Investigation on water content in fresco mock-ups in the microwave and near-IR spectral regions

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ABSTRACT

Water diffusion inside masonry is responsible for the majority of the decay phenomena observed in wall paintings and frescos. Thus, the diagnostics of moisture and water content and their monitoring represent a key issue. In order to preserve the integrity of surfaces of artistic interest, investigations by means of non-destructive techniques (NDT) are preferred over others. The aim of this research is to determine methodologies to quantify the moisture content of frescos by means of the integrated use of two non-invasive techniques, namely Fiber Optic Reflectance Spectroscopy (FORS) in the near-IR region and Evanescent Field Dielectrometry (EFD) in the microwave range. The FORS technique has been employed in order to assess the amount of water adsorbed from the surface by means of an analysis of the reflectance spectra in the Vis-NIR (350-2200nm) range. This technique investigates the electronic and vibrational transitions that are characteristic of each compound and enables their identification. The water content is evaluated on the basis of the 1920 nm and 1450 nm absorption bands. The EFD system consists of a resonant probe connected to a network analyzer. The resonance frequency of the cavity under different moisture-content conditions of frescos is in the 1.0-1.5 GHz range. The device makes it possible to compute, in real time, the moisture content from a measurement of the transmission coefficient (amplitude vs frequency) through the probe. Fresco mock-ups have been prepared in collaboration with the Opificio delle Pietre Dure *in order to recreate most of the possible chromatic shades obtained by mixing iron oxides and hydroxide-based pigments. Measurement were performed by employing both techniques on fresco models after wet-dry cycles obtained by means of poultices with a known water content. The results obtained with these two techniques were compared, and cross relationships between the EFD and FORS data were defined.*

Keywords: NIR, FORS, microwave, EFD, water content, frescos

1 INTRODUCTION

The detection of water content in wall paintings is a critical aspect of their conservation. Within the sector of wall paintings, frescos (*buon fresco*) were painted directly on a wet plastered wall using powdered pigments mixed with water. The late medieval and renaissance periods were characterized by this type of artistic production, particularly in central Italy.

Water diffusion is one the major causes of the decay phenomena observed in wall paintings. Different analytical techniques have characterized the evaluation of chemical and physical parameters related, directly or indirectly, to the moisture content of a given wall and plaster in order to study the interactions between water and the component material of frescos [1]-[6]. The presence of excessive humidity, followed by cycles of dryness, leads to mechanical stress on surfaces and salt crystallization, followed by the detachment of materials. The early detection of the presence of water in the first layers of the painting and just below these is therefore essential in order to avoid and prevent this kind of damage.

In this paper non-invasive techniques based on methodologies in the microwave and near-IR regions are described as strategic tools for measuring the moisture content in frescos. The proposed microwave system, which is based on the Evanescent Field Dielectrometry (EFD), performs a sub-surface measurement with an investigated depth of up to 2 cm. The measurement system uses a special probe that contacts the surface of the material under investigation without damaging it. The probe has a coaxial geometry that consists of an open resonant cavity (an evanescent-field resonator) equipped with a spring device for adapting the probe contact to the surface of the material. The effectiveness and reliability of the method have been validated by means of measurements performed on some reference materials with known dielectric characteristics and thanks to several tests on moistened plaster samples. In situ investigations on several frescos have been carried out using this method, and have proved the usefulness of the approach as a diagnostic tool for investigating the conservation status of frescos and wall paintings ([7], [8]).

Fiber optic reflectance spectroscopy (FORS) in the ultraviolet (UV), visible (Vis) and near infrared (NIR) regions is a non-invasive methodology and a useful technique for analyzing works of art ([10][11]). FORS is used primarily to identify pigments and dyes, to evaluate color and color changes, and to detect alteration products. Electronic and vibrational transitions can be observed in the UV-Vis-NIR spectral range. In the latter case, the transitions are multiple or combinations of vibrational transitions that are commonly detected in the mid-IR. In particular, the 1350-1600 nm and 1750-2000 nm regions show spectroscopic features that are produced by vibrational overtones and combination bands of water and its associated rotational fine structures, respectively. When it is adsorbed in the wall or condensed on its surface, water in liquid phase generates broad and unstructured bands that are due to overtones ($2\nu_3$) and to combinations ($\nu_2 + \nu_3$) of the H_2O fundamental vibrational modes [4].

The depth of penetration of the radiation into painted layers is related to several factors, and depends on the material's chemical composition, refractive index, density and particle size, as well as on the wavelength of the radiation used in the analysis. Hence, in the UV region the depth of penetration into the paint layers can be of a few microns, while in the NIR region it can easily reach one hundred microns. In addition, by moving into the microwave region the penetration can be of a sub-superficial level (a few cm). This means that the combination of the two techniques, FORS and EFD, make it possible to investigate a discrete depth of the wall, and is found to be of great help in the preservation of fresco paintings.

Specifically, EFD and FORS are useful for: (1) periodically monitoring the conditions of frescos, and wall paintings in general; (2) early diagnostics, which thus contributes to the detection of in-depth humidity and/or salts; and (3) providing information on the absorption dynamics of water (or water-based products, carbonation phenomena) in the areas to be treated, during and after restoration interventions.

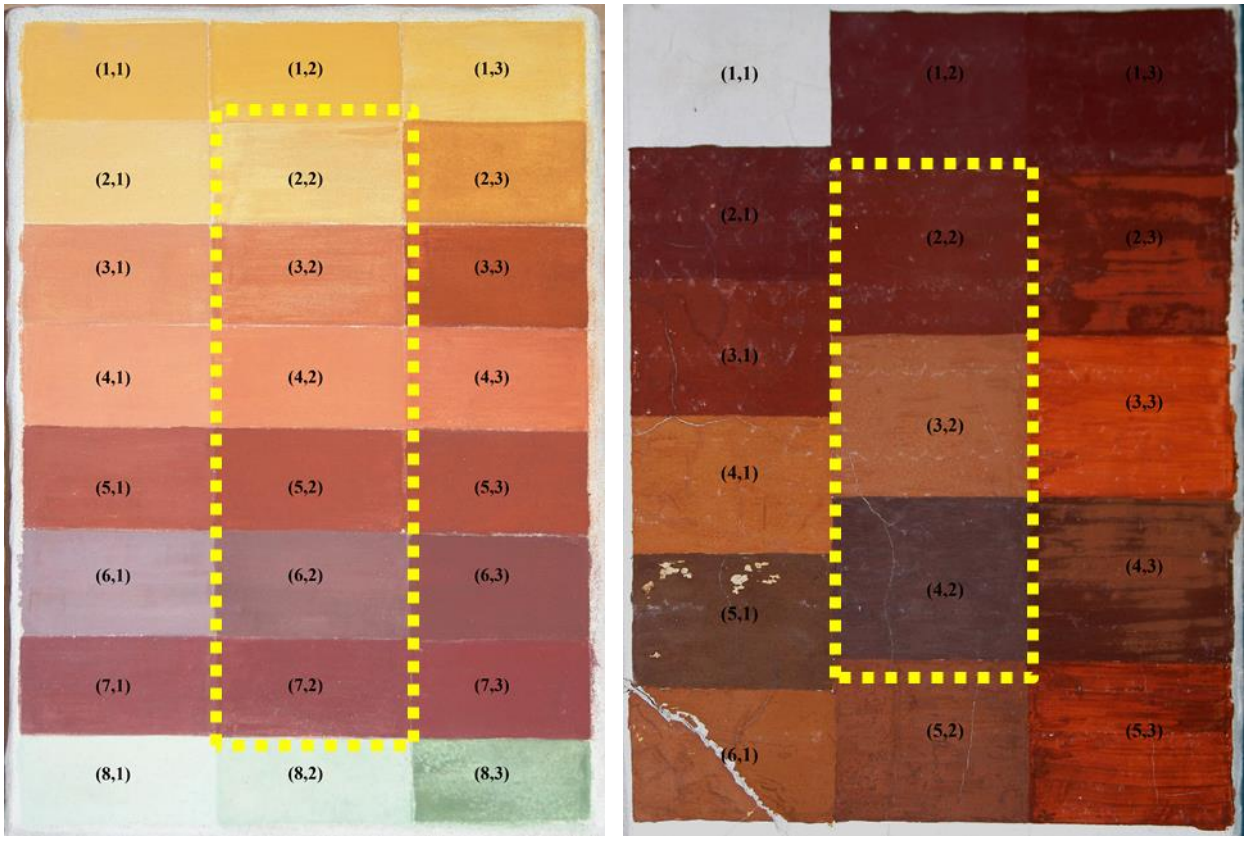
2 MATERIAL AND METHODS

2.1 Mock-up preparation

In collaboration with the *Opificio delle Pietre Dure* (OPD) in Florence, two fresco mock-ups were prepared using several iron oxides and hydroxide-based pigments that were characteristic of a traditional medieval and renaissance palette.

Historical models were prepared following traditional recipes and artists' techniques typically used to paint frescos.

The surface of the board was divided into cells, each one consisting of a different mixture of pigments. Panel 1, which is shown in Figure 1a, was prepared using iron-based pigments. These were spread both in pure form and mixed with San Giovanni white ($CaCO_3$) in ratios of 1:1 and 2:1.
Panel 2 (Fig. 1b) was prepared using binary and ternary mixtures of pigments so as to recreate most of the possible chromatic shades. In particular, for binary mixtures, iron-based pigments were mixed in a ratio of 1:1, with natural Sienna earth pigments first, and then with green earth pigment. Instead, the ternary mixtures were prepared by mixing iron-based pigments in a ratio of 1:1:1 with both natural Sienna earth and green earth pigments.



(a) (b)

Fig. 1: *a) Panel 1 - Mock-up fresco made by spreading the iron-based pigments both pure and mixed with San Giovanni white; b) Panel 2 - Mock-up frescos with binary and ternary mixtures prepared by mixing iron-based pigments with both natural Sienna earth and green earth pigments. The highlighted rectangles delimit the external and central areas*

The pigments used to prepare the fresco panel are listed in Table 1. They include natural earths and ochres consisting of iron oxides and hydroxides commonly used in historic wall paintings. The materials were purchased from specialized dealers and were analyzed preliminarily by means of UV-Vis-NIR FORS, Fourier transform infrared spectroscopy (FT-IR), and powder X-Ray Diffraction (PXRD), in order to characterize their chemical composition and the crystalline phases present.

