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Fresco paintings studied by unilateral NMR

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Abstract

Unilateral NMR has been used to monitor the state of conservation of *frescoes* in the Vasari's house in Florence. The causes of deterioration of ancient *frescoes* are varied, which result in the detachment and crumbling of the painted film from the supporting plaster and in the outcropping of salts. Unilateral measurements of Hahn echo performed on such *frescoes* have allowed a perfect identification of the detachment of the painted film from the plaster. The presence of soluble salts on the pictorial film affects the spin–spin relaxation times, T_2. It is then possible using this technique, to characterize the effect of chemical treatments, of cleansing and consolidation procedures using the distribution of T_2 spin–spin relaxation times.

Keywords: Unilateral NMR; Hahn echo; T_2 relaxation time distribution; Cultural Heritage; *Frescoes*

1. Introduction

The purpose of this paper was to show the use of unilateral NMR relaxometry for a non-invasive analysis of the conservation state of a *fresco* with respect to its supporting wall. It will be shown that the careful acquisition of a Hahn echo [1] on a painted wall can give information concerning the detachment of the painted layer, i.e., the *fresco*, from its support.

Detachment of *frescoes* may derive from many causes, among which are excessive humidity, followed by dryness; thermal stress; fungi attack; negative restoration attempts; chemical or physical instability of the plaster and so on. Whatever the cause, when disjoining occurs between the plaster and the painted film, a dry air chamber is formed and crumbling can then arise with fragmentation of the pictorial film.

We performed an attentive unilateral NMR study on some regions of a *fresco* painted in 1580 by Vasari in Florence. The purpose of our study was to perform a totally non-invasive analysis of the humidity conditions of the *fresco* before restoration to exploit the full potentiality of unilateral NMR in the field of Cultural Heritage.

In the Vasari house there is a large room, which has three windows on the same side and three fully painted walls. The wall on the left with a fireplace is partly restored and it is in a good conservation state; the painted wall on the right side presents crumbling and visible salt crystallization; the central wall appears to be in the worst condition with partial detachment of the *fresco* due to the presence of water pipes, introduced about a century ago, behind the wall.

T_2 measurements have been performed in different regions of the *fresco*; the results of such seem to agree well with current knowledge on the results of different methods of restoration.

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2. Experimental

All measurements were performed with a commercial unilateral NMR "ProFiler" from Bruker Biospin. The NMR "ProFiler" allows non-invasive measurements "in situ" to be performed.

Two probeheads were used; the first one operating at 18.153 MHz with a penetration depth of about 1 mm, the second one at 17.3 MHz with a penetration depth of about 3 mm. The maximum echo signal corresponding to a $\pi/2$ pulse was obtained with a pulse width of 3 μs for the probehead with 1 mm of penetration depth (surface-probehead), whereas for the probehead with a penetration depth of 3 mm (3-mm probehead) the pulse width was found to be 6 μs. The dead time was 15 μs in both cases.

To ensure a non-invasive measurement the probehead was positioned very close to the *fresco*, but not in contact with it. For the NMR analysis, different regions of the painted wall have been selected according to the criteria, advice, and interests of the restorer. The first set of measurements was performed in October 2003, whereas the second, always in the same areas, was carried out four months later. The two sets of measurement accord taking into consideration the experimental error.

Since some pigments used in the painting may be paramagnetic, namely containing metal impurities that might affect the NMR measurements, most of the surface measurements were performed comparing regions displaying the same colour.

The temperature of the room was within 10–15 °C with a relative humidity of about 50%.

The detachment of the painting layer from the plaster was evidenced performing single Hahn echo [1] measurements with an echo time of 20 μs, 2 K of scans. Salts outcropping and the effect of previous restorations were studied measuring the spin–spin relaxation time T_2 with the CPMG sequence [1] acquiring 1024 echoes; starting echo time 100 μs, $2\tau = 100$ μs, 32 K scans.

The analysis of NMR relaxometric data were performed as previously published [2,3]. The distribution of relaxation times was obtained by numerical inversion of the Fredholm integral using a software implemented within the Matlab (The MathWorks) environment [4,5]. In the resulting distribution, the abscissa provides the relaxation time value and the integral corresponds to the normalized spin density.

