Analytical and Bioanalytical Chemistry (2020) 412:1063–1075
https://doi.org/10.1007/s00216-019-02331-x

RESEARCH PAPER

Single-sided NMR: a non-invasive diagnostic tool for monitoring swelling effects in paint films subjected to solvent cleaning

Patrizia Moretti[1,2] · Laura Cartechini[1] · Costanza Miliani[3]

Received: 9 October 2019 / Revised: 26 November 2019 / Accepted: 4 December 2019 / Published online: 21 December 2019

Abstract

During solvent cleaning of a painted surface, the control of solvent diffusion into the painting matrix is a primary concern for conservators. In this work, a comparative systematic study of solvent ingress and of the ensuing swelling phenomenon in paint films due to cleaning treatments was tackled using single-sided NMR. Specifically, the effects of a TAC aqueous solution (triammonium citrate in deionized water) applied in both free and gelled forms (by Klucel® G) on acrylic emulsion and vinyl-based model paints were evaluated. Notably, the NMR measurements (proton spin density depth profiles and transverse relaxation decays) collected before, during, and after these wet-cleaning tests proved that the use of the aqueous gel did not significantly minimize the penetration and the swelling action of water compared with the free solution. Furthermore, swelling effects associated with the use of an organic solvent (ligroin) were evaluated by NMR profilometry on varnished oil and egg-tempera paints. In this case, by comparing the depth profiles collected before and after the solvent treatments, a moderate paint swelling was observed followed by a width reduction of the paint films ascribable to the removed varnish layer.

Overall, the reported NMR results reveal the analytical potentialities of the technique for a non-invasive assessment of the swelling effect of paint films subjected to cleaning (by water or an organic solvent), thereby providing an analytical method in support to the conservators' practice.

Keywords Single-sided NMR · Cleaning of paintings · Swelling · Solvent penetration · Non-invasive monitoring

Introduction

The risks associated with the use of solvents in the cleaning of paintings represent a persistent concern for conservators; therefore, since many years, considerable scientific interest towards this complex issue has been shown. One of the most harmful and encountered effects of solvent cleaning on paint films is swelling. It results from the sorption of the solvent by the paint film that can potentially produce softening of the organic binder, and thus increase the vulnerability of the paint to pigment loss, especially by the mechanical action of swabbing. For several decades, the investigations by N. Stolow on the swelling power of various organic solvents on oil paint films have represented the primary reference source to evaluate this phenomenon [1, 2 and references therein]. Specifically, these swelling data were defined by measuring change in thickness of pigmented and un-pigmented aged oil films on glass supports with a specially designed non-contact instrument [3]. Thereafter, different other analytical approaches have been developed for evaluating the swelling power of several solvents (organic solvents and water) on oil and acrylic paint films; these include gravimetric measurements [4], microscopy methods [5–7], and interferometric techniques [8]. However, these analytical methods are not exhaustive to determine water penetration and swelling effects, and furthermore, although non-destructive, cannot be exploited for in situ investigations.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00216-019-02331-x) contains supplementary material, which is available to authorized users.

✉ Laura Cartechini
laura.cartechini@cnr.it

[1] Istituto CNR di Scienze e Tecnologie Chimiche (CNR-SCITEC), Via Elce di Sotto 8, 06128 Perugia, Italy

[2] Present address: Department of Environment, Constructions and Design (DACD), University of Applied Sciences and Arts of Southern Switzerland (SUPSI), Via Trevano, 6952 Canobbio, Switzerland

[3] Istituto CNR per le Scienze del Patrimonio Culturale (CNR-ISPC), Via Cardinale Guglielmo Sanfelice 8, 80134 Naples, Italy

More recently, non-invasive single-sided nuclear magnetic resonance (NMR) was successfully proposed to investigate paint swelling effects due to solvent penetration, primarily in relation to water cleaning systems. The technique is, in fact, able to provide information about mobility and density of ^{1}H nuclei that can be measured in a sample as a function of the depth (depth profiles) and used for diffusion studies [9]. This information demonstrated to be of great relevance in the heritage science field for non-invasive characterization of paint stratigraphies in master paintings, measurement of the moisture content and profiles in mural paintings and mosaics, or monitoring of stone conservation treatments [10–12].

Concerning swelling studies, single-sided NMR was firstly used to investigate water diffusion into acrylic paints [13]. It is well known, in fact, that aqueous and other polar solvent-based cleaning treatments can significantly impact on this type of paints [14], leading to softening, whitening, and loss of adhesion. This is due to the fact that acrylic paints are made from water-based polymer dispersions and after the drying process form films particularly permeable to water and polar solvents. Furthermore, in modern and contemporary paintings, they are generally applied without a protective varnish coating, and this brings additional risks for the painting surface.

In particular, unilateral NMR was exploited by Angelova et al. in ref. [15] to measure differences of water penetration into acrylic paint films following the application of a range of aqueous gelled systems, used in this study to better control the delivery of liquid with respect to the use of the free solvent. More specifically, the aqueous methylcellulose paste, Pemulen-TR2 and 80PVAc-borax gels, therein tested, were found to allow much higher water ingress into the paint film than that observed in cleaning simulations performed with water-moistened swabs or agar gel. Notably, these data were in disagreement with those obtained in another study [16] by weight measurements of acrylic emulsion-based paints subjected to immersion in deionized water or to swabbing with wet-cleaning systems in both free and thickened forms (Vanzan® and Klucel® G).

Single-sided NMR was also used to visualize and quantify the spatial and temporal distributions of water in reconstructed oil paintings on canvas exposed to different environmental RH% or put in direct contact with water [17].

Preliminary NMR experiments have been also performed to measure penetration effects of organic solvents in traditional oil model paints after cleaning treatments with both free and thickened solutions [18]. Single-sided NMR was, then, applied to study long-term effects of cleaning tests (measurements 1 week after the treatments) made by use of organic solvent- and aqueous-based gels to remove a degraded PVA restoration paint from the alkyd original layer of a sculptural environment fragment [19].

More recently, NMR relaxometry was proposed in combination with solid-phase microextraction (SPME) and FT-IR spectroscopy to follow varnish removal from oil paints using green solvents in innovative gel formulations [20]. The study was aimed at evaluating entry and retention of the solvent in the paint layer during time spans of hours and investigating modifications of the elasticity of the binder after the treatments.

The limited number of these early studies has shown that NMR-MOUSE is a very promising technique to monitor the penetration of solvents—in particular water—into paint films during cleaning treatments and to study long-term effects on mechanical properties of the material (change in stiffness and embrittlement). Nevertheless, the great disparity of the tested systems and materials and some incongruences of the obtained results from different researches clearly evidence the need for a more methodical analytical NMR approach to produce comparable experimental findings.