Table 1*: Pigments used for the production of the historic fresco mock-ups.*

PIGMENT	COMPANY	CHEMICAL COMPOSITION
Yellow ochre	Bizzarri	Iron hydroxide [goethite α-FeO(OH)], bound to a matrix made

		up of quartz, calcite and clay minerals
Natural Sienna earth	Zecchi	From 45 to 70% of iron hydroxide, [goethite α-FeO(OH)], 0,1-1% of manganese oxides (MnO_2, MnO), alluminosilicates [Kaolin $Al_2Si_2O_5(OH)_4$]
Burnt Sienna earth	Zecchi	Calcination of natural Sienna earth at a temperature higher than 200 °C
Red ochre	Zecchi	Iron oxide [hematite, α-Fe_2O_3] bound to a matrix made up of clay minerals, quartz and calcite.
Hematite	Zecchi	Iron oxide [Hematite α-Fe_2O_3]
Caput mortum	Zecchi	Hematite (α-Fe_2O_3) bound to a matrix made up of clay minerals, quartz and calcite, with impurities of Zn, Cu, Mn e Al.
Morellone	Zecchi	Hematite, iron oxide [Hematite α-Fe_2O_3]
Green earth	Zecchi	Iron, potassium, manganese and aluminum silicates and iron oxide.

The EFD and FORS measurements were performed on the panels a few years after their preparation. Five sets of measurements (from T0 to T4) were performed, starting from room temperature conditions (T0) and then by subjecting both panels to a cycle of wetting and drying as follows:

- T0: Measurements on the surface at ambient conditions (23°C and 65% RH);
- T1: Measurements after removal of the poultice. The poultice, consisting of Arbocel® BC 200 and distilled water, was applied for two days to the surface of both panels. The poultices were spread over a sheet of Japanese paper and covered by means of plastic wrap to help the water adsorption and to slow down the water evaporation;
- T2: Measurements 24 hours after removal of the poultice;
- T3: Measurements 5 days after removal of the poultice;
- T4: Measurements 3 weeks after removal of the poultice.

Three EFD and FORS measurements were performed on each cell of the panels, and the average data were reported.
The experimental techniques are described in the following sections.

2.2 Evanescent Field Dielectrometry (EFD) system

Since water is a strongly polar material in comparison to mortar, which is weakly polar, the contrast between the permittivity of water (ε'~80) and that of mortar (ε' ~ 5 to 15) can be derived by means of dielectric spectroscopy.
The EFD system was designed to obtain such measurements. It is composed of a resonant coaxial probe developed for the measurement of solid materials and operating in the microwave domain (1-1.5 GHz), a Scalar Network Analyzer (SNA), and a computer equipped with a dedicated numerical code (Fig. 2a). The probe consists of a microstrip cavity connected to an open-coaxial probe that is put in contact with the surface of the investigated material. The resonant probe can be modelled by means of the equivalent circuit in Figure 2b.
The measuring lines are loosely coupled to the microstrip resonant line. The C_M capacitor represents the termination capacitance related to the probe loaded by the material under test (MUT). The transmission between the two measuring lines, which corresponds to the scattering parameter (S_{21}), is the measured quantity. The values of the resonant frequency (f_r) and of the quality factor (Q), being the latter inversely proportional to the width of the transmission parameter S_{21}, are useful for investigating the moisture content.

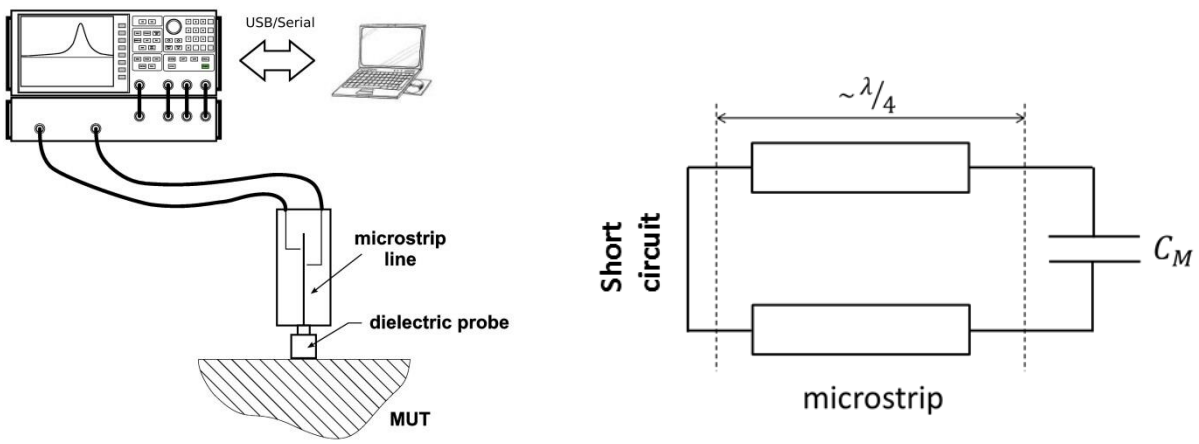


Fig. 2: *(a) Basic scheme of the EFD system. (b) The equivalent circuit of the resonant cavity probe.*

Δf_r and Q were calculated in accordance with the following equation:

$$\Delta f_r = \frac{f_0 - f_r}{f_0} \qquad Q = \frac{f_r}{B} \tag{1}$$

where f_0 is the resonance frequency for the unloaded probe and B is the bandwidth at -3 dB with respect to the resonant peak.

The previous parameters are related to the dielectric constant (ε') and to the dielectric losses (ε'') of the material under investigation.

The moisture content can be defined as the ratio between the mass of water m_W and the weight of the moistened material M.

$$\mathrm{MC} = \frac{m_W}{\mathrm{M}} \tag{2}$$

The above MC definition is "on a wet basis". A different definition, "on a dry basis", uses the dry weight M_d instead of the current weight M, and is directly related to the former.

The existence of a relation between MC and the complex permittivity of hygroscopic materials is well known [12]-[14]. Although a rigorous quantitative relation between them is currently unavailable, the MC value is usually related to a function of the dielectric constant and of the loss factor. By defining such a ψ function, as follows [14]:

$$\Psi = \frac{\varepsilon' - 1}{\varepsilon''} \tag{3}$$

the measured moisture content becomes a function of MC(ψ).

The ψ function is not independent of the density of the material, and therefore the measurement required a specific calibration for the particular category of material under investigation. The categories of materials for which the calibration already exists are those of plaster, marble, sandstone, limestone and cement.

The relation between MC and dielectric properties could also be found by using the electric parameters Δf_r and Q. This made possible a non-destructive and reliable measurement of MC by means of the EFD system, because a change in the dielectric constant and/or in the dielectric losses of the material facing the resonant probe results in a change in f_r and Q. This relationship was determined by solving the imposition of the resonant condition for the equivalent circuit in Fig 2b (see [1]).

The resonant condition for the circuit in Fig 2b is:

$$\mathrm{Z_0}\ \tan(\beta \mathrm{L}) = \frac{1}{2\pi \mathrm{f_r}\ \mathrm{Re}\{\mathrm{C_M}\}} \tag{4}$$

where Z_0 and β are, respectively, the characteristic impedance and the propagation constant of the microstrip line, and L is the equivalent length of the transmission line without the terminal capacitance.
The function Ψ was determined by the computation of C_M through the solution of the electromagnetic problem of the coaxial probe facing a semi-infinite material [1].

$$\Psi = \frac{f_r}{f_{r0} - f_r} \frac{\epsilon' - 1}{2\epsilon'} \left(\frac{Q Q_0}{Q_0 - Q} \right) \quad (5)$$

The above formulation made it possible to compute parameter Ψ in real time without any need for inverting equation (3). The moisture content (MC) in the investigated material was then related to the function Ψ in accordance with the following simplified equation:

$$MC(\Psi) = \alpha \frac{1}{\Psi} + \beta \quad (6)$$

The constants α and β were obtained by means of dielectric measurements in two different moisture contents: under dry conditions and in saturated conditions.
The accuracy of the measurement performed using the EFD system on several reference samples of plaster conditioned at different moisture content levels was of +/-1%.
With the present probe geometry, the region considered by the measurement was approximately semispherical within the material and had a radius of 2 cm, and the measurable moisture content ranged between 0 and 20% (water mass fraction).
EFD measurements were acquired on both mock-ups by performing three measurements for each cell, in order to reduce eventual errors due to the inhomogeneity of the material.

