

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.

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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 , $2\tau = 100 \mu\text{s}$, 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

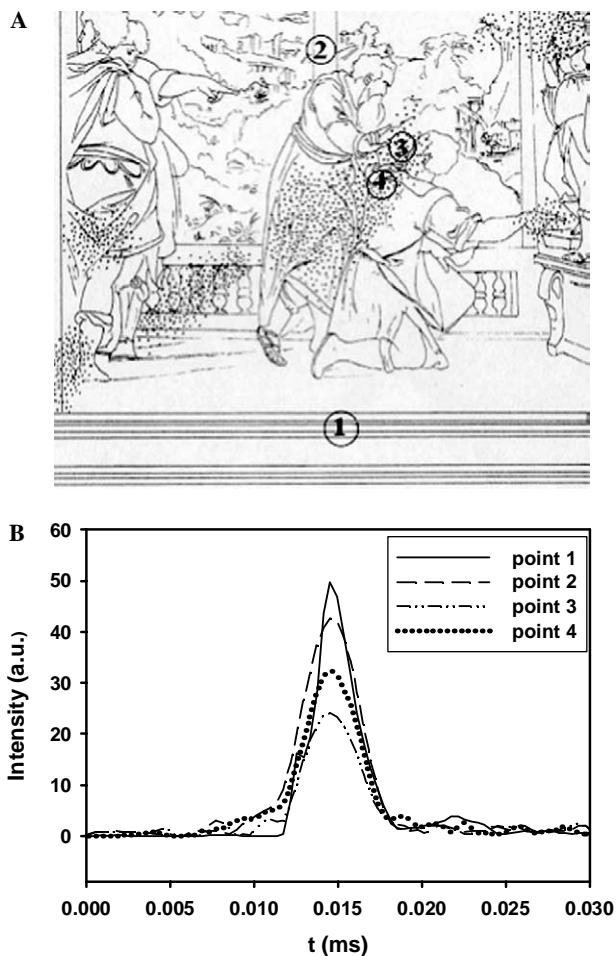


Fig. 1. (A) Computer drawing of the central painted wall. The regions with detachment are shown as spotted areas. The circled numbers are relative to the measured regions. The painted frame in region 1 has exactly the same colour of the column in region 2 (gray-green). Region 3 and 4 show a gray-greenish 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).

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