In this paper, a systematic study by single-sided NMR investigations of simplified model paints cleaned in controlled way has been carried out to develop a reproducible analytical methodology enabling comparable measurements of water penetration into the paint film using free and thickened aqueous solutions. Specifically, NMR measurements (proton spin density depth profiles and transverse relaxation decays) were performed in a non-invasive way before and at different time intervals after wet-cleaning simulations on two types of synthetic paint films: acrylic emulsion paints, herein used as term of comparison with similar previous NMR studies cited above, and vinyl-based paints that, so far, have received much less attention by scientific community about cleaning effects [16].

Furthermore, preliminary results are here reported on the use of single-sided NMR to investigate the solvent effects caused by the use of an organic solvent on varnished paints. In particular, the feasibility of the technique has been explored to follow solvent penetration and paint swelling using ligroin for the removal of a natural varnish applied to models of oil and egg-tempera paints.

In all the NMR experiments here presented, homologous paint samples and reproducible cleaning procedures were carefully used in order to have thoroughly comparable measurements for correct interpretation of the results. It is worth to say that the study of the solvent cleaning effects on long-term physical and mechanical changes of the investigated paints was out of the scope of this research, as NMR relaxometry has been already demonstrated to be particularly suitable for this application [18, 20].

Materials and methods

Model paints

A set of paint mock-ups were produced in duplicate on glass slides in order to have a support free of hydrogen protons detectable by NMR. Specifically, modern ready-made paints of titanium white mixed with acrylic emulsion (Liquitex) or vinyl (Flashe – LeFranc & Bourgeois) were employed to assess the swelling effect due to aqueous cleaning systems. Cleaning experiments were executed on the acrylic emulsion and vinyl paints about 2 months after their preparation, when touch-dry. The effects of organic solvents were, instead, studied on mock-ups with a finishing layer of dammar (Maimeri) applied on touch-dry paint films made of lead white (Sigma-Aldrich) in mixture (1:1 wt%) with the traditional binders whole egg and cold-pressed linseed oil (Zecchi). Varnish was left to dry about 2 months for egg and 8 months for oil before the NMR study.

Cleaning systems

For the modern paint samples (acrylic and vinyl paints), an aqueous solution containing triammonium citrate (TAC) in free and gelled forms, with hydroxypropylcellulose (Klucel® G) as thickener, was tested. The use of TAC was motivated by the results obtained by Ulrich et al. [13] that observed a decrease in water penetration into acrylic paint films by adding a salt (NaCl and ammonium citrate dibasic). In detail, 0.25 g of powdered TAC (Sigma) was dissolved in 25 mL of deionized water and used as free solution or gelled adding 1.25 g of Klucel® G (CTS) (formulations according to refs. [21, 22]).

The swelling effects in traditional varnished oil and egg paints were investigated using ligroin (100–140 petroleum ether, Bresciani) as cleaning solvent. Specifically, this organic solvent was selected for its lower evaporation rate compared with other solvents generally used in the cleaning practice [23].

Profile NMR-MOUSE

NMR measurements were performed using a portable and non-invasive profile NMR-MOUSE® (Bruker Minispec) interfaced with a single-sided sensor developed by the RWTH Aachen University (Germany) [24].

The sensor consists of a U-shaped permanent magnet arrangement able to generate, in the probed area and 3 mm away from the radiofrequency (RF) coil, a static magnetic field with an extremely uniform gradient. The working frequency is 17.6 MHz. The NMR signal is collected from a thin slice centered 5 mm above the device and parallel to its surface, where the field strength is 0.411 T and the gradient is 20 T/m perpendicularly to the scanner surface. The slice volume, about 10×10 mm^2 along the lateral directions, depends on the geometry of the radiofrequency coil of the sensor, while the measurement parameters determine the thickness in the depth direction (*range* from 180 to 2.3 μm). The sensor is mounted on a stepper-motor driven lift that allows shifting the sensitive volume in small steps and with a maximum spatial resolution of 10 μm through the sample's depth up to 3 mm inward. For each slice, the magnetization decays (longitudinal (T_1) and transverse (T_2) relaxation decays) of ^{1}H are collected with a multi-echo train by a CPMG (Carr, Purcell, Meiboom, and Gill) sequence [25]. For simplicity, the effective transverse relaxation time $T_{2,\mathrm{eff}}$ measured and discussed in this paper, is denoted as T_2. In NMR profilometry, the transverse decay time T_2 is generally used to have an estimation of the molecular mobility in the materials as that due, for example, to translational motion of molecules in liquids present in the cavities/pores of the sample matrix. Low mobility correlates with short T_2, while fast mobility with high T_2 [10]. In this study, T_2 values were extrapolated using a mono-exponential fitting curve for the dry paint films and a bi-exponential fitting curve for the treated samples in order to separate the contributions of the paint film (T_2 short) and of the penetrated water (T_2 long).

Furthermore, T_2 signal strengths depend on the density of the H nuclei; thus, the plot of the measured signal—reduced through partial integration of the echo envelope to a T_2-weighted proton spin density value within the sensitive volume—as a function of the explored sample thickness defines its NMR depth profile. The depth profile, generally, allows counting the number of layers of a paint stratigraphy (if they display different proton densities) and to estimate the thickness of each one, compatibly with the spatial resolution of the technique [10]. In this study, the intensity of each experimental point in the shown depth profiles is obtained from the average of the first four echoes intensity in the acquired echo train.

Reflection FT-IR spectroscopy

In support to the NMR study, reflection FT-IR measurements were performed for the assessment of the varnish removal from the oil and egg paints with a compact portable FT-IR spectrometer (ALPHA, Bruker Optics, Germany/USA-MA) equipped with a SiC Globar infrared radiation source, a Michelson interferometer (RockSolid™ design), and a room-temperature DLaTGS detector.

Non-invasive FT-IR analyses were carried out by an external reflectance module with specular optics (22°/22°) that allows collecting the infrared radiation reflected from a surface at about 1 cm of distance. Sampling areas of ca. 3 mm in diameter were focused through an integrated USB high-

