NMR techniques in Cultural Heritage

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Introduction

Nuclear Magnetic Resonance (NMR) is a powerful tool applied in many fields of research such as chemistry, physics, biology, biochemistry, medicine, material science, and geology, nevertheless the application to cultural heritage is more recent [1].

High resolution NMR spectroscopy is a key tool for the investigation of liquid and solid samples, soft matter, and for detecting possible degradation processes occurring in the analyzed samples. Nowadays new technologies and probeheads such as cryoprobes and microprobes have enabled the NMR analysis of liquid samples down to the µg scale. The amount of material needed for solid state NMR [2] analysis has decreased from about 500 mg at the early times down to a few mg, making NMR a suitable technique for analyzing samples available in a small amount. The sample to be investigated must be placed in a sample holder (a glass tube in the case of analysis in solution or a rotor in the case of solid state or soft matter analysis) and placed in a superconducting magnet. By way of example, Figure 1 shows a superconducting magnet operating at the proton frequency of 600.13 MHz.

It consists of an outer stainless-steel Dewar flask containing liquid nitrogen and an inner Dewar flask containing the superconducting coil immersed in liquid helium. The simplest nmR experiment consists of applying a radio-frequency (r.f.) pulse with a duration of a few microseconds to the sample. As the r.f. pulse is switched off, the nuclei relax back to equilibrium generating an interferogram (amplitude *vs* time) known as free induction decay (FID). Signals in the time domain are converted to signals in the frequency domain (amplitude *vs* frequency) by applying a Fourier transformation to the FID [3]. After this transformation, a spectrum is obtained with peaks of appropriate width and frequency (chemical shift) [4]. To obtain reliable results the magnetic field must be highly homogeneous, and the temperature of the sample must be kept absolutely constant during the analysis. nmR spectroscopy is conside-



FIGURE 1 – A superconducting magnet operating at the proton frequency of 600.13 MHz.

red a non-destructive technique because, after the analysis, the sample may be easily recovered and subject to other types of analysis.

1 High Resolution Nuclear Magnetic Resonance

The identification of soluble organic residues in ancient artworks is a typical application of liquid state high resolution nmR in cultural heritage. In fact, the identification of food residues adhering to the surface or absorbed into the porous structure of pottery provides important information about ancient practices. The preparation of the sample suitable for this type of analysis has required the sampling of a few mg of powder from the center of the pottery, the sonication of the powder in deuterated chloroform ($CDCl_3$) and centrifugation for separating the solubilized sample from the solid residue. With this procedure it has been possible to separate the lipid fraction from the sample without extracting any proteinaceous material or its degradation products. For example, the identification of organic residues in pottery from two Sicilian prehistoric sites of Monte Kronio and Sant' Ippolito, has revealed the presence of animal fats [5], the ^{1}H nmR spectrum is reported in Figure 2.

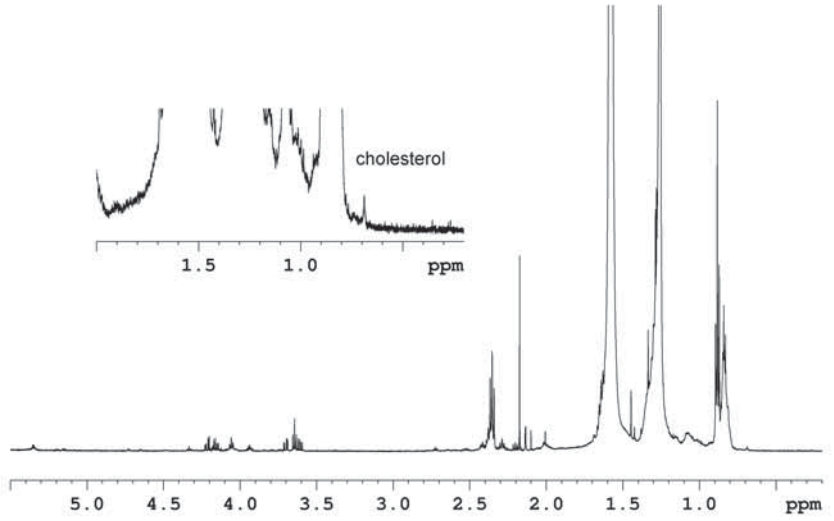


FIGURE 2 – Liquid state ^{1}H nmR spectrum at 600.13 MHz of a sample obtained from Sicilian prehistoric pottery, showing the presence of animal fats. Adapted from [5].

Major signals have been assigned to saturated fatty acids, mono-, di-, and tri-glicerides partially hydrolyzed. Furthermore, a peak between 0.70–0.72 ppm ascribed to cholesterol has been also detected, see the insert in Figure 2.

Since most of materials used in cultural heritage cannot easily solubilazed, solid state nmR spectroscopy provide a suitable technique to analyze materials directly in solid state. In fact, high resolution solid state nmR analysis does not require any treatment of the sample, a solid fragment is inserted in the sample holder and analyzed. As an example, ^{13}C Cross Polarization Magic Angle Spinning (CPMAS) nmR spectroscopy has been applied to investigate the organic binder of a gilded region of a Polyptych painted on a wooden table dated back to the 14$^{\text{th}}$ century and located at Siena picture gallery [6]. Figure 3 compares the spectrum of a fragment of a naturally aged gilded specimen made of albumen and bole on wood (a), with that of a fragment sampled from a gilded region of the ancient Polyptych (b).

Both spectra show the peaks of the wooden support. Specifically, the region between 60 and 105 ppm is dominated by signals mostly assigned to cellulose, the region between 105 and 160 ppm is specific to the aromatic carbons of lignin. Between 10 and 45 ppm both spectra show the same peaks mostly ascribed to methyl and methylene groups of albumen used as mordant in the gilding. Eventually, albumen, carbonyls of acetoxy groups of hemicelluloses, and acid groups of wood contribute to the signal at about 172 ppm. The comparison between the spectrum of the specimen and that of the fragment has allowed to asses the presence of albumen in the original fragment.

