How mobile NMR can help with the conservation of paintings

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1 | INTRODUCTION

The preservation of paintings is crucial to prevent the loss of important artistic information from our past and to ensure future generations will continue to have access to the works of art of past artists. Hence, many organizations and museums focus on protecting and preserving paintings and making sure they are accessible to as many people as possible. This field has captured interest around the world as scientists are getting involved in the diagnosis of degradation of artwork and prevention studies. Two main challenges need to be overcome to preserve the integrity of the object. First, to ensure its conservation and the prevention of its degradation while performing studies on it, a nondestructive method is needed with minimal, or, preferably, no sample collection. Second, the studied objects are often too precious and unmovable, thus taking them to a laboratory and perform studies on them there is not an option.[1–3]

For many decades, nuclear magnetic resonance (NMR) has been extensively used for chemical structure elucidation and materials characterization purposes.

Abstract

The conservation of paintings is fundamental to ensure that future generations will have access to the ideas of the grand masters who created these art pieces. Many factors, such as humidity, temperature, light, and pollutants, pose a risk to the conservation of paintings. To help with painting conservation, it is essential to be able to noninvasively study how these factors affect paintings and to develop methods to investigate their effects on painting degradation. Hence, the use of mobile nuclear magnetic resonance (NMR) as a method of investigation of paintings is gaining increased attention in the world of Heritage Science. In this mini-review, we discuss how this method was used to better understand the stratigraphy of paintings and the effect different factors have on the painting integrity, to analyze the different cleaning techniques suitable for painting conservation, and to show how mobile NMR can be used to identify forgeries. It is also important to keep in mind its limitations and build upon this information to optimize it to extend its applicability to the study of paintings and other precious objects of cultural heritage.

KEYWORDS

cultural heritage, mobile NMR, NMR-MOUSE, painting conservation, paintings, pigments, portable NMR, unilateral NMR
When mobile NMR sensors, such as the NMR-MObile Universal Surface Explorer (MOUSE)\textsuperscript{41} and the Bruker ProFiler,\textsuperscript{[4,5]} came into light as NMR tools for nondestructive characterization and study of cultural heritage objects, they became invaluable additions to the heritage scientist’s toolkit. Mobile NMR, also known as single-sided NMR, unilateral NMR, and portable NMR, is one of the first transportable stray field NMR sensors consisting of permanent magnets and surface coils used to excite and detect signals up to a distance of 25 mm from the magnet’s surface. These sensors can measure longitudinal ($T_1$) and transverse ($T_2$) relaxation times, proton density, and self-diffusion coefficients at different depths with a depth resolution as low as 10 $\mu$m.\textsuperscript{[1]} The main limitation of these sensors is that the resultant magnetic field is inhomogeneous, which restrains the type of NMR experiments that can be done; however, information relevant to cultural heritage can still be extracted from the experiments recorded with mobile NMR.\textsuperscript{[1,2,6]}

The two primary commercial mobile NMR sensors currently employed in cultural heritage studies are the Profile NMR-MOUSE\textsuperscript{®} and the Bruker ProFiler\textsuperscript{®}.\textsuperscript{[4,5]} Although both sensors are commercially available, there are certain different features that characterize each magnet. The Profile NMR-MOUSE, being a later development, brings forth specific improvements, both in the magnet geometry and its associated mechanical parts. Although the Bruker ProFiler is only capable of recording NMR experiments at certain defined depths—1, 3, and 5 mm—the Profile NMR-MOUSE has extended capabilities of recording the experiments at different depths in the sample with a micro-metrical resolution, thus enabling the full acquisition of depth profiles. This feature is very advantageous for analyzing precious objects of cultural heritage, allowing for the noninvasive characterization of the stratigraphy of the object.