2.3 FORS (Fiber Optics Reflectance Spectroscopy)

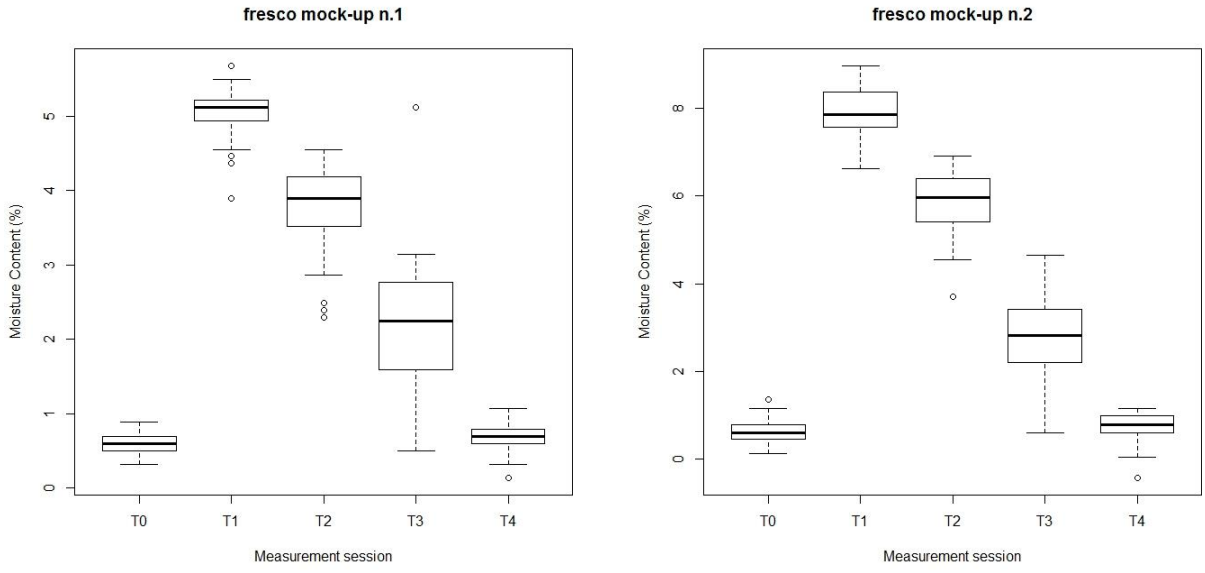
FORS measurements in the 350-2200 nm range were performed using two single-beam Zeiss spectroanalyzers, model MC601 (190-1015 nm range) and model MC611 NIR 2.2WR (910-2200 nm range), housed together in a compact and portable chassis for in situ analyses. The data acquisition step was 0.8 nm/pixel for the 1024-element silicon photodiode array detector (MCS601), and 6.0 nm/pixel for the 256-element InGaAs diode array detector (MCS611 NIR 2.2 WR). The radiation between 320 nm and 2700 nm, which was provided by a voltage-stabilized 20W halogen lamp (module Model CLH600), was conveyed to the sample by means of an anhydrous quartz optical-fiber bundle that also transported the reflected radiation to the detectors. The backscattered radiation, in fact, was collected using fiber optics, and was first directed onto the dispersive elements (gratings) and subsequently onto the detectors. The fiber optic bundles consisted of two extended coaxial cylinders: the inner one ("core") had a high refractive index, while the exterior one ("cladding") had a lower refractive index. Radiation was reflected through the fiber optics because of the difference in the refractive indexes. For the sake of protection, the optical fibers were usually coated with a jacket made of a non-optical material, such as metal or plastic.
The geometric measurement of the probe-head was 0°/45°/45° (0° radiation sent to the surface and 45° the back-scattered radiation from the surface that was sent to both spectroanalyzers). This configuration made it possible to work in diffuse reflectance by collecting the radiation scattered at 45° with respect to the incident light, thus avoiding specular reflected radiation. The latter was the radiation that was reflected without interacting with the bulk of the material analyzed, and so did not carry any information on the chemical composition of the investigated area. Calibration was performed by means of a 99% Spectralon® diffuse reflectance standard. The reflectance spectrum of the analyzed surface (paint) is reported as the percentage of reflected radiation versus the wavelength. Three measurements were acquired for each cell of the panel, so as to obtain average information about the distribution of the water over the cell area. Each measurement was the average of three acquisitions, in order to increase the signal-to-noise ratio.
As previously reported, UV-Vis-NIR FORS in the cultural heritage field is primarily used to identify pigments and dyes, evaluate color and color changes, and to detect alteration in products. In some cases, it may be necessary to integrate other analytical techniques. However, in conjunction with other techniques,

FORS can also be a very useful tool for locating areas for micro-sampling, or in extending local data from micro-analyses to a broader scale, thus reducing the extent of the micro-sampling.

Fig. 3: *FORS measurements on mock-up.*

3. RESULTS AND DISCUSSION

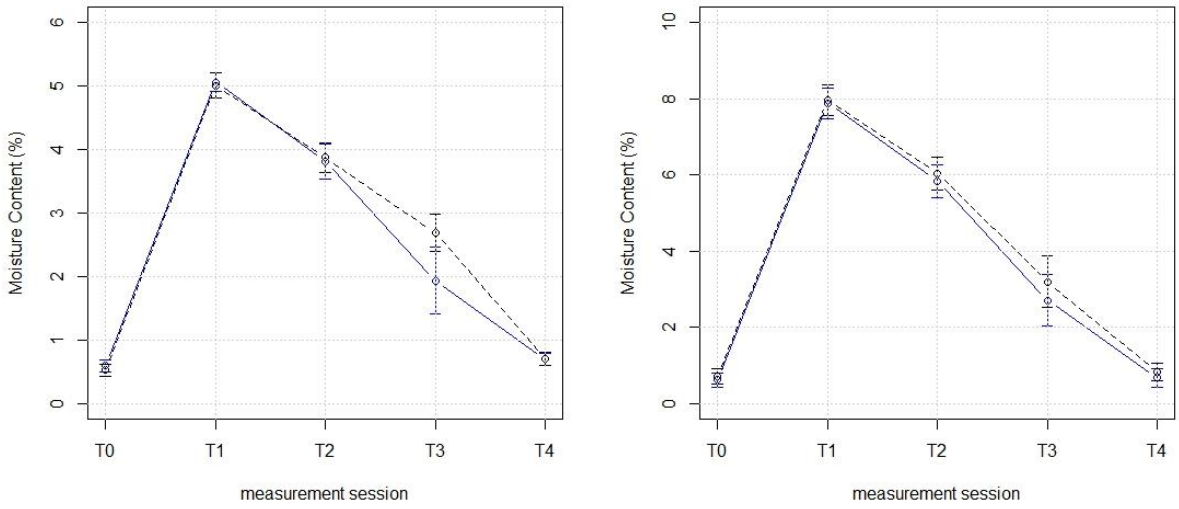
The measurements were performed under environmental conditions (23°C and 65% RH) before the mock-ups were wetted (T0) and at other times (T1-4) after the poultice had been removed.
It should be noted that, even if some uncertainties existed regarding the cells prepared with pigments that showed impurities in the metals (see Table 1), the EFD results obtained in terms of MC were not affected by the type of pigment mixtures.
The boxplots for the EFD results obtained on both fresco mock-ups are shown in Figure 4. Panel 2 appears to be wetter than Panel 1, but the MC values returned to their initial levels for both panels 3 weeks after removal of the poultice (T4). The higher values of MC for Panels 2 could possibly be related to a difference in porosity. The data dispersion was higher at times T2 and T3 with respect to times T0 and T4, because the conditions were not in equilibrium with the environment.



(a) (b)

Fig. 4: *Boxplot of MC measurements performed at different times on panel 1 (a) and on panel 2 (b)*

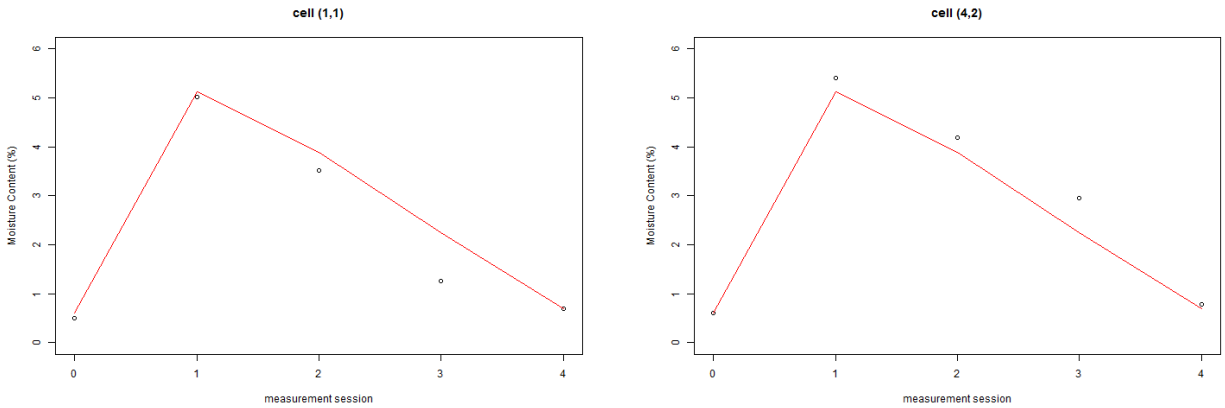
Figure 5 shows the MC differences between mean values in the measurements performed on perimetral cells and internal cells (external and internal to the frame in fig.1a, b) related also to the standard deviation. This strong variation, visible at time T3, was due to a different drying pattern at the center and at the edges. This difference was related to the larger size of the evaporation surface on the outside than the inside areas.



(a) (b)

Fig. 5*: Average MC values (with error bar) measured on the external cells (solid line) versus the average MC values (with error bar) measured in the central cells (dotted line). (a) fresco mock-up 1, and (b) fresco mock-up 2.*

In particular, this dissimilarity could be confirmed by comparing the results obtained on mock-up 1 for the cell (1,1) on the top-left edge with the results for the cell (4,2) at the center of the panel. In Fig. 6a it can be seen how the MC results for T2 and T3 were lower than those for the reference line of the average MC obtained for mock-up 1. On the contrary, in Figure 6b the MC values for the cell (4,2) exceeded the reference line, thus demonstrating the edge effect in the evaporation process. A similar behavior was verified in mock-up 2, while no correlation was found with the pigments.



(a) *(b)*

***Fig. 6**: MC values measured on the single cell (°) versus the mean values of MC (solid red line) obtained for fresco mock-up 1.*

Within the spectral region from 1200 to 2200 nm, the water had specific absorption bands, as shown in Figure 7 at 1900 nm, due to the combination of stretching and deformation vibration bands for H_2O, and a second one at 1450 nm related to the first overtone of the OH stretching vibration bands [3], [4], [6], [15]-[17].

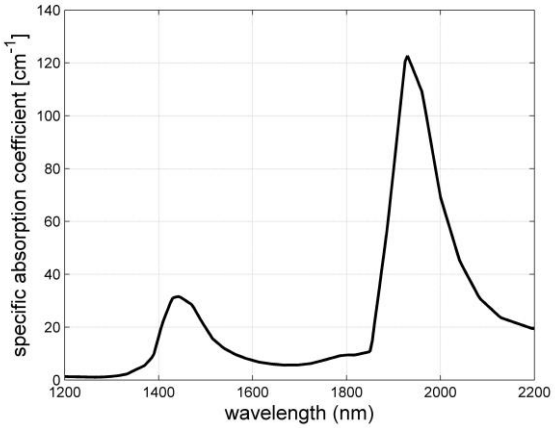
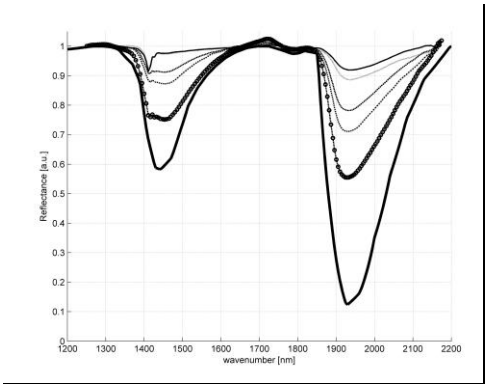


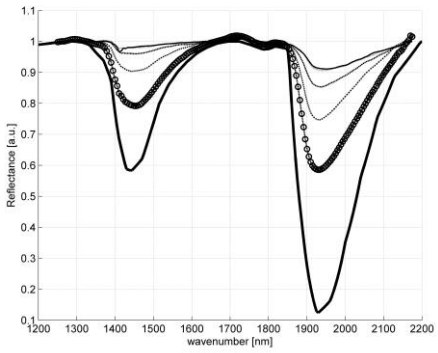
***Fig. 7**: Specific absorption coefficient of water from K.F. Palmer, 1974 [18].*

Figure 8 includes FORS spectra in the same spectral range measured under ambient conditions (T0) and at different moisture-content levels (T1-4), compared with the spectrum of pure water from Palmer, 1974 [18] shown in fig.7, elaborated and plotted in reflectance mode. Spectra on the dry fresco showed a sharp and intense band at around 1415 nm, due to the presence of $Ca(OH)_2$ that had not been completely transformed into $CaCO_3$. However, the presence of this absorption band may have had only a slight effect on the results.