Another example is the usage of ^{13}C CPMAS nmR spectroscopy for characterizing and distinguishing amber from different geographical and botanical origin. Among organic gems having a gemological value, ambers are fashionable ones widely used

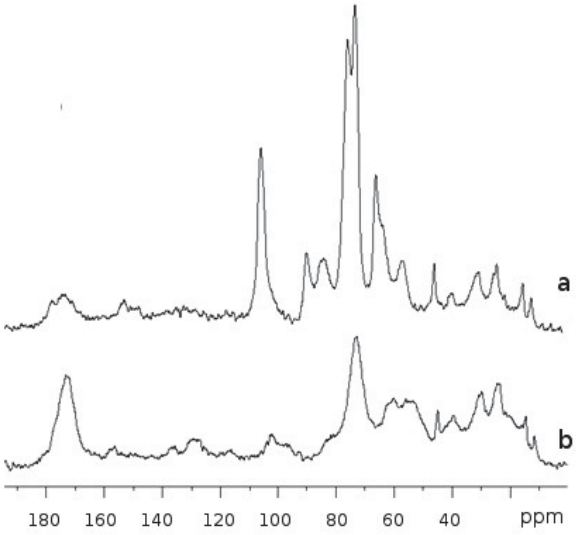


Figure 3 – ^{13}C CPMAS nmR spectra of a fragment obtained from a purposely prepared specimen made of albumen, bole and wood (a) , and a fragment obtained from a gilded region of an ancient Polyptych (b). Adapted from [6].

since ancient times for manufacturing jewels and decorative object. The determination of geographical origin may help to draw maps of cultural and trade networks and provide information on the authenticity of artworks.

Previous studies have demonstrated that nmR spectral features allow the distinction of five groups of amber based on their paleobotanical origins [7, 8]. In ^{13}C nmR spectra of amber, three regions can be detected : single-bonded carbons (δ 10–90), double bonded carbons (δ 105–155), and carbonyl and carboxyl carbons (δ 170–200). The relative intensity of peaks of di- and tri-substituted alkene carbons (δ 128 and 140) and peaks of exomethylene carbons (δ 110 and 150) can be used for evaluating the maturity of fossil resins. The relative intensity of signals of exomethylenes decreases with increasing resin maturation.

Recently ^{13}C CPMAS nmR has been applied to differentiate Sicilian amber (Simetite) with respect to Baltic and Domenican amber [9]. Figure 4 shows the spectra characteristic of Simetite (a), Baltic (b), and Domenican (c) amber.

In details, in the spectrum of Baltic amber the intensity of the peak at 20 ppm is weaker than in Simetite, at 15 ppm a shoulder due to methyl carbons is observed and the peak at 38 ppm is missing. In addition, the fingerprinting of regions of exomethylenes and carbonyl carbons is different from that observed in Simetite. Specifically, in the region of carbonyl carbons three weak peaks are observed, with a characteristic resonance at ˜170 ppm ascribed to succinic acid (see Figure 4b).

In the spectrum of Dominican amber (Figure 4c), the peak at 20 ppm is weaker than in Simetite and a shoulder at 15 ppm, absent in Simetite spectrum, is observed,

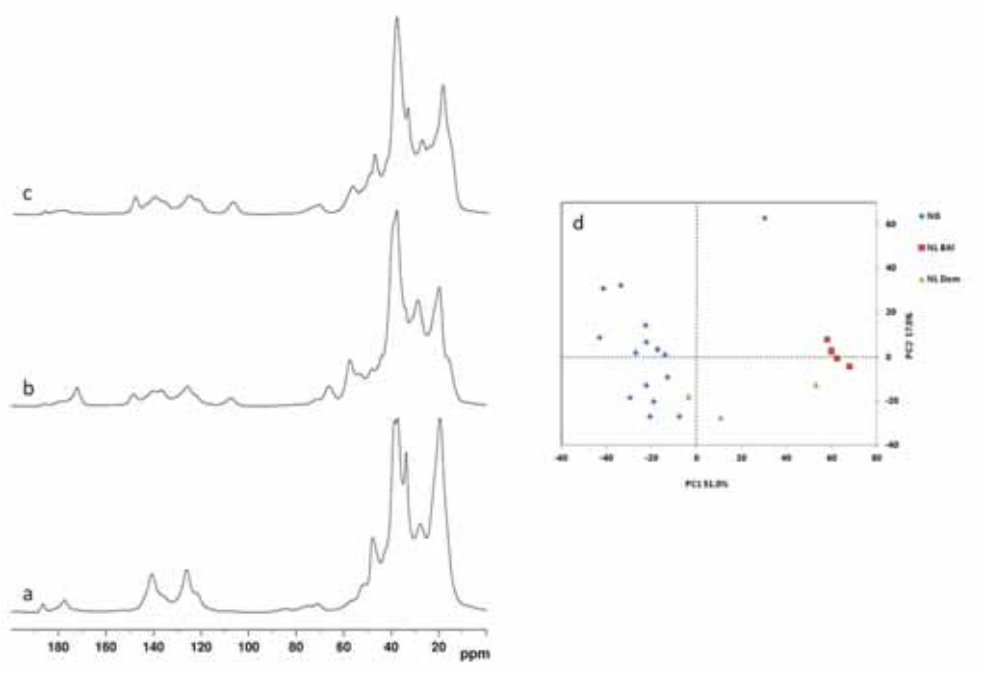


Figure 4 – ^{13}C CPMAS nmR spectra of Simetite (a), Baltic (b), and Domenican (c) amber. (d) PCA analysis of ^{13}C CPMAS nmR spectroscopic data, scores of the principal component variables PC1 and PC2. Adapted from [9].

moreover, a shoulder at ~35 ppm is detected. Finally, the fingerprinting of the region of exomethylenes is very different from that observed in Simetite, while in the functional group region a broad and weak peak related to the carbonyl resonance at about 170 ppm, can be observed (Figure 4c).