Paintings are the artistic reflection of the artist’s mentality and views, and they often speak volumes about the times of their creation. Museums proudly display these valuable artistic pieces, making their understanding and preservation paramount. In that context, heritage science, through the various scientific studies done on paintings, provides details relevant for the conservation of those paintings. This would also ensure the showcasing conditions do not negatively affect their preservation. Moreover, forensic science is also employed in the study of paintings, where it is being used to detect forgeries. This review will discuss some of the work done using the unilateral NMR sensors mentioned above in several contexts regarding paintings, such as identifying stratigraphy, aiding in dating and cleaning of paintings, recognizing forgeries, and more.

2 | STRATIGRAPHY OF PAINTINGS

Pigments, binders, varnishes, and primers are some of the components of an intricate painting, making their study and identification vital to understanding the painting’s aging process and history. Consequently, this knowledge provides the documentation needed in selecting suitable conservation methods.\textsuperscript{[7]} The mobile NMR’s viability as a noninvasive tool for paintings study was first tested by Presciutti et al.\textsuperscript{[8]} who applied it to a series of old master paintings in Italy to differentiate between the different layers and to measure the thickness of each layer. This was done by observing the differences in proton densities as a function of depth in order to study the stratographies and then, using the relaxation times to differentiate between original and artificial binders. Several other distinguished research groups, as illustrated in the following examples, utilized this concept.

Proietti et al.\textsuperscript{[9]} utilized portable NMR to assess the state of degradation and pinpoint its location on the Moon Surface painting in Rome before recommending a restoration method. The data obtained showed a discrepancy in the length of the longitudinal relaxation time in different regions, from which samples were collected for solid-state NMR analysis. The results obtained linked a shorter relaxation time to a higher degradation of constituent polyurethane, thus, pinpointing regions of higher degradation.

Marchettini et al.\textsuperscript{[10]} used mobile NMR to study a 14th century painting, Adorazione dei Magi, and to characterize the pictorial technique of the artist. Proton densities taken at different depths, starting from the surface and moving to a depth of 5 mm, allowed the identification of three distinct layers consisting of pigments and binders, a preparatory foundation layer, and finally, the wooden back. Intensities collected in several regions of the painting showed consistency between the first two layers but not the third. This difference can be attributed to the potential biologically induced deterioration of the wooden layer. Further studies are still being done on this painting to better understand the techniques used in creating this painting.

Tullio et al.\textsuperscript{[11]} used portable NMR to differentiate between the original (14th century), repainted (16th century), and potentially removed regions during repairs (20th century) of a wooden Sienese painting belonging to a lost Polyptych by Andrea di Bartolo. Understanding these different layers from different eras can aid the conservation and restoration of the painting. Transverse relaxation time ($T_2$) measurements helped identify the three constituent layers of binder, primer, and wood. The degradation is observed by analyzing the transverse relaxation times, its effect being seen through a shortening of the $T_2$.
similar to the results published by Prioetti et al. Comparing the data obtained in this study to that of the Adorazione dei Magi leads to the identification of the pictorial techniques and painting materials used by the artists.

Furthermore, Prioetti et al.\textsuperscript{[9]} used portable NMR to identify the origin and to date the different layers of a Byzantine icon attached to a wooden panel. Examining the proton density allowed the identification of three different painting layers belonging to three different times of creation of each layer. The surface of the icon, which was initially thought to be a copy of the Madonna Hodigitria, was dated to the 19th century; however, a second painting underneath it was dated back to the 13th century, and finally, the last one, making up the painted faces of the Virgin and Child’s mantle was dated to the 5th century. Further examination of the Virgin and Child’s faces showed that only that segment was removed from the original painting and glued onto the wooden support.\textsuperscript{[7]} All these studies indicate that portable NMR is an excellent tool for the noninvasive characterization of stratigraphy and understanding the painting techniques and materials, which can help with the conservation and restoration procedures.