Reflectance spectra are presented in order to illustrate the variation in the NIR spectra during wetting in mock-ups. The spectra in figure 8 demonstrate that the intensity and shape of the hydration bands were modified as a function of the sample moisture content. As expected, reflectance spectra measured under environmental conditions contained weaker features at ~1450 nm and ~1950 nm than did spectra recorded under moist conditions.



(a)



(b)

***Fig. 8**: NIR reflectance spectra acquired in the 1200-2200 nm range on cell (1,1) in (a) and on cell (4,2) in (b) at different times. The (—) solid line stands for T0; the (-o-) solid line with marker stands for T1; the (-.-) dashed and dotted line stands for T2; the (--) dashed line stands for T3, and the (...) dotted line, for the T4, thicker solid line for pure water (—) elaborated from K.F. Palmer, 1974 [18].*

The EFD and FORS results were compared with each other. The EFD values were compared with the ones related to the areal integral of the two bands, at approximately 1450 nm and 1950 nm, respectively, of the FORS spectra.

The results are reported in Table 2 for both mock-ups. In particular, the following was considered: a perimeter cell [cell(1,1) for mock-up 1 and cell(1,3) for mock-up 2] versus a central cell [cell (4,2)] for fresco mock-up 1 and cell(3,2) for fresco mock-up 2. The column labelled "ratio" refers to the ratio between the integral on bands 2 (1621-2181 nm) and 1 (1320-1650 nm). The ratio was not constant, even if it seemed that, for higher moisture concentrations in the mock-ups as defined by EFD, the FORS Band2/Band1 integral ratios showed values that were lower than 3.2, while lower moisture-concentration levels corresponded to integral FORS Band2/Band1 ratio values that were often greater than 3.4, apart from several data for cell(1,1) in mock-up 1. These FORS values could possibly have been due to the fact that most of the water absorbed on the inner surface of the fresco mock-ups was concentrated in the first tens of microns from the surface of the samples. Indeed, FORS Band 1 should have been associated approximately with the more external part of the thickness of the samples than FORS Band 2 was. The latter, which was at higher wavelengths than the former, may have penetrated more deeply into the sample stratigraphy, thus resulting in a relatively less intense band than Band 1.

***Table 2**: Comparison between the MC obtained using the EFD system and the integrals of band 1 (1320-1650 nm) and band 2 (1621-2181 nm) in the FORS spectra.*

Fresco mock-up 1							
Cell(1,1)				Cell(4,2)			
MC	Band 1	Band 2	Ratio	MC	Band 1	Band 2	Ratio
0,5	5,1	12,5	2,5	0,6	2,7	16,3	6,0
4,6	41,0	93,1	2,3	5,4	32,6	83,7	2,6
2,4	18,9	54,3	2,9	4,2	13,6	43,1	3,2
0,8	13,2	37,7	2,9	2,9	5,6	25,3	4,5
0,69	4,57	20,13	4,40	0,79	2,96	16,82	5,68

Fresco mock-up 2							
Cell(1,3)				Cell(3,2)			
MC	Band 1	Band 2	Ratio	MC	Band 1	Band 2	Ratio
0,69	3,42	15,55	4,55	0,69	6,17	20,98	3,40
8,7	18,49	57,14	3,09	8,13	43,05	105,06	2,44
5,87	16,56	47,49	2,87	6,06	28,86	79,47	2,75
2,48	7,98	33,62	4,21	3,42	13,11	44,49	3,39
0,88	4,79	20,71	4,32	0,98	7,08	25,64	3,62

The values of the integral calculated for each band versus the MC obtained using EFD for the same cells of Table 2 are plotted in Figure 9. A linear regression was applied to the data acquired for each cell. The measurements under the initial conditions (ambient conditions, T0) and in the wetted state (T1) were not affected by the non-uniform distribution of water, because it was assumed that there was no water gradient from the surface toward the interior. On the other hand, at T1 and T2, the effects of the deeper water influenced the EFD response, and the MC value was higher than the expected spectral integral value, because the FORS measurements could reach approximately one hundred microns in depth within the material and were limited to the surface if compared with the EFD measurement.

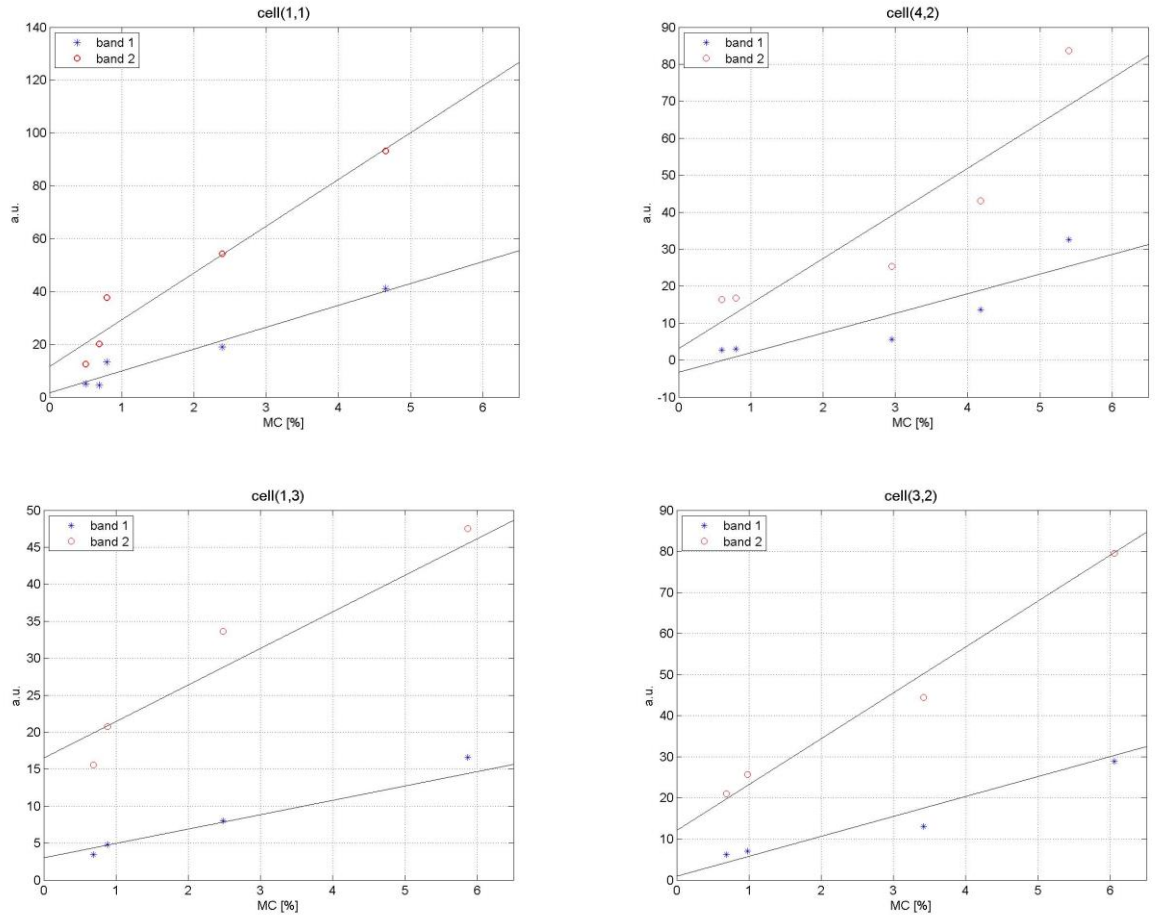


Fig. 9*: Plots of the results of the linear regression between the integral, calculated for each band, and the MC determined using the EFD method.*

CONCLUSIONS

This work is focused on an investigation of the adsorption mechanism of water in wall painting and on an evaluation of the water adsorbed from a surface by different techniques, namely EFD and FORS. The former made it possible to obtain information on the moisture content on a volume inside the material, while with the latter it was possible to focus the measurement on the surface, down to a depth of approximately one hundred microns.

Tests were performed on fresco mock-ups prepared by spreading iron-based pigments in binary and ternary mixtures in order to recreate some of the possible chromatic hues obtainable by mixing iron oxide- and hydroxide-based pigments.
Measurements by means of the EFD method in the microwave range and FORS in the NIR were performed under ambient conditions and after wet-dry cycles involving poultices having a known water content. Data were acquired five different times under different conditions.
The data processing acquired each time made it possible to observe that the peak values in the reflectance spectra related to the bands of adsorbed water increased as the water contribution increased. This result was expected, but can also be used as a piece of strategic information in combination with the result of the EFD measurements relative to an assessment of water distribution in a given material, in particular on wall painting, by using a non-invasive methodological approach. By combining the aforementioned techniques, it is possible to understand, for example, whether the presence of humidity in the wall is caused by internal water circulation (rising dampness, capillarity, some sort of infiltration) or whether, on the other hand, the moisture is due to environmental condition (condensation phenomena on the surface), thus distinguishing the results obtained in relation to the depth of the investigation measurement method.

Further aspects of this study could be the application of both systems to mock-ups prepared with different pigments, in order to assess the efficacy of the methods and to confirm the data acquired in this study.