Actually, the obtained spectra have permitted to distinguish Simetite from the other resins.

The principal component analysis (PCA) has been applied to nmR data, obtained from the integral of the major peaks, allowing to cluster Simetite samples with respect to Baltic and Domenican amber samples and to group Simetite samples in two sets, depending on the maturity, see Figure 4d. The first two PCs account for 68.8% of the variability within the data, PC1 providing for 51% and PC2 for 17.8%. In the Simetite group, the PC2 has allowed to discriminate ambers based on the maturation degree, in fact all samples lying below the horizontal line are younger than those lying above this line. Principal Component Analysis (PCA) is a dimension-reduction procedure that can be used to reduce a large set of variables to a small set that still contains most of the information in the large set. It transforms a number of correlated variables into a smaller number of uncorrelated variables called principal components. The principal components are linear combinations of the original variables weighted by their contribution to explaining the variance in a particular orthogonal dimension.

Specifically, the first principal component (PC1) accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

2 Low Resolution Nuclear Magnetic Resonance : portable single-sided nmR

High resolution nmR spectroscopy requires sampling, however in many cases precious artworks cannot be sampled at all. Often the analysis of precious artworks must match rigorous requirements :

(1) The amount and the number of samples collected (if possible) must be reduced to a minimum.

(2) Non-destructive and non-invasive analysis is advisable.

(3) Often objects to be analyzed cannot be brought in laboratory.

(4) The state of conservation of objects should be monitored over the time, that is to say the monitoring should be repeated over time.

In this context, a breakthrough for application of nmR to cultural heritage has been the development of portable single-sided nmR sensors [10, 11, 12, 13], which allow one to study in situ arbitrarily sized objects non-invasively and non-destructively, combining open magnets and surface r.f. coils to generate a magnetic field external to the sensor and inside the object under investigation. Although the magnetic field of these sensors is highly inhomogeneous, it is possible to measure the proton density, longitudinal (T_1) and transverse (T_2) relaxation times, and the self-diffusion coefficient (D), and even to collect correlation maps such as (T_1, T_2) or (T_2, D) of unmovable and precious artworks [12]. Because in the presence of inhomogeneous field the nmR signal decays quickly, the signal must be recovered stroboscopically [14]. As a consequence, the nmR signal is the signal resulting after applying an Hahn echo pulse sequence. It must be noted that the inhomogeneous field is a further source of relaxation which makes the transverse relaxation time shorter than that measured in a homogeneous field. In fact, in the presence of magnetic field gradient, the transverse relaxation time does not depend only by spin-spin interaction but it is also controlled by molecular diffusion in the magnetic field gradient which, in the case of portable NMR is very strong (14.28 T/m). The diffusion through the gradient results in a more rapid loss of coherence than is expected for the usual spin-spin interaction [15]. The shortening of the transverse relaxation time can be minimized by using an echo spacing as short as possible.

Figure 5a shows a 2 kg palm-size portable single-sided nmR sensor. To change the depth of measurement inside objects, the tuning frequency of these devices must be electronically switched. At this aim, probe heads tuned at different frequencies must be used. The sensor consists of a U-shaped permanent magnet obtained mounting two antiparallel magnets on an iron yoke with the r.f. coil positioned in the gap [14], see Figure 5b. With this geometry, the magnetic field is external to the device allowing the measurement of large objects without any sampling.

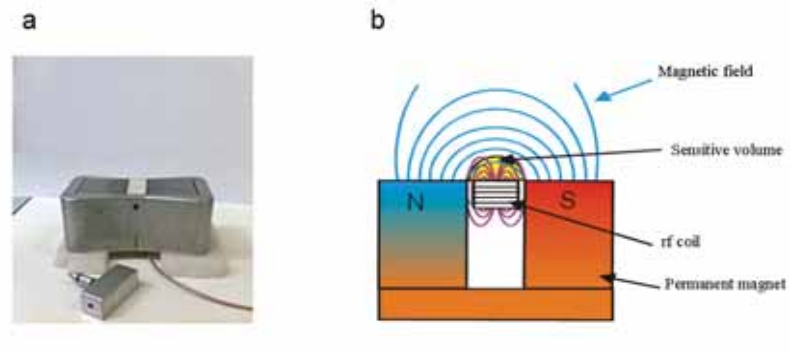


FIGURE 5 – (a) A 2 kg palm-size portable NMR sensor. (b) Two antiparallel magnets are mounted on an iron yoke with the r.f. coil positioned in the gap, the sensitive volume is external to the device allowing the analysis of large object without any sampling. Adapted from [14].

A recent improvement of portable single-sided nmR devices [16] has been the development of sensors able of scanning depths up to 2.5 cm, producing depth profiles with micrometric spatial resolution, see Figure 6a. These devices generate an inhomogeneous magnetic field with an extremely uniform magnetic field gradient to resolve the near surface structure of arbitrarily large samples. To improve gradient uniformity, the device was optimized at a fixed depth from the sensor varying the relative position of the excited slice inside the sample. This is achieved by displacing the sensor using a high-precision lift that repositions the sensor with respect to the sample. Figure 6b shows such a device consisting of two permanent magnets polarized along y direction, and two permanent magnets polarized along –y direction, the sensor is mounted on a precision lift [16]. The use of these sensors in the cultural heritage field has opened a number of new possibilities.

2.1 Portable NMR to detect moisture in wall paintings

In recent years portable NMR has been applied to analyze several ancient artworks, since many objects belonging to cultural heritage are composed by hydrogen. Depending on the issue to be evaluated, portable NMR has been involved to monitor the moisture content in masonry and wall paintings ; to map the state of conservation in wooden artworks ; to analyze the stratigraphy in paintings as well as to evaluate the effectiveness and performances in cleaning, consolidation and protective treatments on porous materials [1].