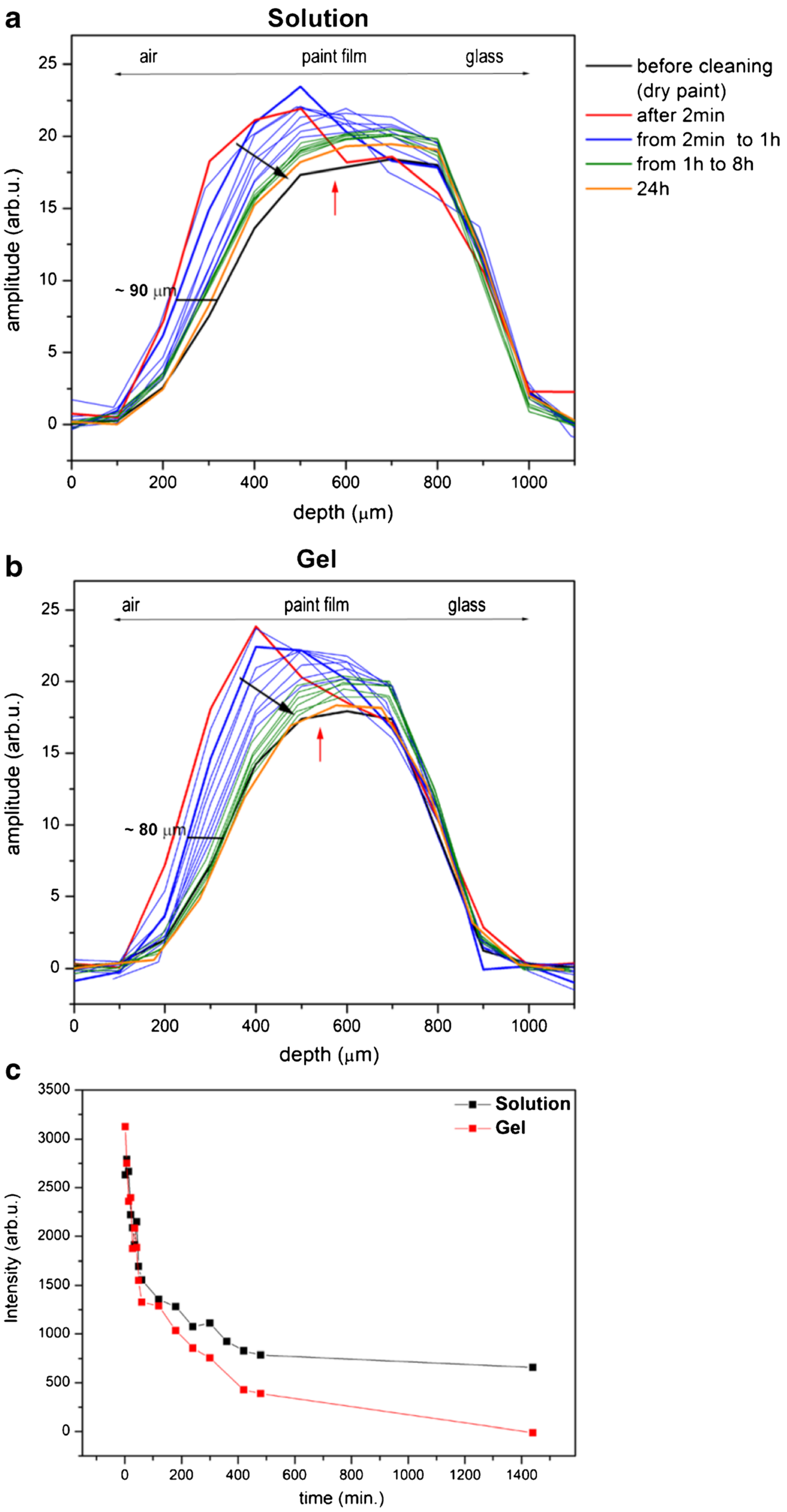

Fig. 1 Depth profiles collected on the acrylic emulsion model paint for the **a** solution and **b** gel cleaning tests (the same legend as for **a**). The water diffusion trend (black arrows) and the estimated swelling effect (calculated with respect to the FWHM) are shown. Red arrows refer to the depth selected for the acquisition of the CPMG decay curves. **c** Difference plots calculated as difference between the areas of the depth profiles collected after the two cleaning tests at different time intervals and the depth profiles collected before them (dry paints)

resolution video camera, and reflectance spectra, expressed in pseudo-absorption units [A′ = log(1/*R*); *R* = reflectance], were collected in the spectral range from 7000 to 375 cm^{-1}, with a spectral resolution of 4 cm^{-1} and using an average of 186 scans. Spectra from a flat gold mirror were used for the background correction.

Experimental methodology

In NMR depth profiles, the presence of a solvent in the paint film produces a detectable increase of the hydrogen proton density that is plotted as a function of the sample depth (see as example in Fig. 1a). In this way, the distribution of the solvent along the sample thickness is determined with micrometric spatial resolution. Furthermore, the increase of the film thickness owing to the formation of more free volume to accommodate the solvent molecules produces an enlargement of the depth profile which in turn provides an estimation of the paint swelling. In addition, measurements of variations in transverse relaxation decay profiles (T_2) collected at a fixed sample depth can be also related to the presence of the solvent.

In this study, two types of single-sided NMR setups were used for the modern and traditional model paints, respectively.

To quantitatively monitor the presence of water into the modern paint samples, depth profiles and transverse relaxation decays were measured before and after the application of the aqueous cleaning systems. Each model paint was placed on top of the device with the painted side facing outwards and fixed by means of adhesive tape to avoid possible shifts during the cleaning tests. These were carried out by the same person through gentle swabbing (40 mg of cotton per swab), using the same amount of deionized water (250 μL) for both solution and gel, as well as the same application time (1 min) and area dimension in order to obtain thoroughly comparable results. The gel was applied by cotton swab, and it was removed by using two dry swabs after 1 min of contact with the painted surface. The common procedure of wet clearance of the gel, instead, was intentionally avoided to obtain a direct comparison between the amount of water penetrated into the paint films from the free solution and its thickened form.

To yield consistent and meaningful results, each NMR experiment encompassed measurements of depth profiles and transverse relaxation decays on different areas of the same model paint tested for the two different treatments: free solvent or gel system. Reproducibility and accuracy of the measurements were validated by repeating each experiment twice using model paint replicas (results are shown as Supplementary Material).

NMR measurements of depth profiles were acquired by setting echo time = 0.034 ms and relaxation delay = 0.2 s and varying the number of scans. Specifically, before each wet-cleaning test, a single profile of the untreated dry paint film was recorded with 512 scans, while for the post-treatment profiles, a range of scans from 16 to 512 was progressively set to monitor over time the presence of water into the paint film. The shorter acquisitions (worse signal-to-noise ratio) were used immediately after the wet-cleaning treatments to follow water penetration in a short time span. The NMR-probed volume was moved through the thickness of the samples by steps of 100 μm with a resolution of 200 μm. According to these setting parameters, at each step, the probed volume was about 20 mm^3 with partial overlapping between successive measurement steps.

Transverse relaxation decays (CPMG echo decay curves) were collected on homologous areas of the same model paint sample and using the same cleaning procedure as that for the measurement of the related depth profiles. CPMG decay curves were collected maintaining the lift position fixed at specific depth beneath the painted surface selected on the basis of NMR depth profiles (selected depth indicated with a red arrow in Figs. 1a, b and 3a, b). Specifically, the CPMG decay curves were recorded on the untreated samples with 2048 echoes, while, after the application of the aqueous cleaning systems, 256, 512, and 2048 echoes were progressively set in order to reduce acquisition time and to follow water penetration over time. Profile and decay measurements were started immediately after the solution/gel treatment of the model paints and repeated until almost complete evaporation of water.