Similarly to the study of oil paintings, single-sided NMR can also be applied for the study of wall paintings. It is important to preserve and protect wall paintings that can be affected by uncontainable environmental conditions. It has been proven to be a valuable tool in distinguishing layers of detached mural paintings, known as strappo. In this process, the painting is detached and fixed to the new support. The challenge with this technique is that it can be difficult to identify the materials used during the process, as they all become part of the artifact. Thus, Tullio et al.\textsuperscript{[12]} used solid-state NMR and portable NMR to detect and identify the materials of different layers of a separated Nubian strappo. Relaxation times and proton density data, obtained through single-sided NMR measurements, helped reduce the invasive sampling needed for the solid-state NMR experiments used to identify the organic materials present in each layer and to distinguish the original from the other strappo constituents. Interestingly, six layers were identified, with only the first one belonging to the original painting and the others having been added during the process of removing the painting from its original place and placing it on its new backbone.

Similarly, Prioetti et al.\textsuperscript{[13]} applied proton NMR depth profiling to an ancient strappo Nubian painting from Sudan dated to the 10th century. The resulting data were compared with the ones acquired from other Nubian paintings from churches around the world and found that the artists used indigenous materials for paintings and that they had undergone similar strappo processes. The variation in proton density in the recorded depth profiles indicated the presence of six different layers. The first layer displayed the highest inconsistency due to variability in the level of materials used for the consolidation of the different regions. Following this study, a protocol was established that diminished the need for invasive studies to analyze the multifaceted strappos.

Another case where the single-sided NMR has been successfully applied to study the layered structure of wall paintings is the fresco La Madonna della Carcere in Volterra, research conducted by and Blümich et al.\textsuperscript{[14]} This was done by analyzing the proton density and mobility in different layers of the wall paintings, which made possible the identification of the adhesive layer present beneath the paint layers, both for the original painting and for the restored one. This study illustrates how mobile NMR is a great tool to study wall paintings, revealing details about their stratigraphy with the potential of discovering hidden wall paintings.

### 3 | PAINT LAYER INSIGHTS

The analysis of pigments along with knowledge of the factors affecting the painting’s films and pigments can be used to assess the aging of the painting and, by extension, to help identify if it is a forgery or not based on the different aging processes in naturally versus artificially aged paintings. Single-sided NMR provides a noninvasive method of collecting pigment and film data without the need to remove samples from the paintings. The various factors leading to aging have been examined by several research groups, as exemplified below.

Udell et al.\textsuperscript{[15]} studied the effects of using linseed oil and water-mixable oil paint on the rate of paint film curing by studying the physical and chemical properties of the films. In this research study, they evaluated multiple paint samples with varying compositions and aging degree in order to record the corresponding curing times and extent of curing. It was noted that the use of water-mixable oil paints containing an emulsifier reduced the curing rate, compared with paints that did not have an emulsifier, and resulted in less cross-linked paint films at different time intervals. Additionally, the higher permeability of water into young paint films (1 month) compared with aged films (2–50 years) was observed by Angelova et al.,\textsuperscript{[16]} providing further insight into the swelling process of paint and how differently aged films behave when exposed to water. The water moisture content at different depths was analyzed using unilateral NMR. The data were used to assess the water’s penetration into different paint film-coated canvas through five different surface conservation treatments. The difference
Aging is a normal process that all artwork undergoes due to exposure to environmental factors such as temperature, humidity, lighting, and pollutants. However, art forgers use techniques like ironing or baking to accelerate the aging and to mimic the natural aging process. In a recent paper, Blümich[20] discusses how artificial aging leads to physical changes in the pigment binders, making them more brittle. The author then describes how portable NMR could be used to identify forgeries based on the observed differences in $T_2$ relaxation times between naturally and artificially aged pigments. In his paper, he studied and compared values obtained from naturally aged paintings to those of forgeries created by the talented forger Wolfgang Beltracchi, concluding that—artificially aged pigments were more brittle with the pigments having comparatively shorter $T_2$ values. Studies on pigments and varnishes have seen a growing interest in forensics science, and historical dating of paintings as studying the aging process can help answer many unanswered questions about the provenance of paintings.

