Diagnostics and monitoring of moisture and salt in porous materials by evanescent field dielectrometry

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Abstract

Moisture and salts are the main causes of decay of porous materials, like wall paintings, stones, plasters and cement-based artefacts. Water is the ‚driving force' of decay, such as the detachment of the painted layer, the whitening of surfaces due to the crystallization of salts (efflorescence), and the weakening of the cementing binder. Early diagnostics of water content and detection of the presence of soluble salts inside the material is a key issue for understanding the degradation processes in such kind of materials and for improving their schedule maintenance. In this contribution a non-invasive microwave system based on evanescent field dielectrometry is described. The method was tested in the laboratory on moistened plaster samples, some of them containing salts at different concentrations. Measurements on water-saturated and oven-dry samples provide the basis for calibrating the instrument for on-site measurement of masonry structures, wall paintings and concrete historical buildings too. The obtained results prove the usefulness of the method as a tool for diagnostics and for monitoring the effectiveness and durability of restoring interventions.

Keywords: sub-surface investigation, moisture and salt content, dielectrometry, resonant technique, SUSI© system, plaster, stone, concrete.

1. Introduction and research aims

In this contribution the authors describe the Evanescent-Field Dielectrometry (EFD) system called SUSI©* for determining the water content and detecting the presence of soluble salts inside porous materials, and present its application. The water and salt content are key issues for the maintenance of works of art, such as wall paintings, stone artefacts, masonry and cement-based artefacts.

The SUSI© system is an electromagnetic (EM) diagnostics method based on the existence of the relation between physical characteristics, in particular water content, and the complex permittivity of hygroscopic porous materials.[1-6]

EM diagnostics methods can be usefully employed for such tasks, when applied with non-destructive modalities. Among the EM tools, dielectric spectroscopy appears as an eligible technique, i. e. the study of the spectral response of the dielectric permittivity of porous materials can help in determining their state of conservation. In particular, thanks to the dielectric contrast between water and dry material, the presence of moisture is easily detectable. Moreover, ionic conductivity – related to the presence of salts in solution – is measured as well.

A system for dielectric spectroscopy is generally too complex and too expensive to be used for real-time monitoring. Narrow-bandwidth, resonant dielectrometry is a viable solution, because it allows to realize portable, low-weight instruments independently measuring the moisture and salt content. Humidity content mea-

** Italian acronym for Sensore per la misura di Umidità e Salinità Integrato, integrated sensor for measuring humidity and salinity* surements based on EFD techniques have been developed for the diagnostics of wall paintings, masonry and cement-based materials.[7-11]

In particular, water inside building materials is known to be the main source of damage in masonry for the following reasons:

- water diffusion inside masonry and its evaporation from the surface can deteriorate the finish of the surface, and in the presence of a wall painting may degrade the painted layer or the preparation layer – detachment and loss of cohesion;

- the water diffusion can induce the growing of microorganisms on the exposed surfaces that induce biodeterioration;

- or, if the support contains salts, a high risk of whitening and salts crystallization could appear as water diffusion affects the surface.

A sub-surface diagnostic can reduce and prevent such kinds of risks. The same result could be obtained by sampling the support in depth, but this practice can't be applied on surface or material with artistic value (wall paintings, monumental stones, etc.). For example, if we want to assess the effectiveness and durability of a desalination treatment on a wall painting, we have to monitor the residual quantity of salts in the substrate. The availability of a non-invasive and portable tool for sub-surface investigation of moisture content and for detecting the presence of salts, like the SUSI system, can be of great help in the preservation and quality control of the treatment.

The SUSI system has been successfully used in the past for the following applications:

(1) – preliminary screening of state of conservation of the support - maps of moisture content and salts content can be achieved for focusing the sampling[9];

(2) – monitoring the effectiveness and durability of restoration or maintenance interventions[10];

(3) – giving insight about the absorption dynamics of water-based products in areas to be treated during the restoration phase.[8]

2. Materials and methods

The SUSI is based on EFD technique that operates in the microwave range. The diagnostics parameters achieved by this instrumentation are the moisture content (MC) and the Salinity Index (SI) related to the presence and amount of salts. A photo of the system is shown in *Figure 1*. It consists of a two-port resonant probe developed for measurements on solid materials, connected to a scalar network analyser (SNA) for measuring the sensor response (the S21 scattering parameter).[7] The system is completed by a numerical code, running on a PC.