Determining the amount, course and distribution of moisture is a fundamental step in the conservation of wall paintings. Processes such as leaching, transport, accumulation, solute precipitation and fractionation, and biological colonization depend on the moisture content of the masonry which is subject to seasonal variation and environmental conditions. The porous mortar backing of wall paintings may provide an easy route for the flow of diluted salt solutions. Salts which crystallize on the wall surface cause the whitening of the painted layer (efflorescence), and sometimes crumbling and fretting of the wall. The plaster-pigment adhesion is affected by the volumetric expan-

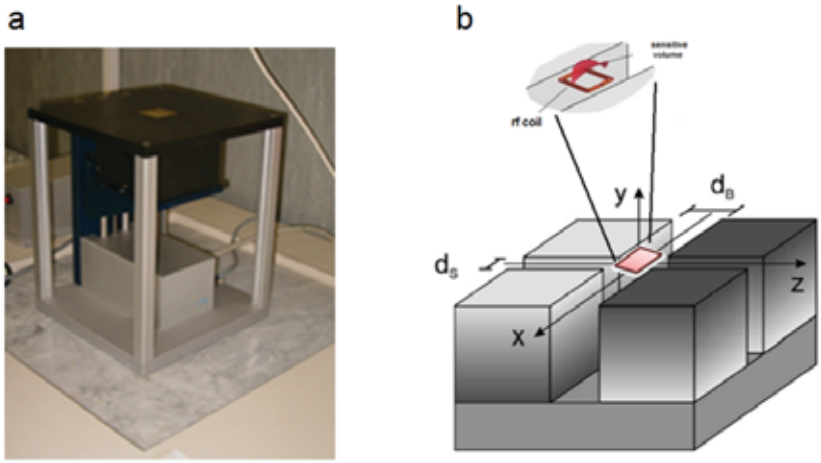


Figure 6 – (a) A portable single-sided nmR device able of scanning depths up to 2.5 cm, producing depth profiles with micrometric spatial resolution. (b) The sensor is constituted of two magnets polarized along y direction, and two magnets polarized along –y direction. Adapted from [16].

sion associated with the crystallization of these salts which may lead to disintegration of the painted surface. In the case of wall paintings important factors must be taken into account, among these the difficulty of controlling potential deteriogens, such as moisture and pollution, the vulnerability of extremely thin painted surfaces forming the interface between the plaster and the environment, and the proximity of places crowded with people to the wall painting. Despite its importance, the determination of water distribution in wall paintings is a difficult task. Methods currently used to get information about the presence of moisture are electrical conductivity, IR thermography (IRT), and gravimetric tests. However electrical conductivity may be affected by the presence of salts, IRT does not allow a quantitative evaluation of moisture, and gravimetric tests require the drilling of solid cores, which is forbidden in the case of precious artworks such as wall paintings.

The development of portable single-sided nmR sensors has allowed non-destructive and non-invasive mapping of water distribution in historical walls. Figure 7 shows a portable NMR sensor measuring the water distribution in ancient Aurelian Roman walls in Rome. The sensor is applied to one side of the object to be measured preserving its integrity.

A portable single-sided nmR sensor has been used to map moisture distribution in *Saint Clement at Mass and the Legend of Sisinnius* wall painting dated back to 1080, located in the second hypogeous level of St. Clement's Basilica, Rome about six meters under the road level [17]. Figure 8 shows a portable NMR sensor measuring moisture in the wall painting. The microclimate of this level is typical of hypogeous buildings, with very high levels of relative humidity (>90%) and rather low temperature over the year. A watercourse under the foundations of the basilica causes the rising damp in the walls of the archaeological site. The masonry and wall paintings show the typical



FIGURE 7 – A portable single-sided nmR sensor measuring moisture in Aurelian walls, Rome.

degradation caused by high humidity, including salt efflorescence, encrustations, and biological colonization. The damage to the wall painting was so severe that the reduction of moisture and its stabilization was mandatory before planning any restoration.

NMR measurements have been carried out choosing a matrix of points on the painted surface. The area of each experimental point was 2 x 5 cm, which matched the dimension of the sensor. Collected data have been processed to obtain contour plots where x and y are the coordinates of the measured area of the painted wall and z is the integral of the nmR signal, which is proportional to the water content. In these maps, the difference in the moisture level is shown as a gradient of color, red indicates the lowest water content, while dark blue indicates the highest water content.

Figure 9a shows the moisture distribution maps collected at a depth of 0.5cm in 2008 before an intervention to reduce the capillary rise of water through the wall, Figure 9b shows the map obtained in 2009 four months after the intervention, and Figure 9c shows the map obtained in 2010 seven months after the intervention. A suitable calibration procedure [17] of the nmR signal has allowed to assign to each area of the map the exact amount of moisture, the scale on the right side is the



FIGURE 8 – Portable single-sided nmR sensor measuring the moisture content in *Saint Clement at Mass and the Legend of Sisinnius*, wall painting in St. Clement's Basilica, Rome.

percentage of moisture assigned to each color of the map. The maps have given a clear image of the path of rising damp. After the intervention, the maximum water content measured in November 2009 and February 2010 has been found to be about 3% lower than that measured in February 2008 before the intervention. The moisture distribution maps obtained four and seven months after the intervention have clearly shown a lower rise of moisture and a net reduction in wet areas.

2.2 Portable NMR to investigate degradation in ancient wood

Wood is a complex natural composite material consisting of cellulose, hemicelluloses, lignin, and water.

Evaluation of the degree of deterioration of ancient wooden artworks is of interest for archaeology, archaeometry and conservation science.

Portable NMR has been used to investigate the state of conservation of a wooden panel of an Egyptian sarcophagus (XXV-XXVI dynasty, Third Intermediate Period) [18], see Figure 10.

Specifically, relaxation times have been measured. Because the wood of the panel was determined to be yew wood by optical microscopy, the transverse relaxation times measured on the inner and outer side of the panel have been compared with those measured on a piece of seasoned yew wood.