Concerning the NMR measurements on the varnished model paints, depth profiles were recorded by setting echo time = 0.045 ms, relaxation delay = 0.15 s, and a smaller step size of 50 μm to increase spatial resolution (resolution of 70 μm). Furthermore, a high number of scans (512) were set for all the measurements to improve the signal-to-noise ratio at this step size. The resultant measuring time for a whole profile was approximately 15 min; this hampered a short-term monitoring of the system and the collection of transverse relaxation decays. Regarding the solvent cleaning procedure, ligroin was applied by swabbing until appreciating varnish removal by the naked eyes.

Results and discussion

Acrylic emulsion model paints

For the model paints consisting of titanium white in acrylic emulsion, a sequence of NMR profiles was collected to monitor the water ingress for 8 h after the application of the free TAC solution (by swabbing). Twenty-four hours after cleaning, a further depth profile for each treated areas was acquired. Figure 1a and b show the depth profiles obtained for the two cleaning systems, while for a better estimation of the extent of water ingress, Fig. 1c presents the difference plots obtained by subtraction of the area of the depth profile collected before each treatment from the areas of the depth profiles collected after it.

More in details, in the sequence of profiles collected after the treatment with the free aqueous solution, compared with the dry paint profile (Fig. 1a, black line), an increase of the signal amplitude due to the presence of water can be noticed. Then, the sequence of profiles registered within 1 h from the application of the TAC solution (indicated with blue lines in Fig. 1a) allowed us to follow up water migration from the surface deeper into the paint, showing the involvement of all the film thickness. The broadening of the post-treatment profiles towards the air-paint interface suggests a swelling phenomenon of the paint film. Nevertheless, in the first profile collected about 2 min after the wet swabbing test (Fig. 1a, red line), the presence of residual water on the treated surface, although not visible to the naked eyes, cannot be excluded. For this reason, an estimation of the transversal swelling of the paint film was made considering the profile acquired ca. 7 min after the treatment (Fig. 1a, thicker blue line); it results in an increase of the film thickness of about 90 μm on a total thickness of ca. 800 μm (11%). Then, from 1 to 8 h after the cleaning (green lines in Fig. 1a), the signal amplitude due to water diffusion inside the painting matrix slowly decreases. The profiles collected after 8 and 24 h (Fig. 1a, green and orange lines, respectively) show slightly higher signal amplitude than the untreated model paint, suggesting the possible presence of residual water. This is further confirmed by the difference plots in Fig. 1c (black symbols) at 24 h after the cleaning test.

The same experimental methodology was exploited to monitor the water ingress after the application of the thickened TAC solution in a different area of the same acrylic emulsion model paint. Also, in this case, a significant increase of the signal amplitude was observed at 2 min after the gel removal, followed by a progressive penetration of water through the paint layer and by a gradual reduction of the signal intensity during the following hours (Fig. 1b); also, the corresponding swelling effect (ca. 80 μm at 7 min) was found similar to what was seen using the free solution.

Nevertheless, from the sequence of profiles (Fig. 1a, b) and from the difference plots (Fig. 1c), a lower water retention was noticed in the paint film treated with the gel system. This finding may be ascribed to a confinement action exerted by the solvent thickener on water diffusion. However, an effect on solvent evaporation speed due to the smaller thickness of the paint film in the area treated with the gel with respect to the one treated with the free solution (ca. 500 μm vs 590 μm, respectively) cannot be excluded; the repetition of the experiment on the paint replica seems to confirm this finding (see Electronic Supplementary Material (ESM), Fig. S1).

The transverse relaxation measurements (CPMG echo decay curves) were acquired before and after the application of the TAC in free and gelled solution maintaining the lift position fixed at a specific depth inside the paint film (red arrows in Fig. 1a, b). The CMPG decay curves and the corresponding fits are plotted in Fig. 2 for the data measured at 10 min, 30 min, 1 h, and 8 h after the application of the solution (Fig. 2a) and of the gel (Fig. 2b). The T_2 values extrapolated from the fits are reported in Table 1.

The plots show a very similar trend of the transverse relaxation decays: in the first 10 min, higher signal intensity and slower transverse relaxation due to the proton mobility of the water molecules are observed (Fig. 2, red curves; Table 1, T_2 long). Progressively the decay curves display a faster relaxing component similar to the one due to the acrylic network of the dry paint film. The data collected after 8 h (Fig. 2, orange curves) show a slightly slower relaxation with respect to the dry paint (Fig. 2, black curves), which suggests the possible presence of residual water at the depth of the measurement.

NMR measurements of water diffusion into the acrylic emulsion paint films and the resulting swelling after the treatment with the TAC solution remark the significant

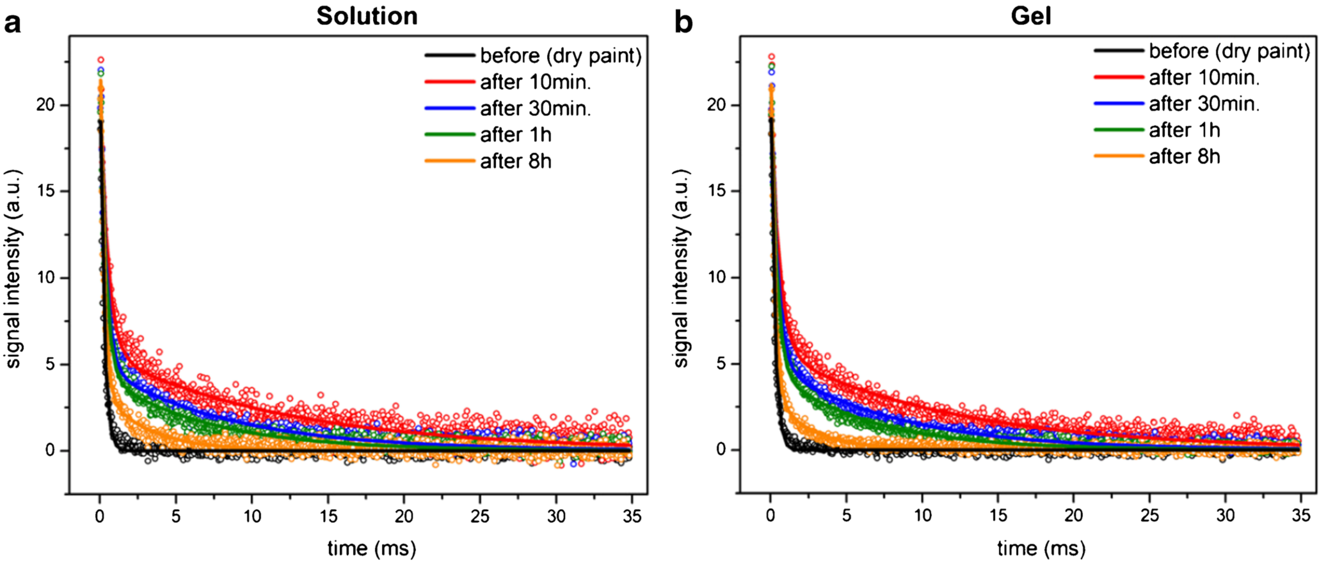

Fig. 2 CPMG echo decay curves and corresponding fits acquired at different time intervals on the acrylic emulsion model paint (at the depth indicated by the red arrows in Fig. 1a, b) after **a** the solution and **b** the gel cleaning tests