The probe (on the bottom left side) is an open resonant cavity able to check the material without damaging it.[7] Both, the

Figure 1: The SUSI© system (US Patent Specification 7,560,937 B2)

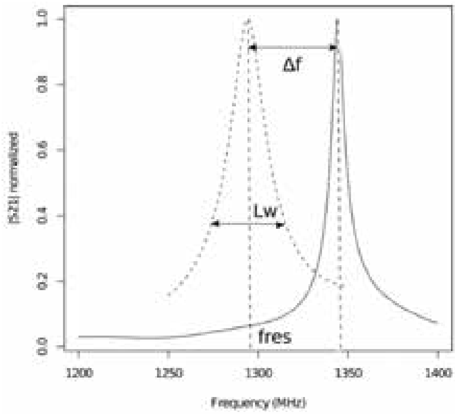

Figure 2: Principle of the SUSI© system

MC and SI related to the material in contact with the probe are calculated in real time by means of the numerical code.

The measurement principle is shown in *Figure 2*. The normalized S21 measured on the material (dashed line) allows to calculate the shift of the resonance frequency (Δf) with respect to the response in air (solid line), and the width L_w at 3 dB or the quality factor Q of the bell-shaped curve. The resonance frequency ranges between 0.9-1.5 GHz for stone materials. The probed volume directly depends on the size and geometry of the sensor; in this case the investigated volume is approximately a semi-spherical volume of 2 cm radius within the material.

The diagnostic parameters (MC and SI) are directly computed from the measured quantities Δf and Q, by resorting to a calibration procedure.[8] The dielectric permittivity, if needed, can be obtained offline by an inversion procedure involving the development in orthogonal modes at the coaxial opening.[7]

The MC parameter has been demonstrated to be linearly related to Δf [8]:

$$MC = \alpha\Delta f + \beta \qquad (1)$$

Therefore, the „calibration" parameters α and β relative to a material can simply be obtained by two measurements, on a dry sample and on a water-saturated one.

The salinity index SI is related to the quality factor Q of the resonant probe. Q can be simplified as the sum of the reciprocals of an „unloaded" term, depending on the geometry and on the electric/dielectric properties of the materials constituting the microstrip cavity, and of a „loaded" term depending only on the dielectric properties of the material facing the sensor. Operatively, SI is computed by using the following expression:

$$SI = \frac{f_r f_0}{2\Delta f^2}\Delta\left(\frac{1}{Q}\right) \qquad (2)$$

where fr is the resonance frequency measured on the material, f0 is that in air, and $\Delta(Q^{-1})$ is the variation of the reciprocal of Q among air and material conditions.

SI has a relatively simple link with the loss tangent (tan δ) of the material. Following a definition for SI used in soil science[12], in terms of the dependence of material electrical conductivity (σ_c) on its dielectric constant (ε'_c)

$$SI = \frac{\partial \sigma_c}{\partial \varepsilon'_c} \qquad (3)$$

and using the relation between conductivity and dielectric losses, the following expression for SI, in terms of the saturation degree S of the porous media, for a given porosity φ (the water content is φS), is obtained:

$$SI = K\frac{\partial \varepsilon''_c}{\partial S}\left(\frac{\partial \varepsilon'_c}{\partial S}\right) = K\tan\delta + K\varepsilon'_c\frac{\partial \tan\delta / \partial S}{\partial \varepsilon'_c / \partial S} \qquad (4)$$

with K an arbitrary constant. Eq. (4) states that SI includes a linear term in the tan δ and a function of tan δ, ε'_c and S.

The relation between (4) and (2) can be obtained by specifying a dielectric model for the material under investigation. In terms of a simple three-phase model[13], using the so called Complex Refractive Index Method (CRIM), the composite material is represented as a mineral/water/air mixture with a complex permittivity given by:

$$\varepsilon'_c = \left[(1-\phi)\varepsilon_m^{1/2} + (1-S)\phi\varepsilon_a^{1/2} + \phi S\,\varepsilon_w^{1/2}\right] \quad (5)$$

where ε_m is the permittivity of the solid matrix, ε_a and ε_w are those of air and water, respectively. Although developed for one-dimensional layered structures, the CRIM model can be demonstrated to satisfy the Hashin & Shtrikman bounds[14] and, therefore, to be a coherent model also for more complex structures.

Figure 3 shows the dependence of SI computed by (4), with ε'_c given by (5), on the saturation degree and on the conductivity of a saline solution filling the solid matrix, for a frequency of 1 GHz and for a porosity φ = 20%. The SI is arbitrarily normalized, choosing a value for the K constant in (4), such as to assume a full-saturation value of 10 for a conductivity of 10 S/m. We observe that the SI slightly depends on the saturation degree, i.e. on the water content, but SI values relative to different material conductivities are very well separated.