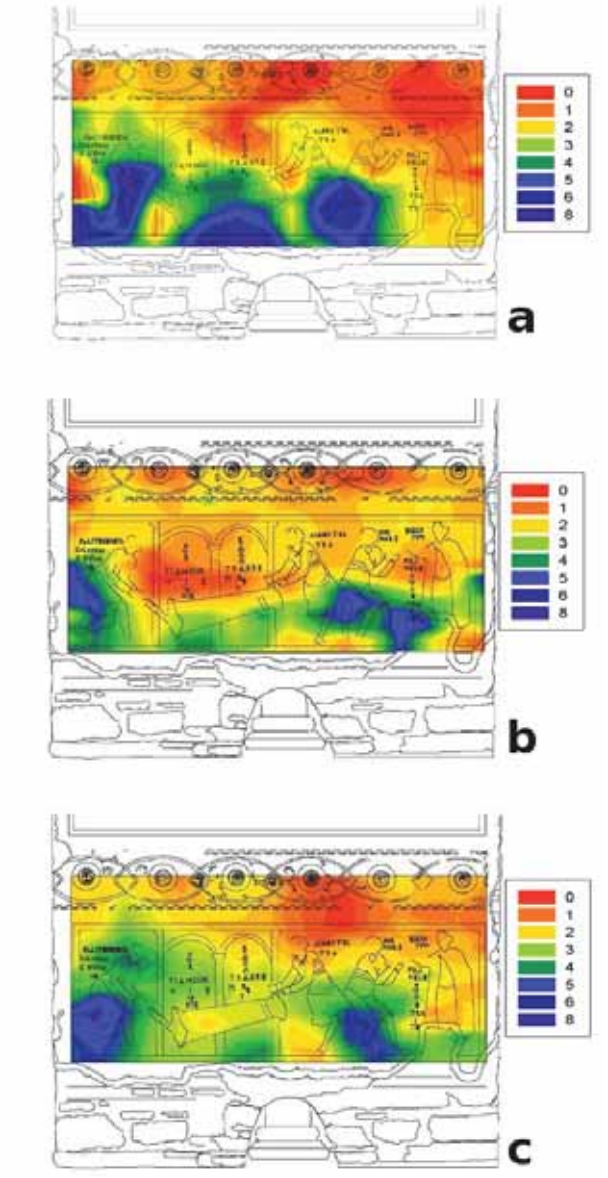


Figure 9 – Moisture distribution maps obtained by portable NMR at a depth of 0.5 cm. (a) Map obtained in February 2008 before the intervention to reduce capillary rise of water through the wall. (b) Map obtained in November 2009 four months after the intervention. (c) Map obtained in February 2010 seven months after the intervention. The scale on the right side is the percentage of moisture assigned to each color of the map. Adapted from [17].

The analysis of transverse relaxation times in seasoned wood has enabled the detection of three water compartments, namely cell water with a short T_2 value, and lumen



FIGURE 10 – The inner side of the panel of a wooden Egyptian sarcophagus dated back to XXV–XXVI dynasty, Third Intermediate Period. Adapted from [18].

water with medium and long T_2 values. Note that transverse relaxation process may display mono- or multi-exponential trends, in fact the decay of the magnetization may be fit to the following equation :

$$y = \sum_{i=1}^{n} W_i \exp\left(\frac{-t}{T_{2i}}\right)$$

where T_{2i} and W_i are the transverse relaxation time and the corresponding population of the i^{th} component respectively, and n is the number of components. By applying an inverse Laplace transformation to experimental data, a distribution of relaxation times is obtained. This procedure allows to obtain water component and distribution in wooden manufatcs.

Water in different internal compartments is related to the size and proportion of wood tissue, see Figure 11. It has also been shown in literature that T_2 relaxation times in wood are clearly represented by applying an inverse Laplace transformation to decays obtained with the CPMG sequence.

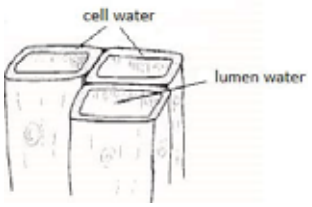


FIGURE 11 – Sketch representing the location of water in a wood cell.

CPMG decays measured on the inner and the outer side of the wooden panel of the sarcophagus are reported in Figure 12a and compared with the decay measured on a piece of seasoned yew wood, the corresponding distributions are shown in Figure 12b. In this representation, peaks are centered at the corresponding most probable T_2 values, while peak areas correspond to the populations of T_2 components. The loss of water occurring in the wood of the sarcophagus is clearly observable, as in seasoned yew wood the distribution displays three peaks resulting from cell water and lumen water in two different environments, whereas in the inner and outer sides of the panel the peak centered at the longest T_2 value is missing. Also, the relative amount of more

confined lumen water measured on both sides of the panel is definitely lower than that measured in seasoned yew wood. Therefore, the ageing of the panel is associated with an evident loss of lumen water. In addition, the longest T_2 component measured on the outer side of the panel clearly shifts to a value shorter than that measured on the inner side, indicating that the wood of the outer side experienced a more pronounced degradation than the wood of the inner side. This is in line with a previous observation indicating the transverse relaxation time as a suitable parameter for evaluating the state of degradation of cellulose-based materials [19].