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Investigation on water content in fresco mock-ups in the microwave and near-IR spectral regions

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ABSTRACT

Water diffusion inside masonry is responsible for the majority of the decay phenomena observed in wall paintings and frescos. Thus, the diagnostics of moisture and water content and their monitoring represent a key issue. In order to preserve the integrity of surfaces of artistic interest, investigations by means of non-destructive techniques (NDT) are preferred over others. The aim of this research is to determine methodologies to quantify the moisture content of frescos by means of the integrated use of two non-invasive techniques, namely Fiber Optic Reflectance Spectroscopy (FORS) in the near-IR region and Evanescent Field Dielectrometry (EFD) in the microwave range. The FORS technique has been employed in order to assess the amount of water adsorbed from the surface by means of an analysis of the reflectance spectra in the Vis-NIR (350-2200nm) range. This technique investigates the electronic and vibrational transitions that are characteristic of each compound and enables their identification. The water content is evaluated on the basis of the 1920 nm and 1450 nm absorption bands. The EFD system consists of a resonant probe connected to a network analyzer. The resonance frequency of the cavity under different moisture-content conditions of frescos is in the 1.0-1.5 GHz range. The device makes it possible to compute, in real time, the moisture content from a measurement of the transmission coefficient (amplitude vs frequency) through the probe. Fresco mock-ups have been prepared in collaboration with the Opificio delle Pietre Dure *in order to recreate most of the possible chromatic shades obtained by mixing iron oxides and hydroxide-based pigments. Measurement were performed by employing both techniques on fresco models after wet-dry cycles obtained by means of poultices with a known water content. The results obtained with these two techniques were compared, and cross relationships between the EFD and FORS data were defined.*

Keywords: NIR, FORS, microwave, EFD, water content, frescos

1 INTRODUCTION

The detection of water content in wall paintings is a critical aspect of their conservation. Within the sector of wall paintings, frescos (*buon fresco*) were painted directly on a wet plastered wall using powdered pigments mixed with water. The late medieval and renaissance periods were characterized by this type of artistic production, particularly in central Italy.

Water diffusion is one the major causes of the decay phenomena observed in wall paintings. Different analytical techniques have characterized the evaluation of chemical and physical parameters related, directly or indirectly, to the moisture content of a given wall and plaster in order to study the interactions between water and the component material of frescos [1]-[6]. The presence of excessive humidity, followed by cycles of dryness, leads to mechanical stress on surfaces and salt crystallization, followed by the detachment of materials. The early detection of the presence of water in the first layers of the painting and just below these is therefore essential in order to avoid and prevent this kind of damage.

In this paper non-invasive techniques based on methodologies in the microwave and near-IR regions are described as strategic tools for measuring the moisture content in frescos. The proposed microwave system, which is based on the Evanescent Field Dielectrometry (EFD), performs a sub-surface measurement with an investigated depth of up to 2 cm. The measurement system uses a special probe that contacts the surface of the material under investigation without damaging it. The probe has a coaxial geometry that consists of an open resonant cavity (an evanescent-field resonator) equipped with a spring device for adapting the probe contact to the surface of the material. The effectiveness and reliability of the method have been validated by means of measurements performed on some reference materials with known dielectric characteristics and thanks to several tests on moistened plaster samples. In situ investigations on several frescos have been carried out using this method, and have proved the usefulness of the approach as a diagnostic tool for investigating the conservation status of frescos and wall paintings ([7], [8]).

Fiber optic reflectance spectroscopy (FORS) in the ultraviolet (UV), visible (Vis) and near infrared (NIR) regions is a non-invasive methodology and a useful technique for analyzing works of art ([10][11]). FORS is used primarily to identify pigments and dyes, to evaluate color and color changes, and to detect alteration products. Electronic and vibrational transitions can be observed in the UV-Vis-NIR spectral range. In the latter case, the transitions are multiple or combinations of vibrational transitions that are commonly detected in the mid-IR. In particular, the 1350-1600 nm and 1750-2000 nm regions show spectroscopic features that are produced by vibrational overtones and combination bands of water and its associated rotational fine structures, respectively. When it is adsorbed in the wall or condensed on its surface, water in liquid phase generates broad and unstructured bands that are due to overtones ($2\nu_3$) and to combinations ($\nu_2 + \nu_3$) of the H_2O fundamental vibrational modes [4].

The depth of penetration of the radiation into painted layers is related to several factors, and depends on the material's chemical composition, refractive index, density and particle size, as well as on the wavelength of the radiation used in the analysis. Hence, in the UV region the depth of penetration into the paint layers can be of a few microns, while in the NIR region it can easily reach one hundred microns. In addition, by moving into the microwave region the penetration can be of a sub-superficial level (a few cm). This means that the combination of the two techniques, FORS and EFD, make it possible to investigate a discrete depth of the wall, and is found to be of great help in the preservation of fresco paintings.

Specifically, EFD and FORS are useful for: (1) periodically monitoring the conditions of frescos, and wall paintings in general; (2) early diagnostics, which thus contributes to the detection of in-depth humidity and/or salts; and (3) providing information on the absorption dynamics of water (or water-based products, carbonation phenomena) in the areas to be treated, during and after restoration interventions.

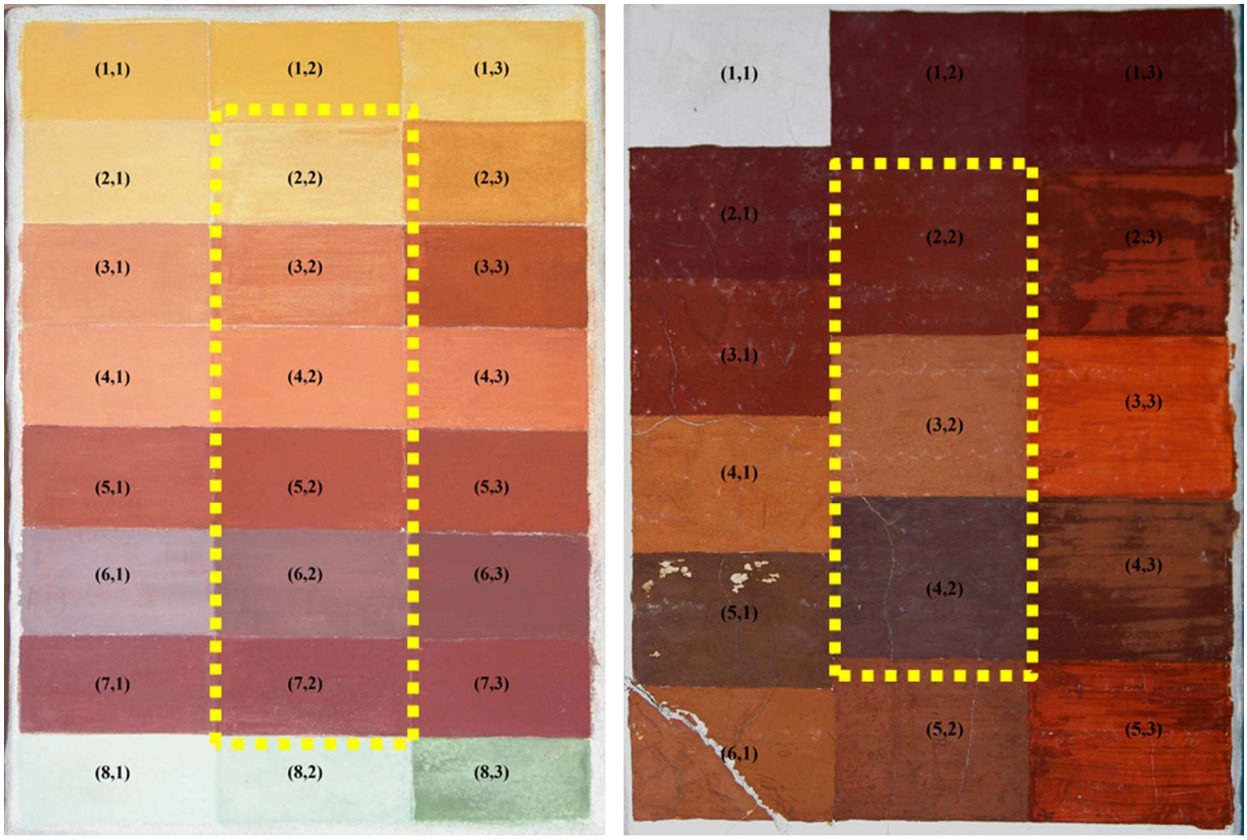
2 MATERIAL AND METHODS

2.1 Mock-up preparation

In collaboration with the *Opificio delle Pietre Dure* (OPD) in Florence, two fresco mock-ups were prepared using several iron oxides and hydroxide-based pigments that were characteristic of a traditional medieval and renaissance palette.

Historical models were prepared following traditional recipes and artists' techniques typically used to paint frescos.

The surface of the board was divided into cells, each one consisting of a different mixture of pigments. Panel 1, which is shown in Figure 1a, was prepared using iron-based pigments. These were spread both in pure form and mixed with San Giovanni white ($CaCO_3$) in ratios of 1:1 and 2:1.
Panel 2 (Fig. 1b) was prepared using binary and ternary mixtures of pigments so as to recreate most of the possible chromatic shades. In particular, for binary mixtures, iron-based pigments were mixed in a ratio of 1:1, with natural Sienna earth pigments first, and then with green earth pigment. Instead, the ternary mixtures were prepared by mixing iron-based pigments in a ratio of 1:1:1 with both natural Sienna earth and green earth pigments.



(a) (b)

Fig. 1: *a) Panel 1 - Mock-up fresco made by spreading the iron-based pigments both pure and mixed with San Giovanni white; b) Panel 2 - Mock-up frescos with binary and ternary mixtures prepared by mixing iron-based pigments with both natural Sienna earth and green earth pigments. The highlighted rectangles delimit the external and central areas*

The pigments used to prepare the fresco panel are listed in Table 1. They include natural earths and ochres consisting of iron oxides and hydroxides commonly used in historic wall paintings. The materials were purchased from specialized dealers and were analyzed preliminarily by means of UV-Vis-NIR FORS, Fourier transform infrared spectroscopy (FT-IR), and powder X-Ray Diffraction (PXRD), in order to characterize their chemical composition and the crystalline phases present.