Table 1 T_2 values extrapolated from the fits of the CPMG echo decay curves shown in Fig. 2 for the acrylic emulsion model paint

Acrylic paint (T_2 dry = 0.3 ms)	Solution		Gel	
	T_2 short (ms)	T_2 long (ms)	T_2 short (ms)	T_2 long (ms)
After 10 min	0.5	12.2	0.5	11.8
After 30 min	0.4	8.5	0.4	8.0
After 1 h	0.4	6.9	0.4	6.4
After 8 h	0.3	3.1	0.2	2.6

vulnerability of this type of materials as also found by Ulrich et al. in similar NMR investigations [13]. The temporal development of water diffusion inside the model paints observed in our study is also in agreement with the relation between water penetration and increase of paint film thickness observed from 1 to 25 min after water sorption in the ATR-FT-IR study by Whitmore et al. [26]. Most important, in our study, similar results were obtained between the free and thickened aqueous TAC solution showing no particular advantage in the use of the Klucel® G–based gel for controlling water penetration. This finding is in agreement with the results obtained in the study by Angelova et al. [15], although different thickeners and shorter monitoring times were considered in our study. A more direct comparison can be made with the results obtained by a multi-technique approach used by Doménech-Carbó et al. [16] who evaluated cleaning systems very similar to ours. Conversely to our findings, they found reduced water swelling effects on acrylic paints after application, dry removal, and clearance procedure of an aqueous gel containing Klucel® G with respect to the use of pure deionized water (monitoring time equal to 150 min). It is worth to note that in the Doménech-Carbó's study, unrealistic free solvent cleaning treatments were applied in terms of both time of contact and way of application (i.e., swabbing for 5 or 30 min or complete immersion of the samples in water). This may explain the disagreement with our results.

Vinyl model paints

The same aqueous systems, TAC in free and gelled solution, used for the acrylic emulsion paint films were applied on the vinyl paint samples and investigated by NMR profilometry. In the depth profiles obtained for these samples before treatment (Fig. 3a, b, black lines), the signal amplitude values were lower compared with those measured for the acrylic films (Fig. 1a, b, black lines) according to the different amounts of hydrogen protons present in the chemical composition. In the profile scan collected on the vinyl paints at about 2 min after the application of the free solution (Fig. 3a, red line), a considerable raise of the signal amplitude was noted, similar to that found at the same step for the acrylic models and showing comparable swelling effects (ca. 60 µm of thickness increase).

The profiles recorded at a longer time to follow the diffusion of water inside the vinyl paint film evidenced the presence of water at 8 h after the wet swabbing test which persisted also at 24 h from the treatment (Fig. 3a, green and orange lines, respectively).

From the NMR depth profiles sequentially collected for the gel cleaning system (Fig. 3b), a trend very similar to that found for the free solution (swabbing) was observed with a comparable swelling effect (ca. 60 µm), although the hydrogen proton density and the water retention by the paint film (Fig. 3c) were found slightly lower.

Considering the transverse relaxation measurements performed at a fixed position inside the film (selected depths indicated with red arrows in Fig. 3a, b), the series of CPMG echo decay curves acquired after the application of both the cleaning systems show similar behavior. The most representative data at 2 min, 10 min, 1 h, and 4 h are plotted in Fig. 4 which shows initial relaxation decays slower than the dry film due to water penetration. After only 1 h from both the treatments, the relaxation decays (Fig. 4, green curves) were significantly faster; therefore, CPMG echo decay measurements were acquired until 4 h, at the time when the decay curves resemble that of the dry paint film (T_2 values reported in Table 2).

Note that relaxation decay registered at 10 min from the gel application appears with a higher intensity than the decay at 2 min (Fig. 4b, blue symbols); this is in agreement to what is observed in the corresponding depth profiles registered between 2 and 10 min (Fig. 3b, blue lines). This finding suggests a possible delay in water penetration into the paint film in the case of use of the gel system.

In general, the vinyl-based model paints, compared with the acrylic films, evidenced more similar water penetration and swelling effects for the two cleaning treatments (confirmed also by the repetition of the experiment on the model paint replica where slightly higher penetration and retention of water were observed for the gel system; see ESM). Furthermore, water evaporation was generally faster for the vinyl models than the acrylic ones, as shown by the difference plots going almost to zero at 24 h (Fig. 3c) and by the CPMG data (Fig. 4 and Table 2) recorded for 4 h, against the 8 h needed for the acrylic samples to achieve comparable decay curves.