3. Results and discussion

3.1. Hahn echo measurements of detachment and crumbling

On the central wall of the room we performed Hahn echo measurements in regions chosen by the restorer on the basis of their different detachment as observed with raking light or soft finger knocking. It must be noted that these methods are still commonly used as a non-invasive source of information.

The wall, analysed with the NMR "ProFiler," showed wide areas of disjoining. A computer drawing of the painted wall, given in Fig. 1A, shows the chosen regions: the circled numbers represent the measured regions; the detachment zones are shown as spotted areas in Fig. 1A. Regions 3 and 4 were chosen in the detached areas. Region 1 was chosen far from any detached area whereas region 2 was close to a detached area.

In Fig. 1B the result of Hahn echo experiments, performed on the four different regions using the surface-probehead, are shown. A net decrease of the Hahn echo intensity has been found in the regions, where detachment occurs (3 and 4), see Fig. 1B. A detectable decrease

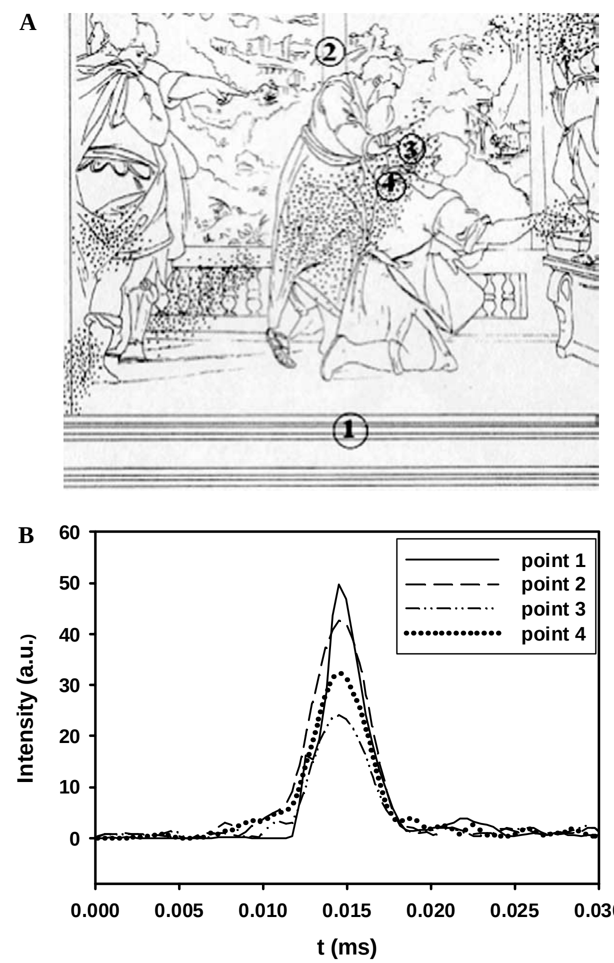

Fig. 1. (A) Computer drawing of the central painted wall. The regions with detachment are shown as spotted areas. The circled numbers are relative to the measured regions. The painted frame in region 1 has exactly the same colour of the column in region 2 (gray-green). Region 3 and 4 show a gray-greenish colour. (B) Single echo experiments performed in region 1 (solid line); region 2 (long dash line); region 3 (dash-dot-dot line); and region 4 (dotted line).

of the intensity of the echo is also observable in region 2, which is located near the detachment zone. It is worthwhile noting that each experiment is easy performed in situ in a fully non-invasive way.

In a well conserved *fresco* an exchange equilibrium between the wall and air humidity is established. In the case of detachment this balance is no longer respected and the cohesion strength between the plaster and the painting layer weakens. Using the surface-probehead it is possible to detect the proton signal from the outer layer of plaster. Therefore, the weaker this signal, the stronger the detachment.

We also performed Hahn echo measurements using the 3 mm-probehead. With this probehead we could measure the proton signal from the deeper layers of the lime mortar (the inner part behind the *fresco*) at a depth of about 3 mm, disregarding the signal from its external layers. Therefore, using this probehead, in the presence or in the absence of detachment of the pictorial film from the plaster, no difference in the intensity of the proton signal is expected. Accordingly, the measurements on regions 1, 2, 3, and 4 do not show any difference in the echo intensity.