Table 1*: Pigments used for the production of the historic fresco mock-ups.*

PIGMENT	COMPANY	CHEMICAL COMPOSITION
Yellow ochre	Bizzarri	Iron hydroxide [goethite α-FeO(OH)], bound to a matrix made

		up of quartz, calcite and clay minerals
Natural Sienna earth	Zecchi	From 45 to 70% of iron hydroxide, [goethite α-FeO(OH)], 0,1-1% of manganese oxides (MnO_2, MnO), alluminosilicates [Kaolin $Al_2Si_2O_5(OH)_4$]
Burnt Sienna earth	Zecchi	Calcination of natural Sienna earth at a temperature higher than 200 °C
Red ochre	Zecchi	Iron oxide [hematite, α-Fe_2O_3] bound to a matrix made up of clay minerals, quartz and calcite.
Hematite	Zecchi	Iron oxide [Hematite α-Fe_2O_3]
Caput mortum	Zecchi	Hematite (α-Fe_2O_3) bound to a matrix made up of clay minerals, quartz and calcite, with impurities of Zn, Cu, Mn e Al.
Morellone	Zecchi	Hematite, iron oxide [Hematite α-Fe_2O_3]
Green earth	Zecchi	Iron, potassium, manganese and aluminum silicates and iron oxide.

The EFD and FORS measurements were performed on the panels a few years after their preparation. Five sets of measurements (from T0 to T4) were performed, starting from room temperature conditions (T0) and then by subjecting both panels to a cycle of wetting and drying as follows:

- T0: Measurements on the surface at ambient conditions (23°C and 65% RH);
- T1: Measurements after removal of the poultice. The poultice, consisting of Arbocel® BC 200 and distilled water, was applied for two days to the surface of both panels. The poultices were spread over a sheet of Japanese paper and covered by means of plastic wrap to help the water adsorption and to slow down the water evaporation;
- T2: Measurements 24 hours after removal of the poultice;
- T3: Measurements 5 days after removal of the poultice;
- T4: Measurements 3 weeks after removal of the poultice.

Three EFD and FORS measurements were performed on each cell of the panels, and the average data were reported.
The experimental techniques are described in the following sections.

2.2 Evanescent Field Dielectrometry (EFD) system

Since water is a strongly polar material in comparison to mortar, which is weakly polar, the contrast between the permittivity of water (ε'~80) and that of mortar (ε' ~ 5 to 15) can be derived by means of dielectric spectroscopy.
The EFD system was designed to obtain such measurements. It is composed of a resonant coaxial probe developed for the measurement of solid materials and operating in the microwave domain (1-1.5 GHz), a Scalar Network Analyzer (SNA), and a computer equipped with a dedicated numerical code (Fig. 2a). The probe consists of a microstrip cavity connected to an open-coaxial probe that is put in contact with the surface of the investigated material. The resonant probe can be modelled by means of the equivalent circuit in Figure 2b.
The measuring lines are loosely coupled to the microstrip resonant line. The C_M capacitor represents the termination capacitance related to the probe loaded by the material under test (MUT). The transmission between the two measuring lines, which corresponds to the scattering parameter (S_{21}), is the measured quantity. The values of the resonant frequency (f_r) and of the quality factor (Q), being the latter inversely proportional to the width of the transmission parameter S_{21}, are useful for investigating the moisture content.

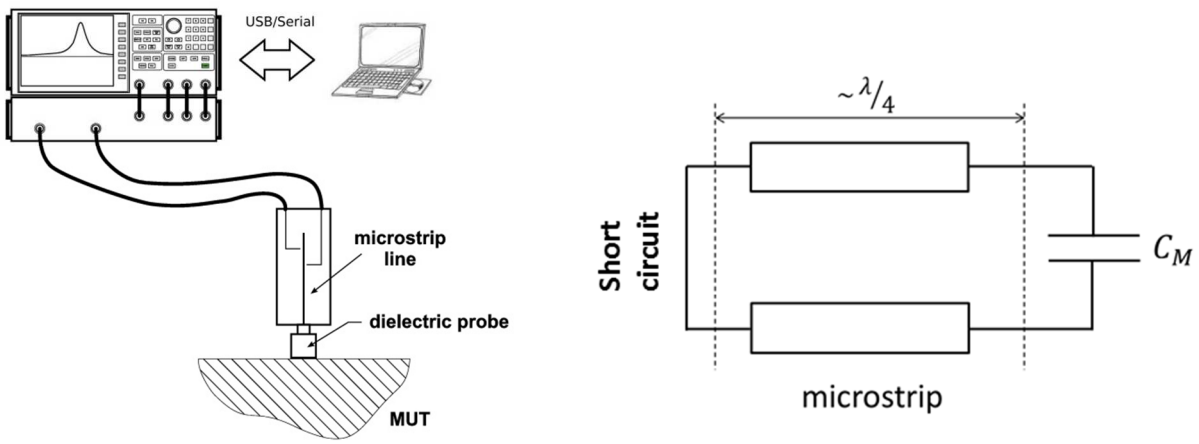


Fig. 2: *(a) Basic scheme of the EFD system. (b) The equivalent circuit of the resonant cavity probe.*

Δf_r and Q were calculated in accordance with the following equation:

$$\Delta f_r = \frac{f_0 - f_r}{f_0} \qquad Q = \frac{f_r}{B} \tag{1}$$

where f_0 is the resonance frequency for the unloaded probe and B is the bandwidth at -3 dB with respect to the resonant peak.

The previous parameters are related to the dielectric constant (ε') and to the dielectric losses (ε'') of the material under investigation.

The moisture content can be defined as the ratio between the mass of water m_W and the weight of the moistened material M.

$$\mathrm{MC} = \frac{m_W}{\mathrm{M}} \tag{2}$$

The above MC definition is "on a wet basis". A different definition, "on a dry basis", uses the dry weight M_d instead of the current weight M, and is directly related to the former.

The existence of a relation between MC and the complex permittivity of hygroscopic materials is well known [12]-[14]. Although a rigorous quantitative relation between them is currently unavailable, the MC value is usually related to a function of the dielectric constant and of the loss factor. By defining such a ψ function, as follows [14]:

$$\Psi = \frac{\varepsilon' - 1}{\varepsilon''} \tag{3}$$

the measured moisture content becomes a function of MC(ψ).

The ψ function is not independent of the density of the material, and therefore the measurement required a specific calibration for the particular category of material under investigation. The categories of materials for which the calibration already exists are those of plaster, marble, sandstone, limestone and cement.

The relation between MC and dielectric properties could also be found by using the electric parameters Δf_r and Q. This made possible a non-destructive and reliable measurement of MC by means of the EFD system, because a change in the dielectric constant and/or in the dielectric losses of the material facing the resonant probe results in a change in f_r and Q. This relationship was determined by solving the imposition of the resonant condition for the equivalent circuit in Fig 2b (see [1]).

The resonant condition for the circuit in Fig 2b is:

$$\mathrm{Z_0}\ \tan(\beta \mathrm{L}) = \frac{1}{2\pi \mathrm{f_r}\ \mathrm{Re}\{\mathrm{C_M}\}} \tag{4}$$

where Z_0 and β are, respectively, the characteristic impedance and the propagation constant of the microstrip line, and L is the equivalent length of the transmission line without the terminal capacitance.
The function Ψ was determined by the computation of C_M through the solution of the electromagnetic problem of the coaxial probe facing a semi-infinite material [1].

$$\Psi = \frac{f_r}{f_{r0} - f_r} \frac{\epsilon' - 1}{2\epsilon'} \left(\frac{Q Q_0}{Q_0 - Q} \right) \quad (5)$$

The above formulation made it possible to compute parameter Ψ in real time without any need for inverting equation (3). The moisture content (MC) in the investigated material was then related to the function Ψ in accordance with the following simplified equation:

$$MC(\Psi) = \alpha \frac{1}{\Psi} + \beta \quad (6)$$

The constants α and β were obtained by means of dielectric measurements in two different moisture contents: under dry conditions and in saturated conditions.
The accuracy of the measurement performed using the EFD system on several reference samples of plaster conditioned at different moisture content levels was of +/-1%.
With the present probe geometry, the region considered by the measurement was approximately semispherical within the material and had a radius of 2 cm, and the measurable moisture content ranged between 0 and 20% (water mass fraction).
EFD measurements were acquired on both mock-ups by performing three measurements for each cell, in order to reduce eventual errors due to the inhomogeneity of the material.