4 | CLEANING OF PAINTINGS

The cleaning process of paintings is an incredibly delicate process that is essential for the removal of potentially damaging layers such as salt deposits or crusts. Classically, the cleaning methods rely heavily on the use of water, and designing new chemical gels to reduce solvent penetration into the artwork is crucial for painting conservation. Targeting of specific stains or deeper contaminiates is being actively researched, with silicates, cellulose, and gelling materials being some of the most common constituents of thickeners. Single-sided NMR can be used to test the mobility of water in some of these materials, like the gels, and in examining the efficacy of different gel formulations in cleaning wall paintings, as done by Proietti et al.[21] Transverse relaxation times of the gels obtained nondestructively using portable NMR showed that water was found in two states: bound water (shorter relaxation time) and free water (longer relaxation time). The group evaluated the efficacy of different cleaning gels based on the proton depth profiles corresponding to the water penetration at different depths. The study concluded that Carbogel gel released the most water, whereas the Gellan gum released the least amount of water, making the latter a better treatment option. Furthermore, they studied the changes in the depth profile signals before and after applying the cleaning treatments to paintings to examine shellac removal and how different techniques affect the thickness of the deposited shellac layer. The reduction in the thickness represented by a weaker post-treatment hydrogen signal was used as an indicator of its removal and of the success of the cleaning treatment.[22]

Understanding how varnishes and film layers affect the treatment of a painting is essential in establishing the best practices for the conservation of the painting. Fife et al.[23] used portable NMR to examine the effect varnishing has on the stiffness of paintings and how it is influenced by the type of treatment solvents used. In their paper, the authors examine the effect solvent-based treatments have by using two paintings The Dinner and The Dance, both of which created by the same artist using the same material and techniques, with the sole difference being that The Dinner, unlike The Dance, underwent several varnishings and varnishing removals. $T_2$ measurements were used to test the extent of solvent penetration on model paintings undergoing different treatments. Two different solvents were tested: free solvent and cellulose gel thickened solvent. This study concluded that the gradient of $T_2$ suggests the stiffness of The Dinner painting and this could be due to the entry of organic solvents and the deposition of resin in the different painting layers during treatment. Additionally,
it was observed that the free solvent affects a wider region of the model, and similarly to the thickened-solvent case, the signal intensity could be used to extract information related to the solvent penetration in painted surfaces.

Cleaning of paintings in such a way that only the layer of grime present on their surface is removed, without interacting with the paint film, is a constant challenge. To assess the solvent penetration and retention during cleaning using different biodegradable solvents and gels, Prati et al.\[24\] proposed a procedure to do this with the least solvent paint film interaction. The role of mobile NMR in this study was to monitor the solvent penetration and retention into the paint film on mock paintings and on a 19th century painting and help assess the best type of cleaning solvents and their optimum concentrations. They also observed that gels reduce solvent penetration and retention and that gels are less harsh on the paintings, compared with other methods.

The cleaning substances used for paintings must be friendly not only to the painting but also to the environment. One cleaning option that fulfills these conditions is the use of gels. Doherty et al.\[25\] proposed another protocol for replacing invasive surface-enhanced Raman spectroscopy (SERS) active gels substrates with the water-soluble active methylcellulose gels, such as MC4000 and MC400. Portable NMR was used to monitor the penetration and removal of the gels from painted surfaces and to study the effect this procedure had on the painting. They found that upon the application of the active methylcellulose gels, an additional layer formed on the painting. According to the NMR measurements, there was no penetration of the gel into the paint layer. The removal of these gels did not decrease the depth of the paint layer, making this method relatively nondestructive. The use of poly-3-hydroxybutyrate (PHB) made from relatively non-poisonous constituents was proposed by Samori et al.\[26\] as another environmentally friendly gel. According to their study, the PHB gel had high efficacy in cleaning the painting without penetration into its layers and can be disposed of by simply dissolving it in water.