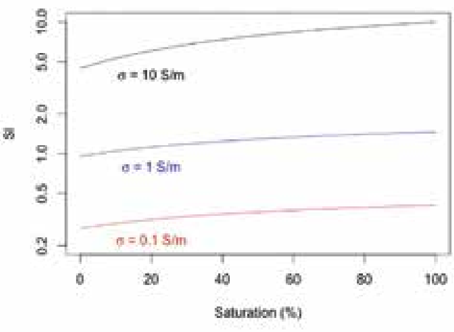

Figure 3: SI versus the saturation degree and the water conductivity

The measured SI, computed by eq. (2), can be easily demonstrated to be related to the dielectric properties as in (4), with a suitable choice of the K constant.

3. Results

3.1. Calibration procedure

The calibration procedure is adopted to relate the measured MC with a water content calculated by gravimetric approach. In this regard, on each type of porous material we can apply the following procedure:

1. Samples in ambient conditions are weighted and measured by SUSI system;

2. Samples are dried in oven at 65°C for three days, until to steady-state condition, then weighted and measured by SUSI system;

3. Samples are water saturated in a vacuum cell with inner pressure of about 2-3 kPa, in order to obtain maximum filling of pores accessible to water, then weighted and measured by SUSI system.

The SUSI measurements are taken when the sample weight reaches steady-state conditions. At least two cycles of drying/wetting should be performed on each sample. Steps 2 and 3 are functional to obtaining the calibration parameters, α and β of eq. (1), for each class of materials.

The calibration procedure for cement mortar samples is described here as an example. *Table 1* summarizes the cement mortar samples made in laboratory and used in this study.

Name	Description	Photo
M1	Size: 4x4x16 cm	
M2	Composition: Portland CEM I cement, binder:sand (weight ratio) : 1:3	
P1	Size: 4x4x16 cm Composition: Hydraulic lime, binder:sand (weight ratio) : 1:3 Size: 4x4x16 cm Composition: Natural prompt cement, no sand	

Table 1: Cement mortar samples made in laboratory

The calibration procedure consists in determining the parameters α and β of eq. (1), relating the SUSI-measured un-calibrated MC (uMC) with the gravimetric MC (MCg) obtained on a dry basis.

Figure 4 shows the calibration curve for sample M1 *(Table 1)*. We observe an uneven spreading of uMC values among samples at low water content. This depends on the characteristics of the surface of the material, less density on the surface than in the bulk, due to a no-homogeneity associated with the sample preparation. This affects the water content in different way in the surface respect to the bulk.

For any given type of porous materials, the parameters α and β can be implemented in the calibration section of the software managing the instrument.

The SI measurement does not require any calibration. Actually, the salinity index is assumed only as a semi-quantitative measure of the salt content, as we are not able to distinguish among salt species only on the basis of the dielectric measurement.

3.2. Application for diagnostics and monitoring

Two applications of the SUSI system for diagnostics and monitoring are briefly described in this sub-section:

- Mapping of the MC and SI on the wall painting of St. Clement at mass and the legend of Sisinnius in the St. Clement Basilica, Rome (Italy)[9];

- The assessment of the effectiveness of an extractive poultice of salts from the wall paintings in the Allori's loggia in the Pitti Palace in Firenze (Italy).[10]

About the first application, the St. Clement Basilica is built on three different levels. The middle level is located below the road level at about 12 m. At this level are located several precious ancient wall paintings. These wall paintings are subject to hard environmental conditions: high relative humidity of the ambient air (about 90% – constant during the year - with a temperature ranging from 12°C to

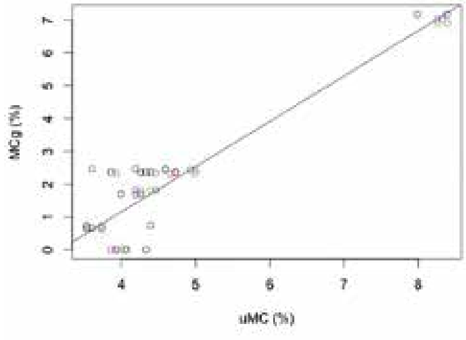

Figure 4: Gravimetric MC (MCg) versus uMC for sample M1

Figure 5: St. Clement at mass and the legend of Sisinnius wall painting. The solid red framework indicates the area investigated by SUSI system and circles represent the points where measurements were performed

22°C), and capillary rise of water from the ground below.[15] On the wall paintings, the typical degradation processes induced by rising damp were present: whitening of the painted layer, salt crystallization, biological microorganism attacks (algae, bacteria, etc.). In particular, on the St. Clement at mass and the legend of Sisinnius, wide areas of salt efflorescence and thick encrustations were present.