2.3 FORS (Fiber Optics Reflectance Spectroscopy)

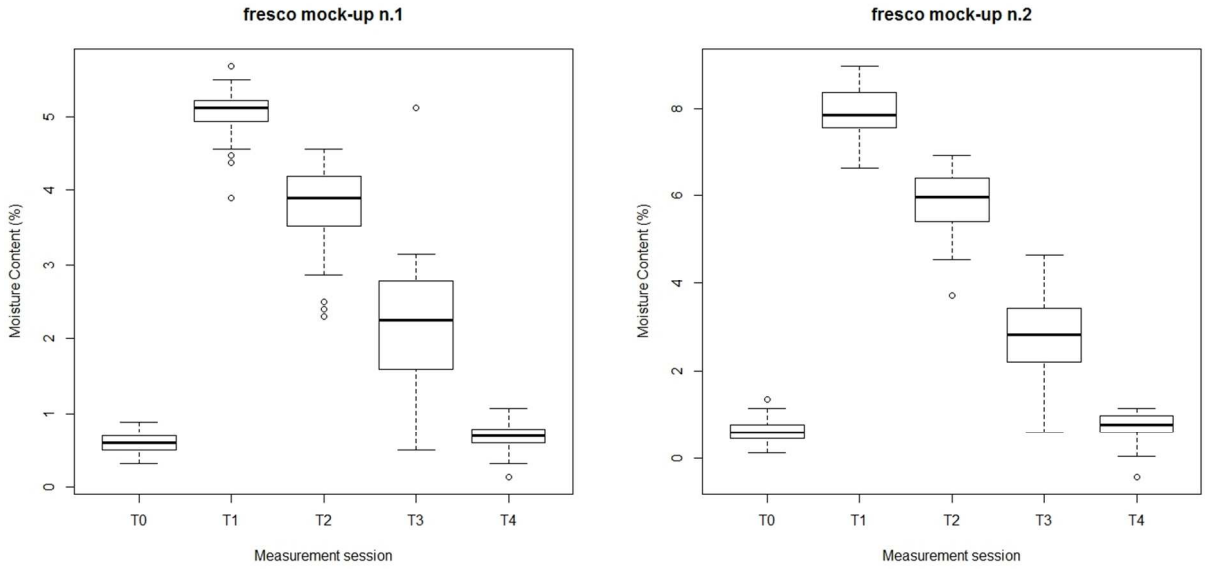
FORS measurements in the 350-2200 nm range were performed using two single-beam Zeiss spectroanalyzers, model MC601 (190-1015 nm range) and model MC611 NIR 2.2WR (910-2200 nm range), housed together in a compact and portable chassis for in situ analyses. The data acquisition step was 0.8 nm/pixel for the 1024-element silicon photodiode array detector (MCS601), and 6.0 nm/pixel for the 256-element InGaAs diode array detector (MCS611 NIR 2.2 WR). The radiation between 320 nm and 2700 nm, which was provided by a voltage-stabilized 20W halogen lamp (module Model CLH600), was conveyed to the sample by means of an anhydrous quartz optical-fiber bundle that also transported the reflected radiation to the detectors. The backscattered radiation, in fact, was collected using fiber optics, and was first directed onto the dispersive elements (gratings) and subsequently onto the detectors. The fiber optic bundles consisted of two extended coaxial cylinders: the inner one ("core") had a high refractive index, while the exterior one ("cladding") had a lower refractive index. Radiation was reflected through the fiber optics because of the difference in the refractive indexes. For the sake of protection, the optical fibers were usually coated with a jacket made of a non-optical material, such as metal or plastic.
The geometric measurement of the probe-head was 0°/45°/45° (0° radiation sent to the surface and 45° the back-scattered radiation from the surface that was sent to both spectroanalyzers). This configuration made it possible to work in diffuse reflectance by collecting the radiation scattered at 45° with respect to the incident light, thus avoiding specular reflected radiation. The latter was the radiation that was reflected without interacting with the bulk of the material analyzed, and so did not carry any information on the chemical composition of the investigated area. Calibration was performed by means of a 99% Spectralon® diffuse reflectance standard. The reflectance spectrum of the analyzed surface (paint) is reported as the percentage of reflected radiation versus the wavelength. Three measurements were acquired for each cell of the panel, so as to obtain average information about the distribution of the water over the cell area. Each measurement was the average of three acquisitions, in order to increase the signal-to-noise ratio.
As previously reported, UV-Vis-NIR FORS in the cultural heritage field is primarily used to identify pigments and dyes, evaluate color and color changes, and to detect alteration in products. In some cases, it may be necessary to integrate other analytical techniques. However, in conjunction with other techniques,

FORS can also be a very useful tool for locating areas for micro-sampling, or in extending local data from micro-analyses to a broader scale, thus reducing the extent of the micro-sampling.

Fig. 3: *FORS measurements on mock-up.*

3. RESULTS AND DISCUSSION

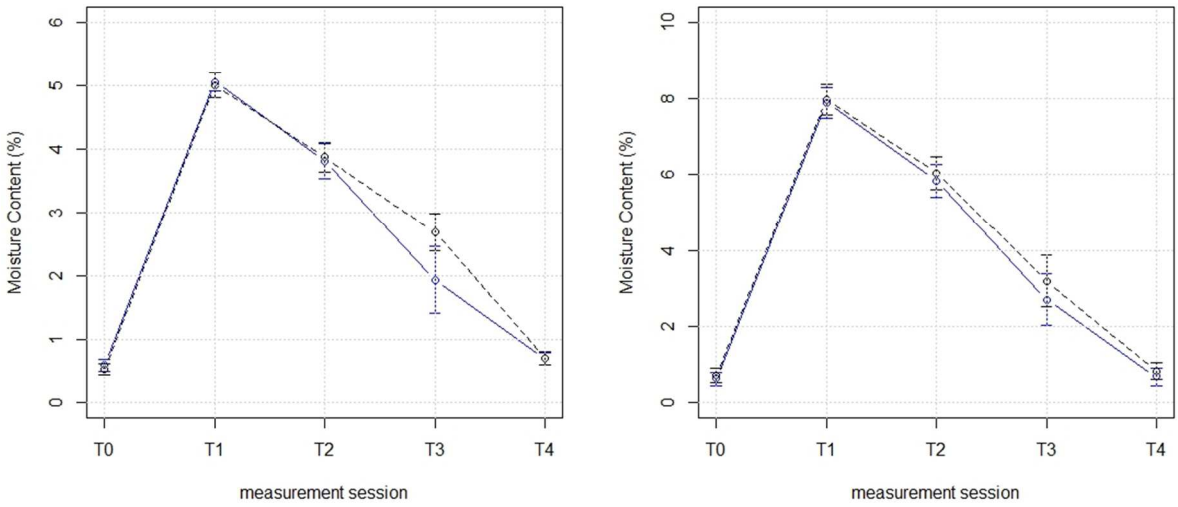
The measurements were performed under environmental conditions (23°C and 65% RH) before the mock-ups were wetted (T0) and at other times (T1-4) after the poultice had been removed.
It should be noted that, even if some uncertainties existed regarding the cells prepared with pigments that showed impurities in the metals (see Table 1), the EFD results obtained in terms of MC were not affected by the type of pigment mixtures.
The boxplots for the EFD results obtained on both fresco mock-ups are shown in Figure 4. Panel 2 appears to be wetter than Panel 1, but the MC values returned to their initial levels for both panels 3 weeks after removal of the poultice (T4). The higher values of MC for Panels 2 could possibly be related to a difference in porosity. The data dispersion was higher at times T2 and T3 with respect to times T0 and T4, because the conditions were not in equilibrium with the environment.



(a) (b)

Fig. 4: *Boxplot of MC measurements performed at different times on panel 1 (a) and on panel 2 (b)*

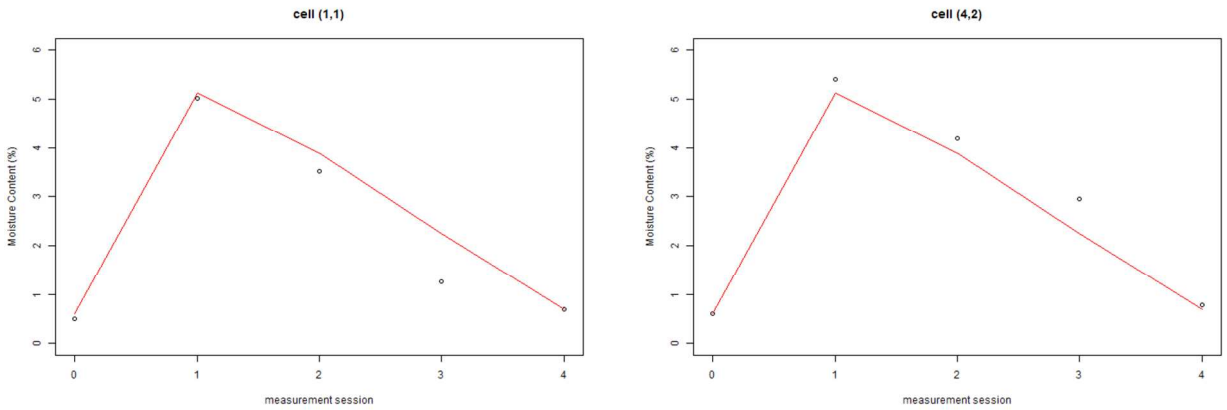
Figure 5 shows the MC differences between mean values in the measurements performed on perimetral cells and internal cells (external and internal to the frame in fig.1a, b) related also to the standard deviation. This strong variation, visible at time T3, was due to a different drying pattern at the center and at the edges. This difference was related to the larger size of the evaporation surface on the outside than the inside areas.



(a) (b)

Fig. 5*: Average MC values (with error bar) measured on the external cells (solid line) versus the average MC values (with error bar) measured in the central cells (dotted line). (a) fresco mock-up 1, and (b) fresco mock-up 2.*

In particular, this dissimilarity could be confirmed by comparing the results obtained on mock-up 1 for the cell (1,1) on the top-left edge with the results for the cell (4,2) at the center of the panel. In Fig. 6a it can be seen how the MC results for T2 and T3 were lower than those for the reference line of the average MC obtained for mock-up 1. On the contrary, in Figure 6b the MC values for the cell (4,2) exceeded the reference line, thus demonstrating the edge effect in the evaporation process. A similar behavior was verified in mock-up 2, while no correlation was found with the pigments.



(a) *(b)*

Fig. 6*: MC values measured on the single cell (°) versus the mean values of MC (solid red line) obtained for fresco mock-up 1.*

Within the spectral region from 1200 to 2200 nm, the water had specific absorption bands, as shown in Figure 7 at 1900 nm, due to the combination of stretching and deformation vibration bands for H_2O, and a second one at 1450 nm related to the first overtone of the OH stretching vibration bands [3], [4], [6], [15]-[17].

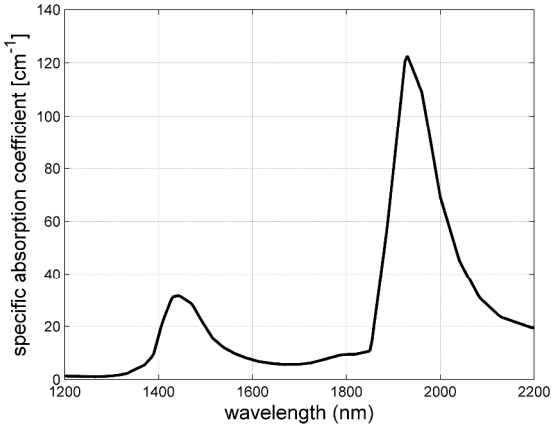
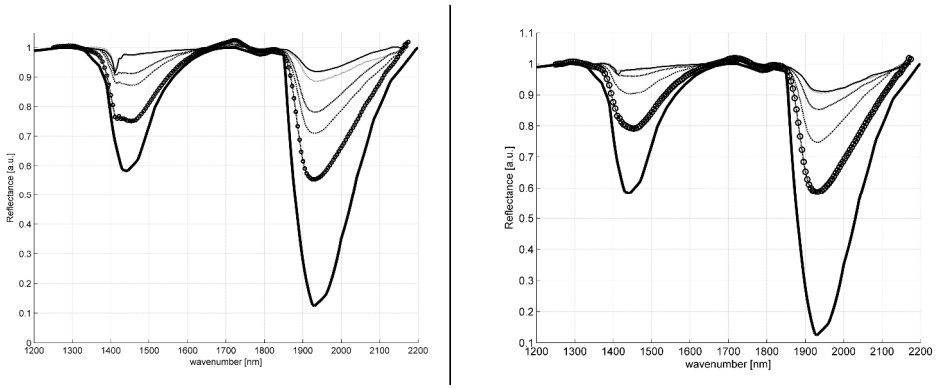


Fig. 7*: Specific absorption coefficient of water from K.F. Palmer, 1974 [18].*

Figure 8 includes FORS spectra in the same spectral range measured under ambient conditions (T0) and at different moisture-content levels (T1-4), compared with the spectrum of pure water from Palmer, 1974 [18] shown in fig.7, elaborated and plotted in reflectance mode. Spectra on the dry fresco showed a sharp and intense band at around 1415 nm, due to the presence of $Ca(OH)_2$ that had not been completely transformed into $CaCO_3$. However, the presence of this absorption band may have had only a slight effect on the results.