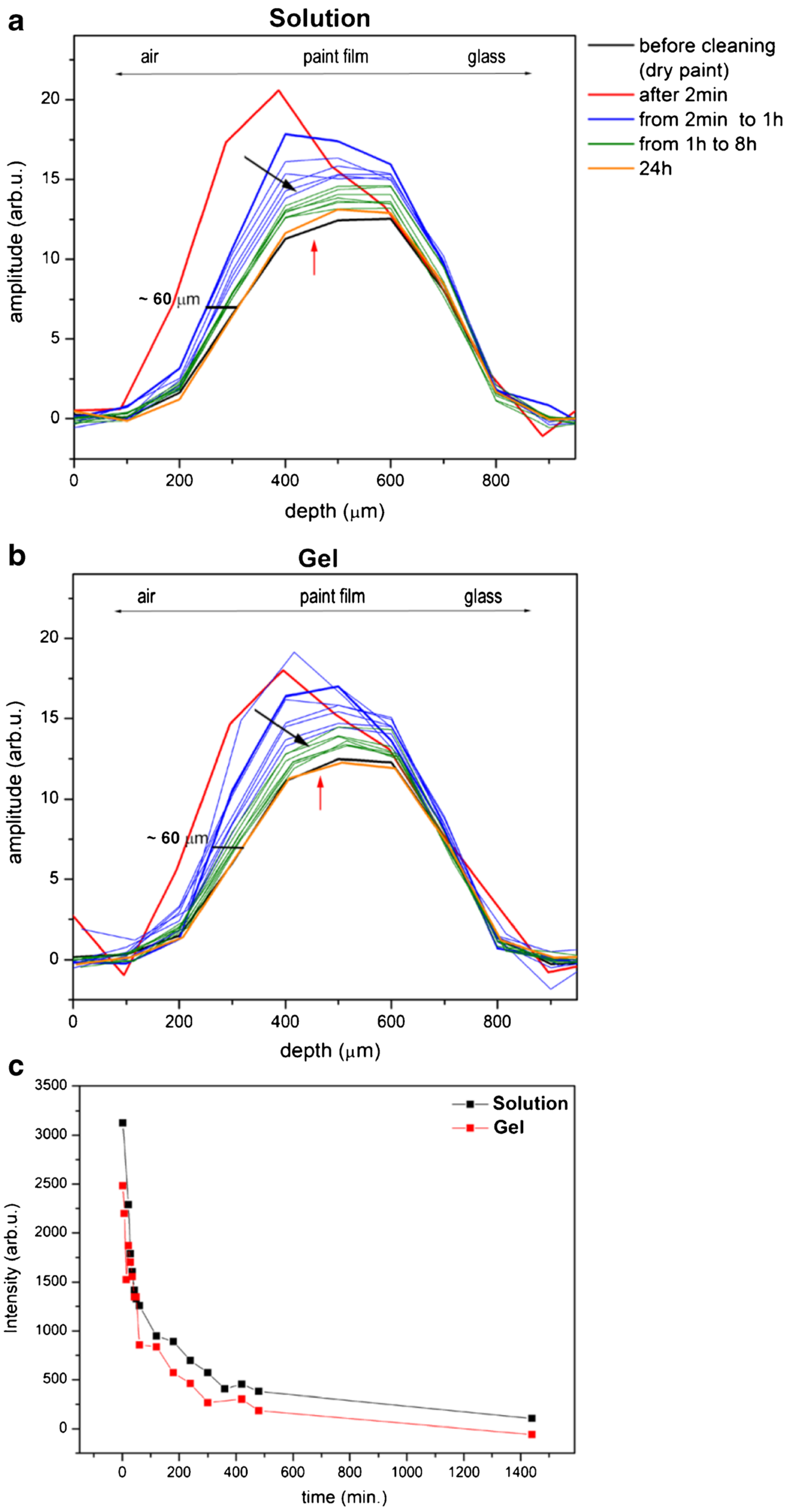

Fig. 3 Depth profiles collected on the vinyl emulsion model paint for the **a** solution and **b** gel cleaning tests (the same legend as for **a**). The water diffusion trend (black arrows) and the estimated swelling effect (calculated with respect to the FWHM) are shown. Red arrows refer to the depth selected for the acquisition of the CPMG decay curves. **c** Difference plots calculated as difference between the areas of the depth profiles collected after the two cleaning tests at different time intervals and the depth profiles collected before them (dry paints)

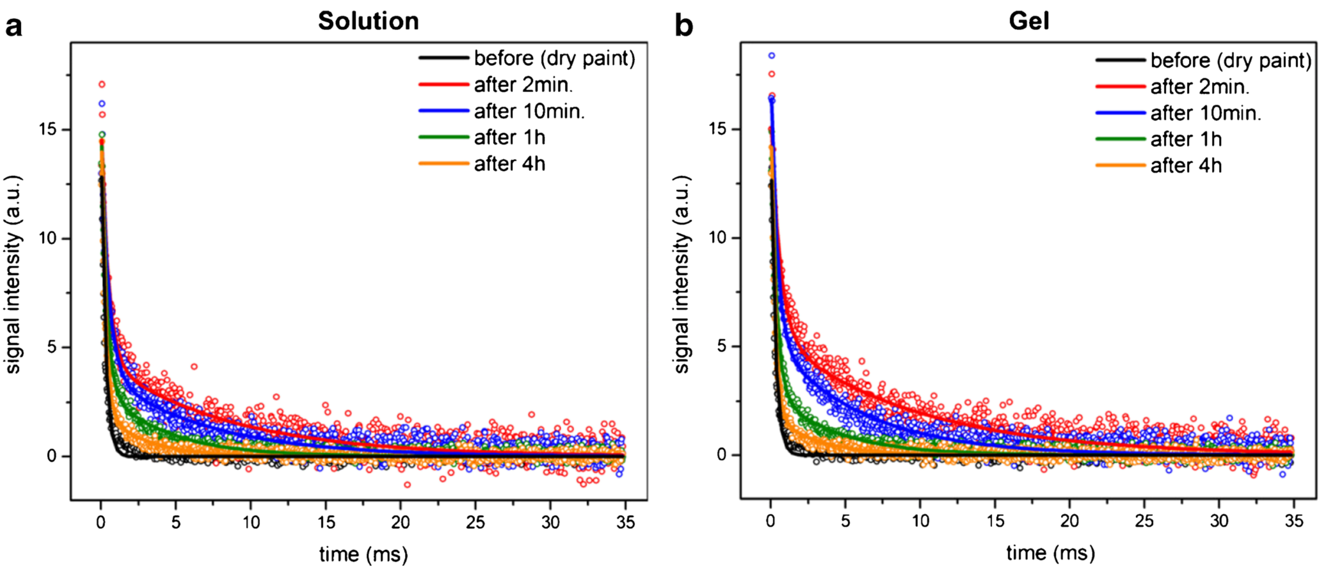

Fig. 4 CPMG echo decay curves and corresponding fits acquired at different time intervals on the vinyl model paint (at the depth indicated by the *red arrows* in Fig. 3) after **a** the solution and **b** the gel cleaning tests

Varnished oil and egg-tempera model paints

The profiles collected for the varnished paint sample made of lead white pigment in linseed oil before and after cleaning with ligroin are shown in Fig. 5. Comparing the dry paint film profile (Fig. 5a, black line) with those collected at 15 min after solvent cleaning and in the following hours (Fig. 5a–c, red, blue, and green lines), a considerable difference in width was noticed along with a small increase of the proton density throughout the all paint depth. The modest temporal variation of the profile width until complete drying pointed out a limited swelling effect of the paint due to solvent penetration. The comparison between the dry paint film profile and that acquired 24 h after the ligroin test (Fig. 5c, black and orange lines, respectively) allowed appreciating a width difference of ca. 115 μm attributable to the removed varnish layer. This, in the untreated sample depth profile, was not clearly distinguished from the underlying oil paint film being displayed as a shoulder at the sample/air interface. The thickness of the varnish layer measured at the optical microscope on a sample cross section taken from this model in a location close to the treated area was found consistent with the NMR finding. The removal of the varnish layer was controlled by infrared analyses carried out in reflection mode with the portable FT-IR spectrophotometer before and after the ligroin treatment (Fig. 5d). In the spectrum acquired after the application of ligroin (Fig. 5d, red line), the carbonyl band at about 1708 cm^{-1} and the signal at 1382 cm^{-1} (asymmetric *stretching* of the methylene group CH_2) [27], both ascribable to the natural resin, suggest the presence of possible varnish residues, not visible by NMR but easily detected by reflection FT-IR [28]. Furthermore, comparing this spectrum with that collected on an unvarnished area (Fig. 5d, dark-yellow line) of the same model paint, in the fingerprint region, the bands of C-O *stretching* and C=C *deformation* modes of the oil binder [29] appear attenuated by the presence of overlaid varnish residues.