To summarize, with the surface-probehead, it is possible to measure the humidity of the plaster, whereas, with the 3 mm-probehead, the humidity of the mortar is measured, disregarding the pictorial film and the plaster and therefore disregarding the detachment. All these measurements were repeated 4 months later, obtaining the same results.

The same measurements were also performed on the right sided wall where crumbling of pictorial film is present. The computer drawing of the wall is shown in the top of Fig. 2. Crumbling is present in region B and not in region A. As expected, we observe a net decrease of the intensity of the Hahn echo in the crumbled region, see Fig. 2, bottom.

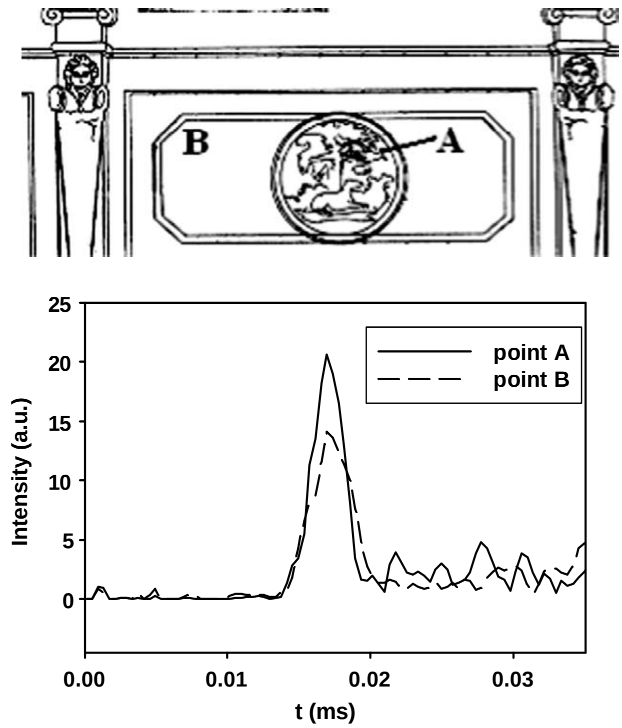

Fig. 2. Top: computer drawing of the right sided painted wall. Crumbling is present in region B, whereas in region A the pictorial film is in a good condition. Bottom: single echo experiments performed in region A (solid line) and in region B (dashed line).

3.1.1. Salts outcropping

Each porous material is in thermal and hygrometric exchange with its surrounding environment. The presence of soluble salts in the mortar of the *fresco* or in air moisture (due to pollution) can cause the occlusion of the porous system of the painting layer and the occurrence of a recrystallization process. The growth of salt crystals within the pores can lead to the formation of salt efflorescence and consequent surface whitening or, indeed, to the crumbling of the painted surface.

On the wall in front of the fireplace, an area is covered by a white film due to the outcropping of salts. In the top of Fig. 3, a computer drawing of the painted wall is shown, along with the chosen regions. Note that regions 6 and 8 do not show any salt outcropping, whereas its presence is noted in regions 5 and 7. In Fig. 3, bottom, we report the result of the Hahn echo experiments performed in these regions. The echo intensity of areas with outcropping salts shows a strong increase of the echo intensity when compared to a similar area on the same fresco free of salts, regions 7 and 8. This increase of intensity may be due to the hygroscopic nature of the outcropping salts. In other regions, however, where salt outcropping is also evident, the intensity of the Hahn echo appears erratic, sometimes more intense and sometimes weaker on respect to the salt free areas, see regions 5 and 6.

Anyhow, since the whitening of the painting is visibly evident, in the case of outcropping salts the Hahn echo measurement is not diagnostic to the restorer.

3.2. T_2 measurements

In some regions of the *frescoed* room we also performed T_2 measurements using a CPMG sequence. For the sake of clarity, we will show either the T_2 decays, or the results obtained by inverting the T_2 decays by solving the Fredholm integral [4,5].