Reflectance spectra are presented in order to illustrate the variation in the NIR spectra during wetting in mock-ups. The spectra in figure 8 demonstrate that the intensity and shape of the hydration bands were modified as a function of the sample moisture content. As expected, reflectance spectra measured under environmental conditions contained weaker features at ~1450 nm and ~1950 nm than did spectra recorded under moist conditions.



(a) *(b)*

***Fig. 8**: NIR reflectance spectra acquired in the 1200-2200 nm range on cell (1,1) in (a) and on cell (4,2) in (b) at different times. The (—) solid line stands for T0; the (-o-) solid line with marker stands for T1; the (-.-) dashed and dotted line stands for T2; the (--) dashed line stands for T3, and the (...) dotted line, for the T4, thicker solid line for pure water (—) elaborated from K.F. Palmer, 1974 [18].*

The EFD and FORS results were compared with each other. The EFD values were compared with the ones related to the areal integral of the two bands, at approximately 1450 nm and 1950 nm, respectively, of the FORS spectra.

The results are reported in Table 2 for both mock-ups. In particular, the following was considered: a perimeter cell [cell(1,1) for mock-up 1 and cell(1,3) for mock-up 2] versus a central cell [cell (4,2)] for fresco mock-up 1 and cell(3,2) for fresco mock-up 2. The column labelled "ratio" refers to the ratio between the integral on bands 2 (1621-2181 nm) and 1 (1320-1650 nm). The ratio was not constant, even if it seemed that, for higher moisture concentrations in the mock-ups as defined by EFD, the FORS Band2/Band1 integral ratios showed values that were lower than 3.2, while lower moisture-concentration levels corresponded to integral FORS Band2/Band1 ratio values that were often greater than 3.4, apart from several data for cell(1,1) in mock-up 1. These FORS values could possibly have been due to the fact that most of the water absorbed on the inner surface of the fresco mock-ups was concentrated in the first tens of microns from the surface of the samples. Indeed, FORS Band 1 should have been associated approximately with the more external part of the thickness of the samples than FORS Band 2 was. The latter, which was at higher wavelengths than the former, may have penetrated more deeply into the sample stratigraphy, thus resulting in a relatively less intense band than Band 1.

***Table 2**: Comparison between the MC obtained using the EFD system and the integrals of band 1 (1320-1650 nm) and band 2 (1621-2181 nm) in the FORS spectra.*

Fresco mock-up 1							
Cell(1,1)				Cell(4,2)			
MC	Band 1	Band 2	Ratio	MC	Band 1	Band 2	Ratio
0,5	5,1	12,5	2,5	0,6	2,7	16,3	6,0
4,6	41,0	93,1	2,3	5,4	32,6	83,7	2,6
2,4	18,9	54,3	2,9	4,2	13,6	43,1	3,2
0,8	13,2	37,7	2,9	2,9	5,6	25,3	4,5
0,69	4,57	20,13	4,40	0,79	2,96	16,82	5,68

Fresco mock-up 2							
Cell(1,3)				Cell(3,2)			
MC	Band 1	Band 2	Ratio	MC	Band 1	Band 2	Ratio
0,69	3,42	15,55	4,55	0,69	6,17	20,98	3,40
8,7	18,49	57,14	3,09	8,13	43,05	105,06	2,44
5,87	16,56	47,49	2,87	6,06	28,86	79,47	2,75
2,48	7,98	33,62	4,21	3,42	13,11	44,49	3,39
0,88	4,79	20,71	4,32	0,98	7,08	25,64	3,62

The values of the integral calculated for each band versus the MC obtained using EFD for the same cells of Table 2 are plotted in Figure 9. A linear regression was applied to the data acquired for each cell. The measurements under the initial conditions (ambient conditions, T0) and in the wetted state (T1) were not affected by the non-uniform distribution of water, because it was assumed that there was no water gradient from the surface toward the interior. On the other hand, at T1 and T2, the effects of the deeper water influenced the EFD response, and the MC value was higher than the expected spectral integral value, because the FORS measurements could reach approximately one hundred microns in depth within the material and were limited to the surface if compared with the EFD measurement.

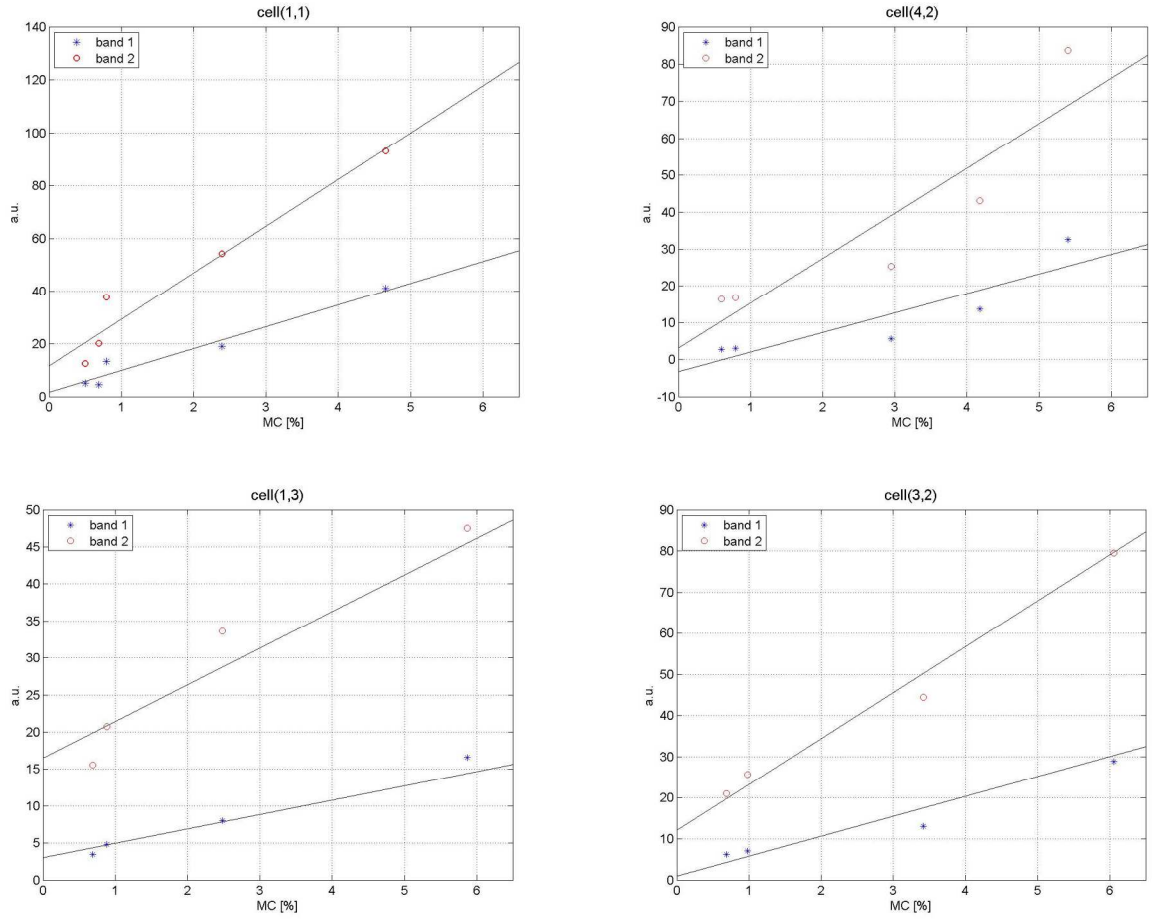


Fig. 9*: Plots of the results of the linear regression between the integral, calculated for each band, and the MC determined using the EFD method.*

CONCLUSIONS

This work is focused on an investigation of the adsorption mechanism of water in wall painting and on an evaluation of the water adsorbed from a surface by different techniques, namely EFD and FORS. The former made it possible to obtain information on the moisture content on a volume inside the material, while with the latter it was possible to focus the measurement on the surface, down to a depth of approximately one hundred microns.

Tests were performed on fresco mock-ups prepared by spreading iron-based pigments in binary and ternary mixtures in order to recreate some of the possible chromatic hues obtainable by mixing iron oxide- and hydroxide-based pigments.
Measurements by means of the EFD method in the microwave range and FORS in the NIR were performed under ambient conditions and after wet-dry cycles involving poultices having a known water content. Data were acquired five different times under different conditions.
The data processing acquired each time made it possible to observe that the peak values in the reflectance spectra related to the bands of adsorbed water increased as the water contribution increased. This result was expected, but can also be used as a piece of strategic information in combination with the result of the EFD measurements relative to an assessment of water distribution in a given material, in particular on wall painting, by using a non-invasive methodological approach. By combining the aforementioned techniques, it is possible to understand, for example, whether the presence of humidity in the wall is caused by internal water circulation (rising dampness, capillarity, some sort of infiltration) or whether, on the other hand, the moisture is due to environmental condition (condensation phenomena on the surface), thus distinguishing the results obtained in relation to the depth of the investigation measurement method.

Further aspects of this study could be the application of both systems to mock-ups prepared with different pigments, in order to assess the efficacy of the methods and to confirm the data acquired in this study.

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