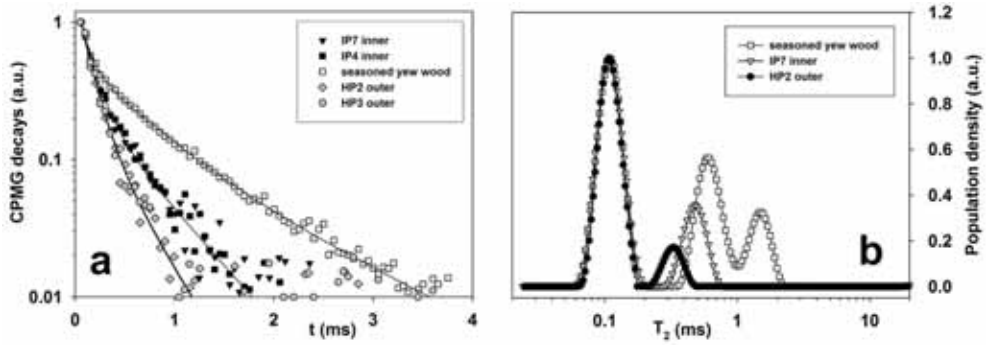


FIGURE 12 – (a) Semi-logarithmic plots of CPMG decays measured on the inner side of the wooden panel, on the outer side, and on a seasoned yew wood. (b) Transverse relaxation time distributions obtained by applying a Laplace transformation to the corresponding CPMG decays. Adapted from [18].

2.3 NMR stratigraphy of paintings

The knowledge of the layer structure or stratigraphy of a wall painting provides information about the materials used and the state of conservation. Usually information about the stratigraphy is obtained by cutting cross-sections from the painting and analyzing them by optical microscopy, scanning electron microscopy, micro-Fourier transform infrared spectroscopy, and other techniques. Recently developed portable NMR sensors permit to obtain, non-invasively and non-destructively, the stratigraphy of a painting [20]. The nmR stratigraphy encodes the amplitude of the ^{1}H nmR signal as a function of the depth scanned. Layers of different materials can be detected and their thickness measured. In fact, the intensity of the signal, indicating the hydrogen content which is different in different materials, enables a layer to be differentiated from another one. An example of the potentiality of this technique is shown in Figure 13 where the stratigraphy of a purposely-prepared tempera wooden specimen (a), and the corresponding optical image (b) are reported. Based on ^{1}H nmR signal intensity, the stratigraphy indicates four well defined layers : the first one is the pictorial layer (0.2 mm thick), the second one the primer (0.5 mm thick), the third one the *incamottatura* (canvas + glue) (1.2 mm thick), and the fourth one is the wood of the panel. It is worth to note that the layers and their thickness match those observed by optical microscopy.

Recently, portable NMR has been used to investigate in situ, non-destructively and non-invasively, the stratigraphic structure and state of conservation of the *Adorazione*

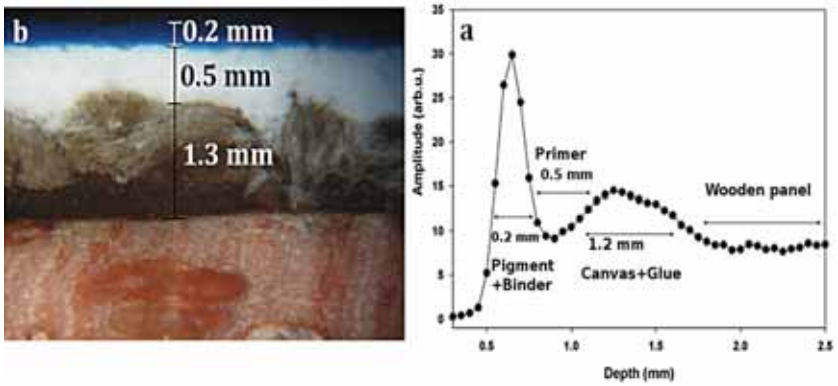


FIGURE 13 – (a) nmR stratigraphy of a purposely prepared tempera specimen showing four layers : the first is the painted layer, the second the primer, the third the incamottatura, and the fourth the wood. (b) The corresponding optical image.

dei Magi, a wooden panel painted by Bartolo di Fredi in the second half of 14th century and located in Siena picture gallery [21], see Figure 14a. Figures 14b and c show the ^{1}H nmR stratigraphies collected by scanning a region of the Virgin mantle (P1), and two regions of the red vest (P7, P9). In P1 three layers have been detected, the first one about 0.6 mm thick has been ascribed to the pigment + binder, the second one about 0.6 mm thick to the primer, and the third one to the wooden table. The CPMG decays selectively measured in layer 1 and 3 exhibit a bi-exponential trend with two T_2 values, specifically T_{2a} of 0.12±0.01 ms and T_{2b} of 0.49±0.01 ms in layer 1, and T_{2a} of 0.11±0.01 ms and T_{2b} of 1.1±0.1 ms in layer 3, whereas the decay selectively measured on layer 2 exhibits a mono-exponential trend with a T_2 value of 0.26±0.01 ms. Because the transverse relaxation time depends on the physicochemical properties of the investigated materials, based on relaxation time values, it is expected to recognize layers constituted of different types of organic materials. In region P7, again three layers have been detected ascribed to the pigment + binder, to the primer, and to the wooden table. In P9, besides these three layers, a fourth layer has been detected ascribed to the canvas + glue constituting the *incamottatura* joining the wooden axes of the table of the painting, see Figure 14c.

2.4 NMR stratigraphy to monitor cleaning treatments

The cleaning of cultural heritage is carried out to remove undesired layers that may induce degradation to the artworks, such as unwanted organic layers, metal stains, crusts, salt efflorescences, or layers due to natural aging [22]. Shellac is a natural organic resin of animal origin that was widely used in the past as a varnish for wall paintings. At present the darkening of shellac over time is a widely spread problem. When shellac ages, it becomes insoluble, changes colour, and becomes very hard to remove. Many old paintings become yellowish due to the shellac coating.