The paint sample made by a film of lead white pigment bound in whole egg and coated with a layer of varnish was examined following two cleaning tests performed by repeating the ligroin application on the same area. Also, in this case, the varnish layer in the untreated sample was not resolved from the underlying paint film in the NMR profile. The profile obtained 15 min after the first test is shown in Fig. 6a (red line). The comparison with the profile obtained for the untreated sample (Fig. 6a, black line) showed no significant change of the width; therefore, in order to ensure a complete varnish removal, a further solvent treatment

Table 2 T_2 values extrapolated from the fits of the CPMG echo decay curves shown in Fig. 4 for the vinyl model paint

Vinyl paint (T_2 dry = 0.3 ms)	Solution		Gel	
	T_2 short (ms)	T_2 long (ms)	T_2 short (ms)	T_2 long (ms)
After 2 min	0.5	8.5	0.6	9.5
After 10 min	0.5	6.9	0.4	6.0
After 1 h	0.3	4.2	0.4	4.2
After 4 h	0.3	2.9	0.3	3.0

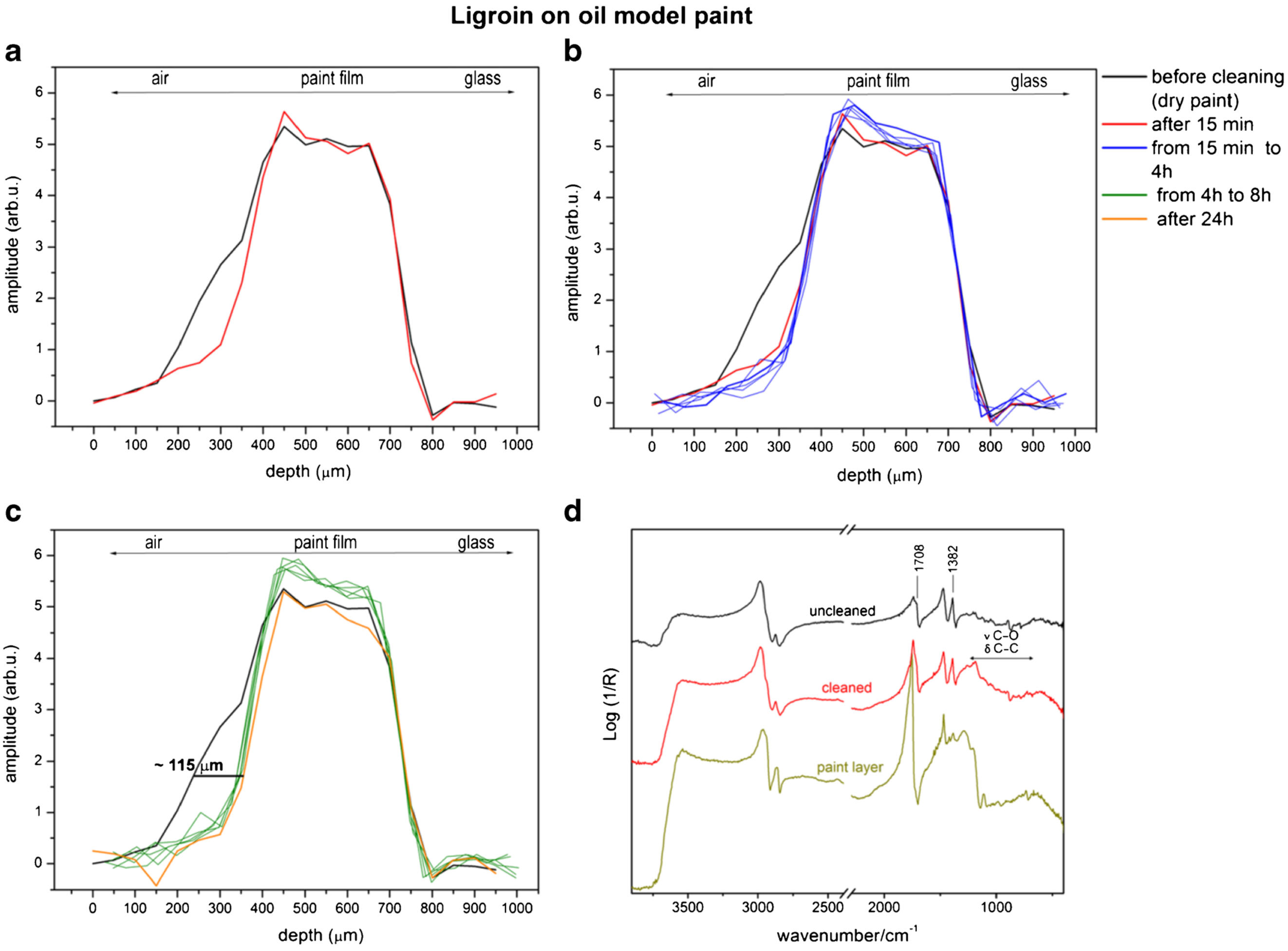

Fig. 5 Depth profiles collected on the oil-based model paint before and after solvent cleaning tests: **a** before and after (15 min) the application of ligroin; **b** after 15 min and from 15 min to 4 h; **c** from 4 to 8 h and after 24 h; the estimated thickness of the removed varnish layer is also shown; **d** reflection FT-IR spectra acquired on the same model before (*black line*) and after (red *line*) the cleaning test in comparison with the spectrum of the unvarnished paint layer (*dark-yellow line*)

was applied. In the profile collected after this second cleaning step (Fig. 6a, blue line), increased signal amplitude was registered due to solvent penetration into the paint film followed by swelling. This latter effect was clearly observed in the measurements collected after the ligroin application up to 4 h (Fig. 6a, b) showing a signal amplitude decrease over time, while simultaneously the air/paint interface moves with a narrowing of the profiles (Fig. 6b, green lines). This is explained with the evaporation of the solvent, followed by a decrease of the swelling phenomenon of the paint film, which in turn progressively allows appreciating a reduction of the paint thickness as a consequence of the removal of the varnish layer. An estimation of the varnish thickness of ca. 60 μm was obtained by comparing the profile of the varnished paint layer with that collected 24 h after the cleaning test (Fig. 6c, black and orange lines, respectively). This finding was confirmed by optical microscopy on a sample cross section from this model. NMR data were also supported by the results of reflection FT-IR measurements performed before and after the application of ligroin (Fig. 6d), which clearly proved the removal of the varnish coating layer. Indeed, in the infrared spectrum collected for the cleaned area (Fig. 6d, blue line), the bands of the natural resin are not present, whereas those referable to the paint layer, a proteinaceous component (p) and lead white (w) (Fig. 6d), are clearly distinguishable.