Through measurements of NMR parameters of samples that contain hydrogen atoms. With these sensors pretuned to the hydrogen resonance frequency, they are only able to analyze samples containing hydrogen. However, these atoms are present in paintings, in different quantities, depending on which layer of the painting is examined. That is precisely the information revealed by the proton density profiles, which provide stratigraphies based on the density of protons in different layers, where the topmost layers containing the different paint layers can be observed due to the presence of hydrogen atoms in the binders used to mix the pigments. Other methods of obtaining stratigraphies, such as microscopy, are available; however, the Profile NMR-MOUSE is capable of revealing this information in a noninvasive way. This is one of the major advantages of mobile NMR. Nevertheless, this advantage is only when the sample contains hydrogen atoms, leading to one of the limitations of these sensors, which is that mobile NMR is currently unable to see other nuclei. Ideally, a technique used in cultural heritage should be multi-elemental, as is the case with X-ray fluorescence, a technique widely used in paintings research, capable of providing concurrent information on several nuclei during one measurement. With future technological improvements, it would be ideal to have the mobile NMR sensors able to record experiments on other high natural abundance nuclei, which could complement the results obtained through proton measurements.

When researching a painting, it is important to extract the most detailed information possible from the entire object. This is where an excellent resolution is crucial. Although the Profile NMR-MOUSE is capable of acquiring experiments with a depth resolution of 10 μm, improvements in the resolution would be required to match the capabilities of other methods. These advancements would enable the higher accuracy stratigraphy information, especially for the cases when the paint layers are very thin. Moreover, these developments, coupled with the development of more advanced sensor positioning systems that would allow for the positioning of the sensor in X, Y, and Z directions, could provide a much more complete picture of the investigated painting.

In the end, although mobile NMR has shown many advantages in studying paintings, improvements can be made in this field to take advantage of even more information that these sensors could provide. Ideally, mobile NMR research should be used in combination with other, preferably noninvasive techniques, such as X-ray fluorescence, Raman, and IR spectroscopy, in order to provide the most comprehensive details of the studied object.

5 | ADVANTAGES AND LIMITATIONS OF MOBILE NMR

The case studies exemplified throughout this mini-review illustrate the broad range of mobile NMR sensors' application to various aspects of paintings research. They illustrate the use of this technique in obtaining information about the stratigraphy of the painting, the analysis of the paint layer, and the cleaning of paintings. How do the mobile NMR sensors provide all this information?
6 | CONCLUSION

In conclusion, on multiple occasions, mobile NMR has proven its value in nondestructively and noninvasively aiding in the study and subsequent preservation of paintings. It is paramount to not only utilize the current techniques available for conducting studies but also to actively work on optimizing and advancing the research methods applicable to cultural heritage objects. However, there are still several limitations that need to be taken into account, namely resolution, limited automation, and acquisition time dependency on coil sensitivity.[1] Efforts are being made to optimize it further, such as the automation of the comparison between different depth profiles of different samples acquired nondestructively by the device, which will significantly reduce the user time needed to process a large data set. This could be extrapolated in the future to include different comparable parameters like the $T_2$ relaxation time, which this review has shown to be a very useful parameter in analyzing paintings.[27]