3.2.1. Detachment and crumbling

In the same regions shown in Figs. 1 and 2 we measured T_1 and T_2 relaxation times. T_1 was measured for obtaining the proper relaxation delay and T_2 with the hope of obtaining useful information on porosity [6–8]. However, these measurements, although quite noisy,

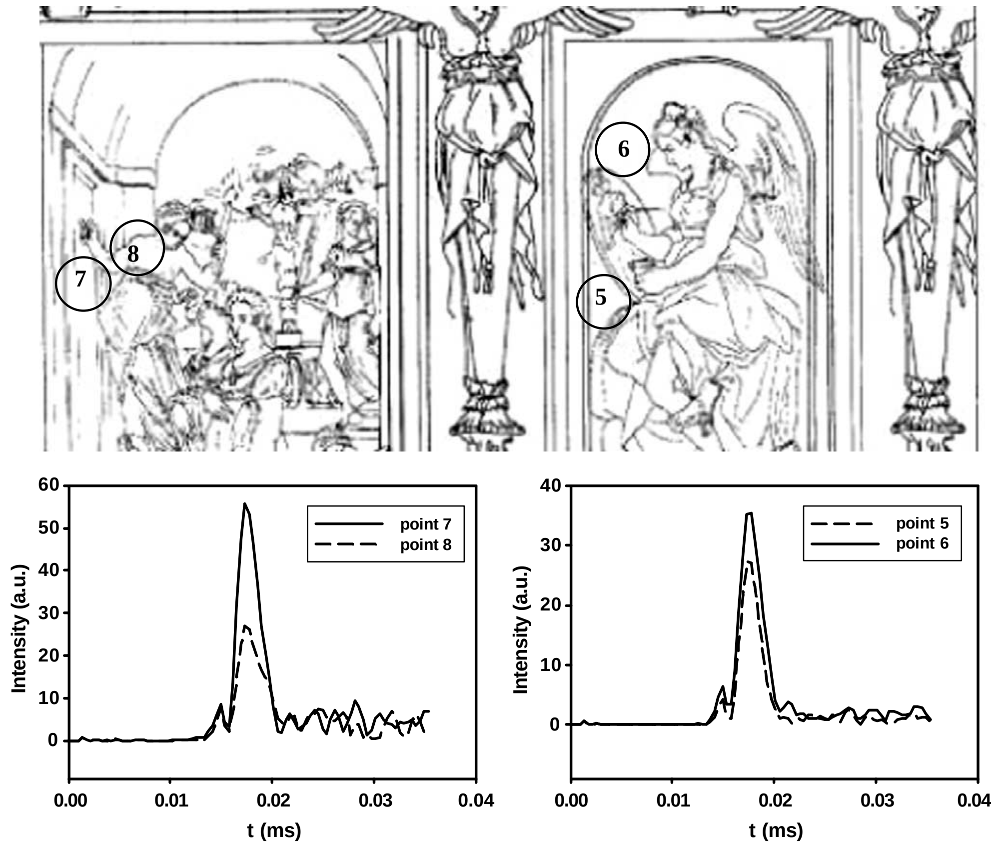

Fig. 3. Top: computer drawing of the right sided painted wall. Outcropping salts are present in regions 5 and 7, whereas in regions 6 and 8 the pictorial film is in a good condition. Bottom: single echo experiments performed in region 6 (solid line) and in region 5 (dashed line); single echo experiments performed in the region 7 (solid line) and in region 8 (dashed line).

show similar values in all regions and do not seem useful or informative.

3.2.2. Outcropping of salts

As previously shown, in regions where outcropping salts are present, the Hahn echo measurement is completely uninformative. However, in these regions T_2 measurements may give information to the restorer [8], in fact, in Figs. 4A and B, some interesting data are noted. Measurements have been performed on the regions 5, 6, 7, and 8 previously shown in Fig. 3.

In region 6, without outcropping salts, the T_2 distribution appears centered at about 0.3 ms, tailed towards longer values, see Fig. 4A; whereas in region 5, where outcropping salts are present, another weak distribution centered at about 2 ms is observed, see Fig. 4A. In Fig. 4B, the T_2 distributions of region 8, without outcropping salts, and region 7, with outcropping salts, are compared. In the presence of outcropping salts, the distribution is broader and centered at longer values than the distribution obtained in the region without salts; the major broadness may be due to moisture adsorbed by the outcropping salts. Therefore, T_2 values may be useful to the restorer to assess the presence of hygroscopic salts in a fast non-invasive way.

