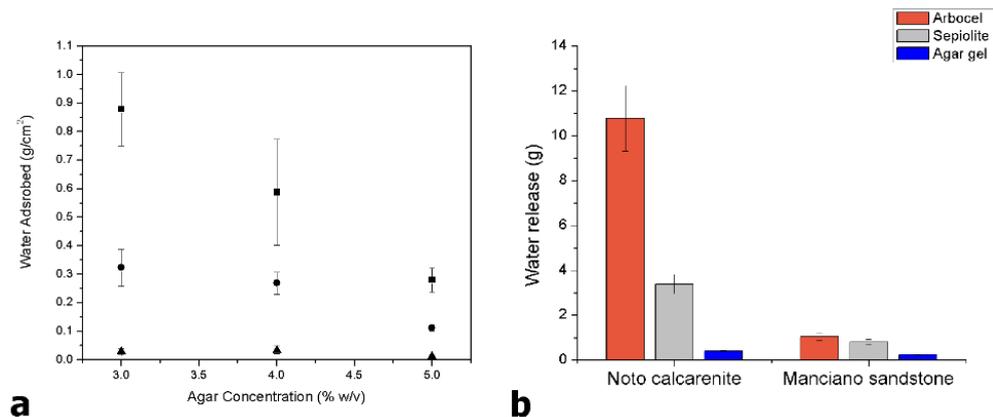


Figure 4 - a) Water absorbed at 30 minutes by agar gel at different concentration on Noto calcarenite (■), Manciano sandstone (●) and Bergamo limestone (▲); b) Water released by paper pulp, sepiolite and agar gel at 3% w/v, on Noto calcarenite and Manciano sandstone.

As it is possible to observe by Figure 4b, in the case of Noto Calcarenite the water released by Arboceel is more or less ten times greater the one released by agar gel; for what concern sepiolite it is the triple. The situation is similar for what concern the other stones, even if is the total amount of water released is lesser than the one measured for Noto Stone; this is certainly due to the total open porosity value of the calcarenite.

Moreover, the preliminary result about the percentage of the water absorbed is estimated and it is around 2.39 % for Noto stone, 1.44 % for Manciano sandstone and 0.12 % for Bergamo limestone.

#### 4. Conclusions

In this research, a systematic study on desalination systems demonstrates that agar gel applied by brush, records the best results in saline extraction capacity if compared to the traditional systems and to agar gel in rigid form too. In general, the agar gel is considered as a *peelable* system, but this statement could be considered correct if the gel is applied in a rigid form and not applied by brush, where some inconveniences about rips have been observed. Moreover, the other systems exhibit a lower extractive capacity and the Japanese paper shall be applied on the treated surface to avoid unwanted residues.

Finally, only one application of the extractive poultices didn't bring in a reduction of the SI on the plaster, so the applications should be repeated several times until to observe an effective reduction in the SI parameter.

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