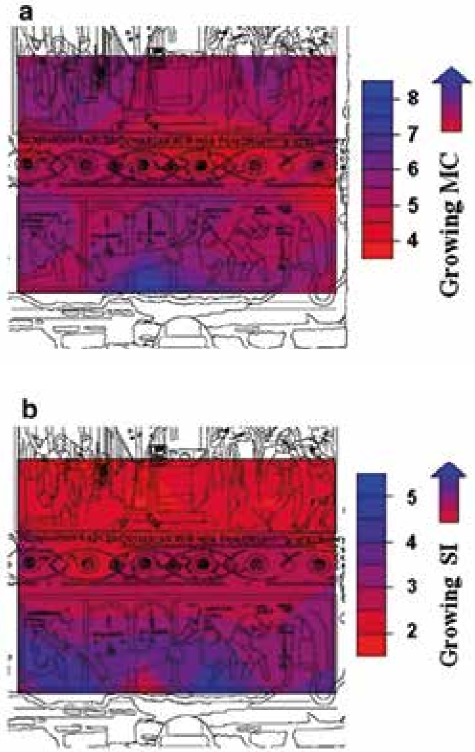

Figure 6: Maps of the distribution of (a) moisture content and (b) of the salinity index

The measurements were performed on the points indicated on *Figure 5*, keeping the sensor in contact with the surface for less than 30 s (the time necessary for the data acquisition). The maps, in terms of MC and SI, are obtained by interpolating the collected data.

SUSI measurements showed that the wall painting exhibited a decreasing gradient of MC from the bottom to the top (until 1.50 m in height) of the investigated area *(Figure 6a)*, ranging from 3.5% (red) to 8% (blue). The SI was higher in the first meter from the floor *(Figure 6b)*, ranging between a minimum of 1.5 (negligible salts) in the upper part of the investigated area to a maximum of 5.5 (quite high salt concentration) in the lower part.

As regards the latest application, the results of tests on the wall paintings at the Allori's loggia in the Pitti Palace in

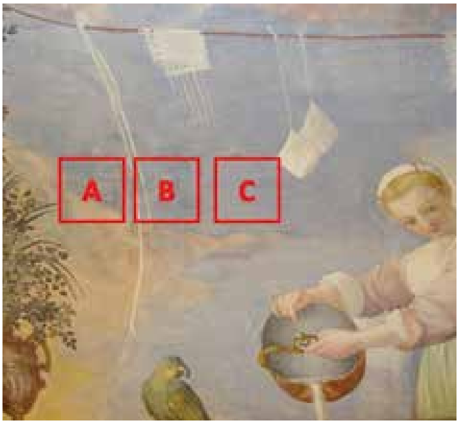

Figure 7: The wall painting of the Allori's small loggia in the Pitti Palace.

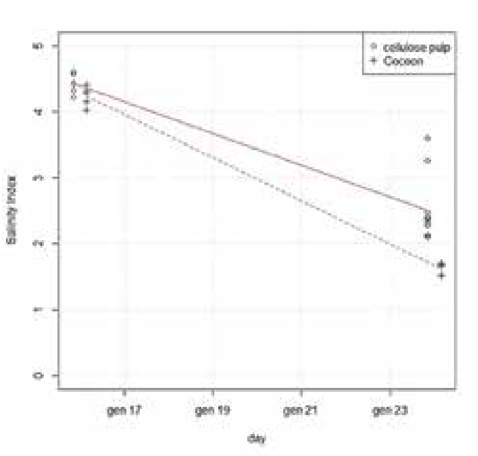

Figure 8: Plots of Salinity Index for two kinds of extractive poultices

Firenze are summarized. *Figure 7* shows the portion of the wall painting where the poultices were applied. On the area labelled with A, a cellulose pulp (bc1000 and bc 200) was applied; on area B the mixing of cellulose pulp, sepiolite clay and sand in different ratios (6 parts of arbocel bw 40/6 parts of sepiolite clay/6 parts of sand was applied); and, on area C the Cocoon® by Westox was applied. The effectiveness of each poultice was evaluated by SUSI measurements applying the following protocols:

a. preliminary measurement by SUSI system before the application of extractive poultices on the selected area on a regular grid;

b. new measurements after from the removal of extractive poultices.

Figure 8 shows the results regarding two kinds of poultice: cellulose pulp and Cocoon. The Cocoon poultice demonstrates a better effectiveness after 7 days with respect to the cellulose pulp, while the poultice made by mixing cellulose pulp and sand didn't provide good results.

4. Conclusions

The SUSI system based on EFD technique can be employed for in situ diagnostics of buildings materials, in particular for diagnosis and monitoring of the presence of water salts up to 2 cm in depth (for the probe used in this work). The resonant approach guarantees an excellent sensitivity on the measurement of the moisture content and also allows to simultaneously and independently detect the presence of soluble salts. A rough quantification of the salt concentration is made based on a Salinity Index, empirically introduced and theoretically justified based on a simple 3-phase model of material. The measurement system, calibrated on samples with proper characteristics (plaster, stone, concrete, etc.), is a promising technique to be applied in diagnosis and monitoring of materials used in historical buildings and artworks.

5. References

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