3.2.3. Cleansing and restoration

Before performing a full cleansing and restoration of the painted surfaces, various attempts were performed using simple well-known procedures. The kind of information required by the restorer regards the state of the humidity on the pictorial film after the different cleansing procedures. All measurements were performed in regions cleaned at least 1-year before.

The most common ancient procedure to fix the pigments and to prevent the crumbling of the *frescoes* consisted in the application of a mixture of several substances such as egg-yolk, animal glue, wax or linseed oil. The degrading processes that occurred to these materials changed the appearance of the *frescoes* and constituted an optimum substrate promoting the growth of fungi and bacteria. Nowadays, in the process of restoration, these materials are removed with water and successively, when necessary, with a water solution containing ammonium carbonate. To study an area where these cleansing procedures were applied, we performed T_2 measurements. The cleaned area is located in the wall in front of the fireside. The analysed regions are indicated in Fig. 5, top, as 9, 10, and 11. In the untreated region 9, the pictorial

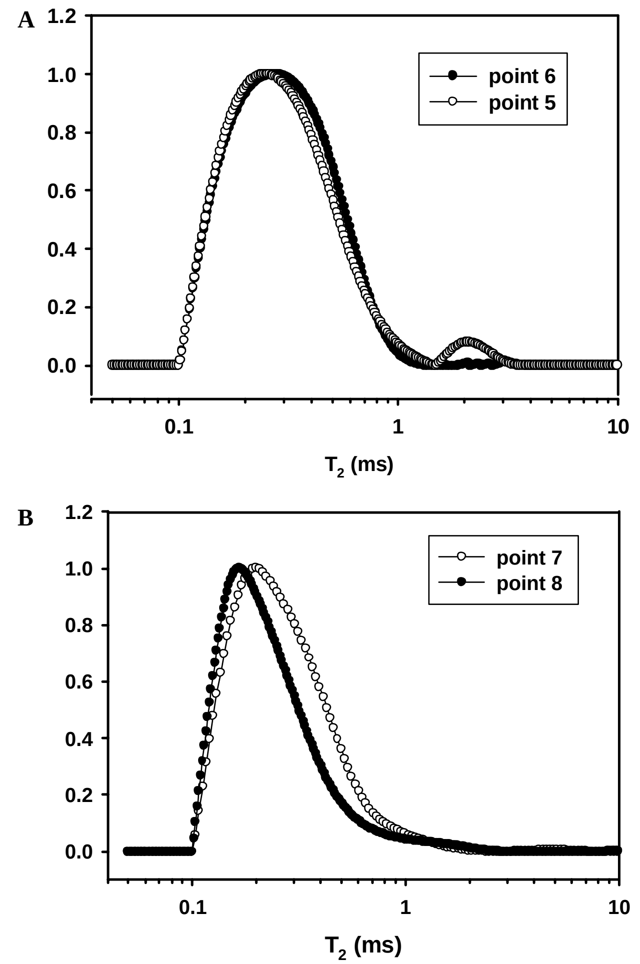

Fig. 4. (A) Relaxation time distributions obtained by inverting CPMG relaxation decays of region 5 and region 6. (B) Relaxation time distributions obtained by inverting CPMG relaxation decays of region 7 and region 8.