^{1}H nmR stratigraphy has been applied to monitor, non-destructively and non-invasively, the effectiveness of a cleaning procedure aimed at removing a shellac coating from a purposely prepared and aged calcarenite specimen [23]. The specimen acts as

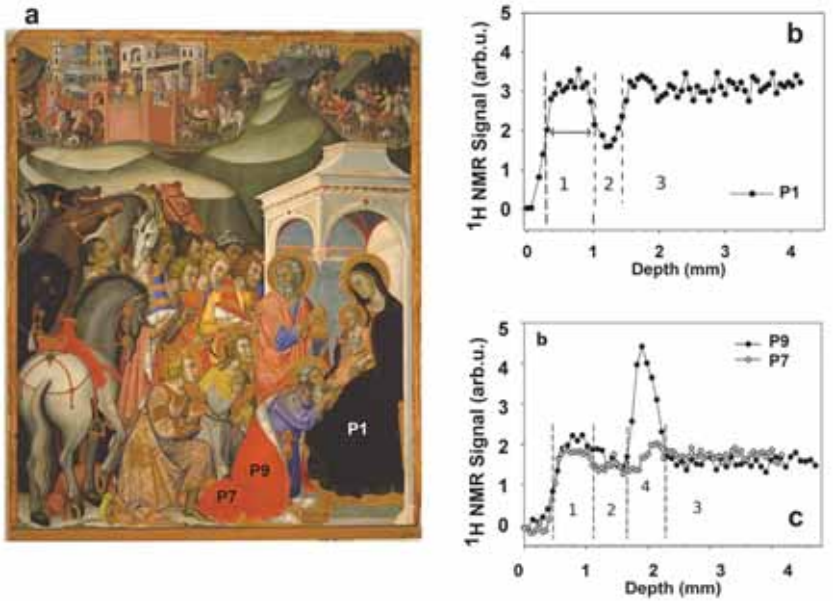


Figure 14 – The painting *Adorazione dei Magi* (1375-1385) by Bartolo di Fredi, Siena Picture Gallery (Italy) (a). ^{1}H nmR stratigraphies collected in P1 (b), and P7 and P9 (c). Adapted from [21].

an inert support to simulate the cleaning of a wall painting. The calcarenite specimen has been scanned before the cleaning treatment (UT), after coating with shellac and aging (T), and after cleaning (TC), see Figure 15.

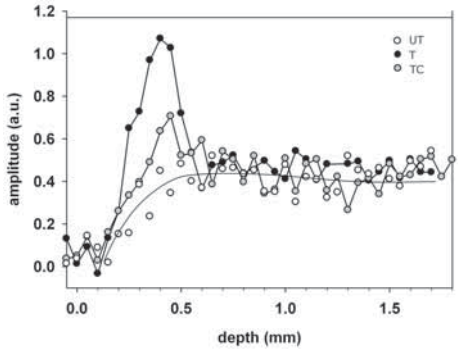


Figure 15 – ^{1}H nmR stratigraphy of untreated calcarenite (UT), calcarenite coated with shellac and aged (T), and calcarenite coated with shellac, aged and thereafter cleaned (TC). Adapted from [23].

Profiles show two layers, one, exclusively due to moisture in the porous structure, with a weak signal amplitude at a depth of more than 0.7 mm, where the three profiles merge together. Between 0.2 and 0.7 mm, the profile of the specimen coated with shellac shows a strong intensity due to the abundance of hydrogen atoms in

shellac. In the same depth range, the intensity of the profile of the specimen coated with shellac and thereafter cleaned has been found to be definitely weaker than before cleaning, due to a decrease in the hydrogen level of shellac. The profile of the untreated specimen was flat. The intensity of the profile between 0.2 and 0.7 mm indicates the efficiency of the cleaning treatment, the more effective the treatment, the lower the level of hydrogens encoded by the profile.

This method may be used to monitor the efficiency of any cleaning procedure aimed at removing any type of organic patina and to measure the thickness of the patina. Very recently this method has been successfully tested *in situ* [24].

2.5 Unilateral nmR to investigate consolidating and protective treatments on porous stones

Stones undergo weathering due to physical, chemical, mechanical, and biological degradation. Exfoliation, erosion, and detachment cause an extensive loss of material from stones. The weathering may also include discoloration, cracking, presence of salts efflorescence and biological colonization. Water is one of the major factors of degradation due to its ability to transport biological and chemical substances in and out of the material, and to cause cracking during wet-dry cycles.

Consolidation is an intervention carried out on stones affected by loss of cohesion in regions located near the surface with the aim of re-building it. The consolidation is usually carried out with the permeation of solubilized substances through the stone. Thereafter consolidation of the material occurs by different mechanisms such as solvent evaporation and chemical reactions. Protection is carried out to prevent the penetration of decay agents through the surface of the stone.

The compatibility with the stone is one of the main prerequisites for consolidating and protective agents.

New multifunctional treatments for stone conservation based on the combined use of TEOS (tetraethoxysilane) and colloidal inorganic (silica) and organic (polytetrafluoroethylene, PTFE) nanoparticles have been reported in literature [25]. These multifunctional treatments allow to exploit the functional properties of colloidal silica able to improve the consolidating efficiency of TEOS-based treatments, and those of colloidal PTFE whose hydrophobic and lubricant effects are well known in several industrial sectors.

Portable NMR has been applied to evaluate the penetration depth of consolidating treatments carried out on Yellow Neapolitan tuffs [25], their ability to impair water absorption, the possible presence of inhomogeneities in treated stones caused by sharp variations of the amount of the absorbed product, and how the treatment may change the open porosity of stones and may affect water diffusion through the porous matrix.

Volcanic tuffs played a fundamental role in the development of the Roman civilization. In fact, the ancient Romans made an extensive use of volcanic tuffs to construct infrastructures, such as bridges, roads, and aqueducts, crucial for the development of the Roman Empire. Since the use of these materials never ceased in the following centuries and is still continuing today, a huge number of monuments built with different

volcanic tuffs have been accumulated. Some are so important for the cultural heritage of Italy and the world that actions are taken to preserve them for future generations.

Volcanic tuffs are rocks composed of a consolidated ash matrix made of particles containing lithic (xenoliths of sedimentary origin and lava fragments), vitric (pumice fragments and glass shards), and crystal clasts (primary and accessory minerals) at different amounts. Large differences in texture and chemical and petrographic compositions are observed among tuffs. In addition to the relative content of clasts, also the nature of the matrix is different, and a broad distinction is made between welded and lithified tuffs. Lithified tuffs, such as Yellow Neapolitan tuffs, are rocks whose original ash matrix has undergone such profound chemical alterations, that authigenic minerals, mainly composed of zeolites, act as binding agents for the material.