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REFERENCES
[1] M. Baias, Magn. Reson. Chem. 2017, 55, 33.
[2] B. Blümich, F. Casanova, J. Perlo, F. Presciutti, C. Anselmi, B. Doherty, Acc. Chem. Res. 2019, 43, 761.
[3] M. Baias, B. Blümich, in Modern Magnetic Resonance, 2018, pp. 1–13.
[4] J. Perlo, F. Casanova, B. Blümich, J. Magn. Reson. 2005, 176, 64.
[5] C. Casieri, S. Bubici, F. De Luca, J. Magn. Reson. 2003, 162, 348.
[6] C. Rehorn, B. Blumich, Angew. Chem. Int. Ed. Engl. 2018, 57, 7304.
[7] N. Proietti, D. Capitani, V. Di Tullio, Sensors (Basel) 2014, 14, 6977.
[8] F. Presciutti, J. Perlo, F. Casanova, S. Glöggler, C. Miliani, B. Blümich, B. G. Brunetti, A. Sgamellotti, Appl. Phys. Lett. 2008, 93.
[9] N. Proietti, V. Di Tullio, D. Capitani, R. Tomassini, M. Guiso, Appl. Phys. A 2013, 113, 1009.
[10] N. Marchettini, A. Atrei, F. Benetti, N. Proietti, V. Di Tullio, M. Mascalchi, I. Osticioli, S. Siano, I. Turbanti Memmi, Surf. Eng. 2013, 29, 153.
[11] V. Di Tullio, D. Capitani, A. Atrei, F. Benetti, G. Perra, F. Presciutti, N. Proietti, N. Marchettini, Microchem. J. 2016, 125, 208.
[12] V. Di Tullio, D. Capitani, F. Presciutti, G. Gentile, B. G. Brunetti, N. Proietti, Anal. Bioanal. Chem. 2013, 405, 8669.
[13] N. Proietti, V. Di Tullio, F. Presciutti, G. Gentile, B. G. Brunetti, D. Capitani, Microchem. J. 2016, 124, 719.
[14] B. Blumich, A. Haber, F. Casanova, E. Del Federico, V. Boardman, G. Wahl, A. Stilliano, L. Isolani, Anal. Bioanal. Chem. 2010, 397, 3117.
[15] N. A. Udell, R. E. Hodgkins, B. H. Berrie, T. Meldrum, Microchem. J. 2017, 133, 31.
[16] L. V. Angelova, B. Ormsby, E. Richardson, Microchem. J. 2016, 124, 311.
[17] V. Di Tullio, N. Zumbulyadis, S. A. Centeno, J. Catalano, A. M. Wagner, C. Dybwodski, ChemPhysChem 2019, 20, 1.
[18] R. Hendrickx, E. S. Ferreira, J. J. Boon, G. Desmarais, D. Derome, L. Angelova, D. Mannes, A. Kaestner, H. Huinink, K. Kuipers, B. Voogt, Stud. Conservat. 2017, 62, 393.
[19] K. Ulrich, S. A. Centeno, J. Arslanoglu, E. Del Federico, Prog. Org. Coat. 2011, 71, 283.
[20] B. Blümich, Concepts Magn. Reson. A 2019, 47A, e21464.
[21] M. Bertasa, T. Poli, C. Riedo, V. Di Tullio, D. Capitani, N. Proietti, C. Canevali, A. Sansonetti, D. Scalarone, Microchim. J. 2018, 139, 306.
[22] N. Proietti, D. Capitani, V. Di Tullio, Magnetochemistry 2018, 4, 11.
[23] G. R. Fife, B. Stabik, A. E. Kelley, J. N. King, B. Blumich, R. Hoppenbrouwers, T. Meldrum, Magn. Reson. Chem. 2015, 53, 58.
[24] S. Prati, G. Sciutto, F. Volpi, C. Rehorn, R. Vurro, B. Blümich, L. Mazzocchetti, L. Giorgini, C. Samori, P. Galletti, E. Tagliavini, R. Mazzeo, New J. Chem. 2019, 43, 8229.
[25] B. Doherty, F. Presciutti, A. Sgamellotti, B. G. Brunetti, C. Miliani, J. Raman Spectrosc. 2014, 45, 1153.
[26] C. Samori, P. Galletti, L. Giorgini, R. Mazzeo, L. Mazzocchetti, S. Prati, G. Sciutto, F. Volpi, E. Tagliavini, Chem. Select 2016, 1, 4502.
[27] C. Rehorn, C. Kehlet, E. Del Federico, W. Zia, T. Meldrum, B. Blümich, Strain 2018, 54, e12254.

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