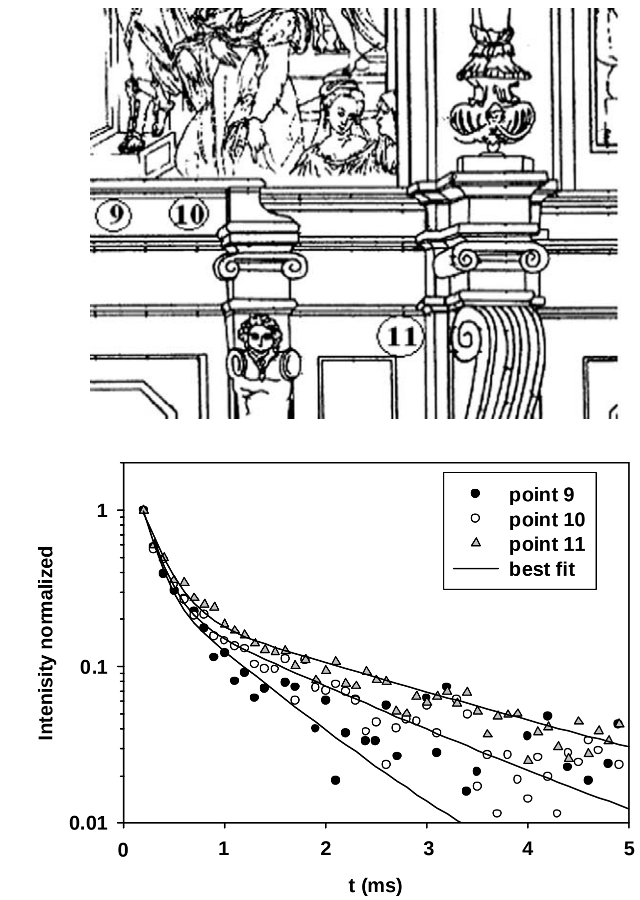

Fig. 5. Top: computer drawing of the right sided painted wall. T_2 decays of regions 9, 10, and 11 obtained applying CPMG sequence. Best fit values of the T_2 decays are:

Region 9: $W_a = 88\%$ $T_{2a} = 0.2 \pm 0.02$ ms, $W_b = 12$ $T_{2b} = 0.85 \pm 0.1$ ms.
Region 10: $W_a = 90\%$ $T_{2a} = 0.2 \pm 0.02$ ms, $W_b = 10$ $T_{2b} = 1.50 \pm 0.1$ ms.
Region 11: $W_a = 88\%$ $T_{2a} = 0.2 \pm 0.02$ ms, $W_b = 12$ $T_{2b} = 2.2 \pm 0.1$ ms.

film appears to be in a good state of conservation even if the mixture of proteic substances used in the previous restoration is still present on the surface. Point 10 was cleaned with distilled water; point 11 was cleaned with distilled water and successively treated with a water solution containing ammonium carbonate. The mild alkaline power of ammonium carbonate allows the removal of the proteic materials. The colour is gray-green in all these regions.

The Hahn echo measurements performed in these regions were poorly informative, showing only that washed regions contain more water than the unwashed ones. On the contrary some useful information was obtained by T_2 measurements. In all measured regions the T_2 decay can be properly analysed by a bi-exponential decay, see Fig. 5, bottom. The fast relaxing T_2 component is 0.2 ms in all regions, whereas the slow relaxing component is found to be 0.85 ms in region 9, 1.5 ms in region 10, and 2.2 ms in region 11. The shorter T_2 values is measured in region 9. It is worth noticing that in this region, the mixture of proteic substances used in the previous restoration is still present. These substances do not allow a correct exchange of moisture between the *fresco* and its environment, consequently the fresco results much dryer. In the region 11, where a ammonium carbonate washing was applied, the longest T_2 values are measured. Note the action of the ammonium carbonate washing. The ammonium carbonate treatment completely removes the layer of proteic substances, allowing a good exchange of humidity between the *fresco* and its surrounding. Region 10, washed only with water shows a T_2 value which is intermediate between the corresponding values measured in regions 9 and 11. To confirm the above data, we chose another three restored regions in which we performed the same measurements. All T_2 results have been confirmed.

Another enquiry, of the restorer, regards the effect of the barium hydroxide used as consolidant after the cleansing [9].

The analysed zone is located on the wall with the fireside. In this area a treatment with barium hydroxide was applied. The aim of the NMR measurements was to verify the consolidating power of the barium hydroxide on *frescoes*.

The analysed regions, 12, 13, and 14, are shown in Fig. 6, top. All these gray-green regions, were cleaned and/or treated at least 1-year previous to the NMR measurements.

In region 12, washed only with water, the pictorial film retains a good state of conservation. The region 13 was washed with water and successively with ammonium carbonate. Region 14 was washed, treated with ammonium carbonate and thereafter consolidated with barium hydroxide.

All regions show a bi-exponential decay of T_2 relaxation data. In Fig. 6, bottom, the T_2 distributions of the relaxation decays are also reported.