Tuffs exposed to atmospheric agents are particularly prone to chemical transformations resulting in a progressive change of their physical, chemical, and geological properties. Because water and in particular wet drying cycling are known to be among the main causes of degradation of tuff, consolidating treatments with also a hydrophobic action are usually preferred in the case of tuffs.

^{1}H nmR depth profiles of tuffs have been measured on water-saturated tuff specimens scanning the specimen from the outer surface to a depth of 10 mm. Basically, the profile encodes the amplitude of ^{1}H nmR signal as a function of the depth scanned.

By way of example Figure 16 compares the profile of an untreated Yellow Neapolitan tuff and those of the same tuff after treatment with TEOS and PTFE nanoparticles (a), and after treatment with silica and PTFE nanoparticles (b).

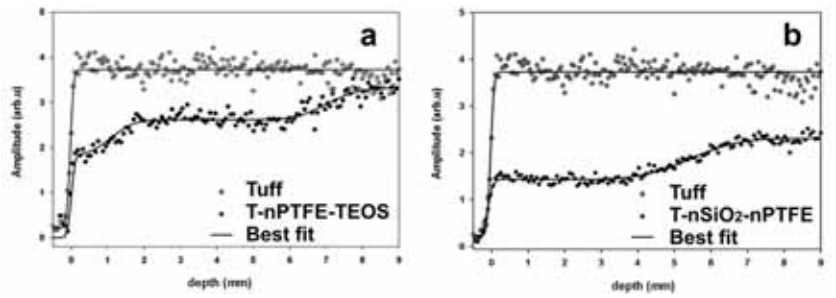


Figure 16 – ^{1}H nmR Depth profiles of untreated tuff compared with profiles of tuff treated with TEOS and PTFE nanoparticles (a), and with PTFE and silica nanoparticles (b). Adapted from [25].

The amplitude of profiles of treated tuffs was found to be definitely reduced with respect to that of the untreated tuff due both to the hydrophobic action of PTFE and pores coating effect that played a role in reducing water uptake. The two profiles have been fit to the following equation :

$$f(x) = \sum_{k=1}^{N} \frac{W_k}{2} \mathrm{erfc}\left[\frac{x_k - x}{\sqrt{2}_k}\right] + q_0 \quad (1)$$

where N is the number of transitions of the amplitude in the depth profile, x_k and $w_k/2$ are the abscissa and the ordinate of k component at the inflection point, respectively, and D_k is the half width of the transition of the amplitude from low to high value. The abscissa at the inflection point x_k is the penetration depth of the treatment, therefore a low x_k value corresponds to a shallow penetration depth of the treatment, while a high x_k value corresponds to a great penetration depth of the treatment. The solid lines through experimental points have been obtained from the best fit procedure. Obtained parameters are reported in table 1.

table 1. Parameters obtained fitting ^{1}H nmR depth profiles to equation (1), the coefficient of determination R^2 is also reported.

Note that the very initial part of the profile is due to surface effects being very close to the water-air-specimen interface, as a consequence parameters x_1, D_1 and w_1 that encode this part of the profile have been no longer considered in the following data discussion.

At penetration depths shallower than 5.42 mm, the amplitude of the profile of tuff treated with PTFE and silica nanoparticles is about one third than that observed in the case of untreated tuff, whereas at deeper depths an amplitude increase is observed followed by another flat region where the amplitude is about one half than that of untreated tuff, see Figure 16b.

The profile of tuff treated with TEOS and PTFE nanoparticles shows an overall amplitude reduction with respect to the profile of untreated tuff. With respect to untreated tuff, at depths shallower than x_2=1.1 mm, the treatment halves the amount of absorbed water. At deeper depths, an amplitude increase followed by a flat region is observed. At depths deeper than 7.03 mm the amount of absorbed water increases again, however remaining slightly lower than that observed in untreated tuff, see Figure 16a.

The slope at the inflection point b_k may be obtained from the first derivative of f(x) calculated at $x=x_k$:

$$b_k = \frac{\mathrm{df}(x)}{\mathrm{dx}}$$

The slope at inflection point encodes the amplitude variation rate of the profile, the steeper the change in slope the highest the b_k value. Moreover, the steeper the amplitude transition, and the more pronounced the inhomogeneity.

All parameters obtained allow the comparison among the different treatments. By way of example the profile of tuff treated with silica and PTFE nanoparticles shows just one amplitude variation with a slope b_2=0.33 mm^{-1}, whereas the profile of tuff treated with TEOS and PTFE nanoparticles shows two amplitude variations encoded by b_2=0.64 mm^{-1} and b_3=0.40 mm^{-1}. Therefore, in this specimen two regions have been detected, one close to the surface where the amount of absorbed water was rather low and another one at a deeper depth where the treatment was not sufficient enough to impair water absorption.

Conclusion

In recent years the interest of the scientific community in characterizing, monitoring and conserving objects belonging to cultural heritage has continuously increased along with the growing awareness that the characterization of artworks, the investigation of the causes of degradation of materials, and the development of new materials and methods for conservation are of fundamental importance in the safeguard of cultural heritage. Because artworks are complex heterogeneous materials, their study requires a methodological approach where micro-destructive, non-destructive, and possibly non-invasive techniques are combined.

In this context, the various examples of application of nmR methodologies for characterizing and monitoring cultural heritage reported here, though not exhaustive, demonstrate that nmR is not confined to a few specific applications, but can be successfully extended to a wide range of different issues regarding cultural heritage. The next promising applications will be the employment of the last recent nmR techniques such as solid-state dynamic polarization DNP and ultra-fast nmR, these techniques provide high resolution spectra requiring much less amount of sample with respect to the traditional nmR techniques.

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