In all regions, the T_2 distribution shows a maximum at about 0.2 ms. In region 12, the distribution is rather symmetric and narrow, whereas in regions 13 and 14 the distribution is tailed towards longer values, more in region 13 than in region 14. Then the ammonium carbonate treatments removes the proteic substances present on the surface of the paint and allows a better exchange of humidity between the *fresco* and its surrounding.

In the region 14, where the barium hydroxide treatment was applied after ammonium carbonate washing, the distribution of relaxation times is shifted again to shorter values. In fact, it is well known that this treatment is able of consolidating a *fresco* [9]; after this treatment a new exchange equilibrium of moisture between the fresco and its surrounding is established. It is well known [9] that the consolidating action of barium hydroxide is explicated through the filling of large pores while small pores are unaffected. On this regards the obtained T_2 distribution may be interpreted as due to lack of water in larger pores. However, this interpretation must be taken with caution because our measurements have been performed far from water saturation [10,11].

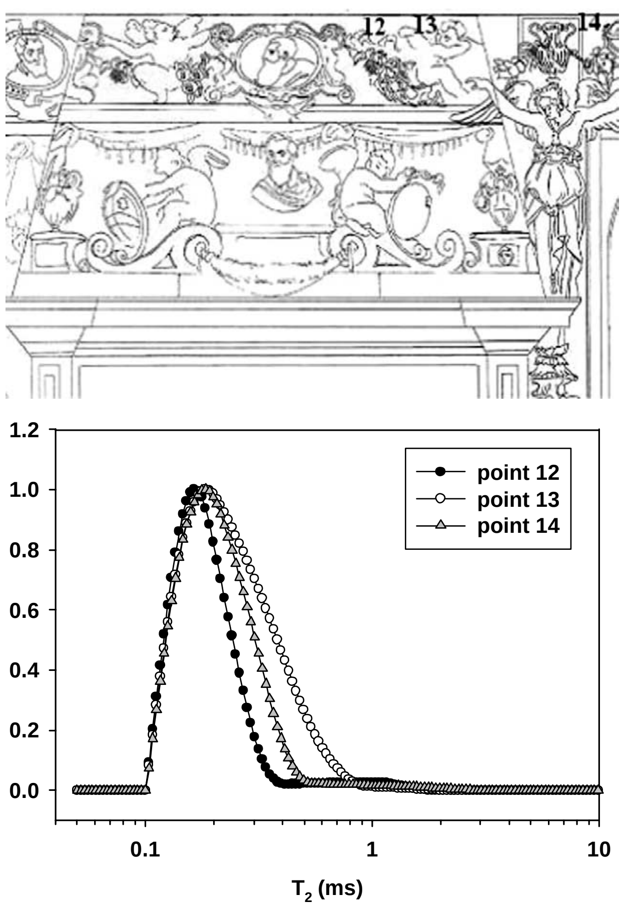

Fig. 6. Top: computer drawing of the right sided painted wall. Bottom: relaxation time distributions obtained by inverting CPMG relaxation decays of regions 12, 13, and 14.

4. Conclusion

In the course of a campaign of measurements in the Vasari's house in Florence, large amount of NMR data using a fully non-invasive unilateral NMR relaxometer was produced. All measurements were aimed at answering precise enquries of the restorer. These regarded the detachment of a historical *fresco* from its supporting wall, the state of humidity in precise regions, and the effects of chemical treatments of the cleansing and consolidation procedures. Using the simple, few parameters obtainable with a unilateral NMR technique we have been able to answer most of these questions. T_2 measurements seem the most significant, for studying in situ the effect of cleansing, restoration, and consolidation procedures.

The simple measurement of the Hahn echo gives direct information about the detachment and crumbling of the pictorial film. It follows that unilateral NMR technique represents an advancement on already used methods. The measurements of the detachment of a painted surface from its supporting mortar is very important to restorers. The intensity of the Hahn echo, that is, the spin density of the water signal, seems to be a suitable method to assess the state of a *fresco* even when other methods do not give clear indications.

It must be pointed out that in this paper, we do not correlate T_2 distribution with the pore size distribution. In fact this correlation can be done only in the case of pores saturated with water; the Cultural Heritage field, does not usually fulfil this condition.

Work is in progress for correlating the T_2 distributions measured under "non-saturation" conditions, with the pore size distribution.

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