Overall, the results from non-invasive NMR monitoring of varnished traditional paint samples clearly evidenced effects of solvent penetration and paint swelling (for the tempera model paint) as a consequence of the treatment with ligroin. On the other side, they showed also the limit of the technique in distinguishing the varnish layer with respect to the underlying paint. This is due to the similar content of protons of the materials and to the limited spatial resolution (70 μm at most) of the instrumentation which is comparable or even larger than the typical thickness of varnish coatings. Nevertheless, the achieved outcomes open new perspectives for the use of NMR for monitoring cleaning treatments of paint surfaces also in the case of employment of organic solvents.

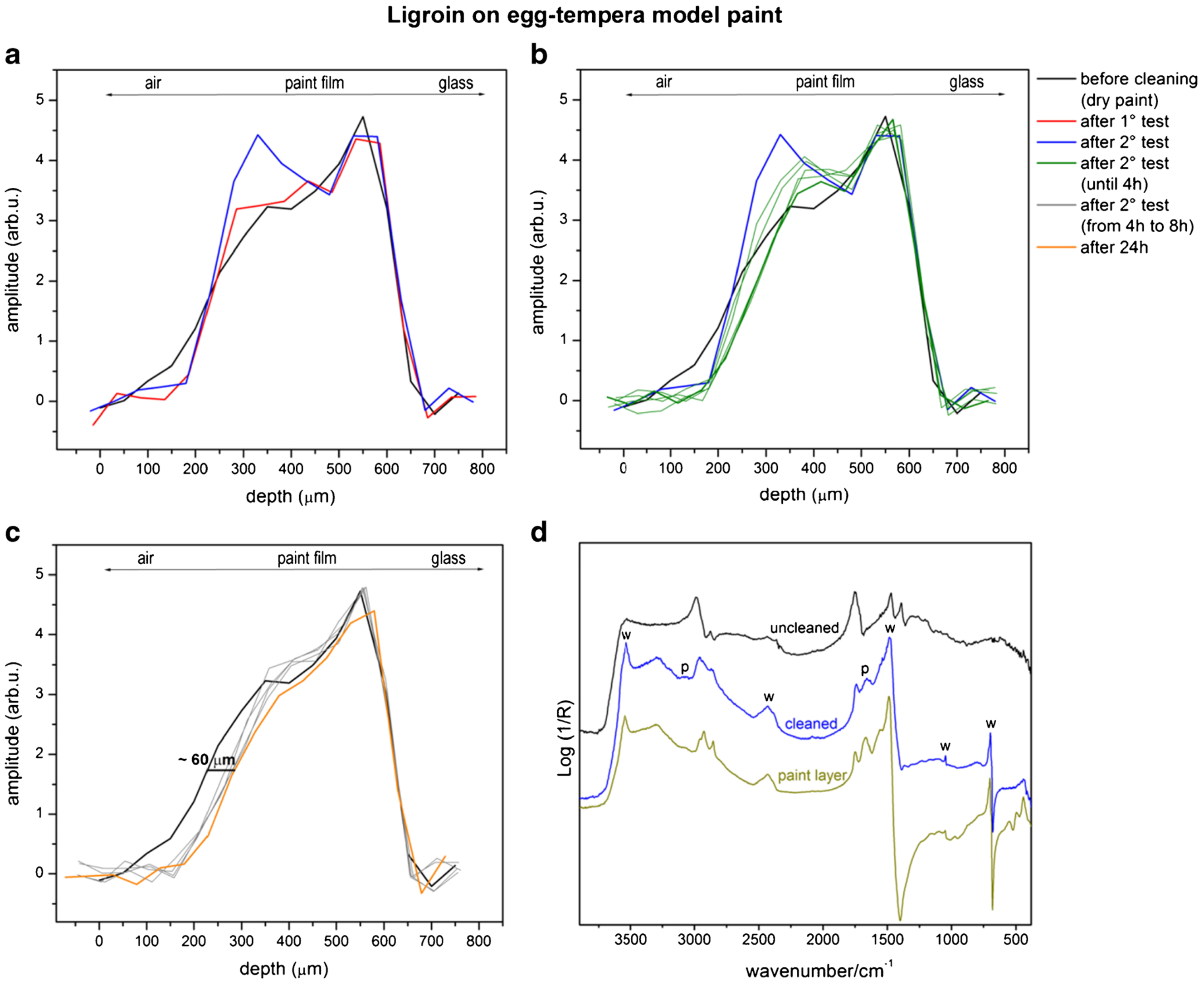

Fig. 6 Depth profiles collected on the egg-based model paint before and after solvent cleaning tests: **a** after 1° and 2° application of ligroin; **b** after 2° test and monitoring until 4 h; **c** from 4 to 8 h and after 24 h; the estimated thickness of the removed varnish layer is also shown; **d** reflection FT-IR spectra acquired on the same model before (*black line*) and after (*blue line*) the 2° cleaning test in comparison with the spectrum of the unvarnished paint layer (*dark-yellow line; p, proteinaceous component; w, lead white*)

Conclusions

In this paper, studies for the use of the mobile nuclear magnetic resonance (NMR-MOUSE®) technique were carried out to assess penetration and swelling effects of solvent cleaning on paint films in a systematic and reproducible way, trying to perform cleaning tests as close as possible to real treatments.

Firstly, NMR investigations were focused on the monitoring of depth penetration and swelling action of water in acrylic emulsion and vinyl-based model paints by testing a TAC aqueous solution in both free and thickened forms (by Klucel® G). The potential of the NMR-MOUSE for the examination of water diffusion and swelling in acrylic paint films was already known from literature. Therefore, in this research, NMR investigations on acrylic paints were carried out for comparison purposes with previous studies and to set up a fully reproducible and controlled procedure to compare free solvent and gel cleaning treatments. The same experimental approach was, then, exploited for the investigation of the less studied water-vinyl paint.

The results from NMR monitoring of the water uptake by the acrylic paint films and of the ensuing swelling effect after the treatment with the free aqueous solution resulted to be in good agreement with what is known from previous studies on the water sensitivity of this type of materials [8, 13, 15, 16, 26]. More interesting was the comparison of the NMR results obtained for the acrylic and vinyl paints: the water uptake by the paint films was found very similar and accompanied by a comparable increase of the transversal paint thickness due to swelling. In fact, in both the systems, an enhancement of the proton spin density values due to water sorption was observed from about 2 min after the swabbing cleaning tests to approximately 1 h when all the paint width was affected by solvent penetration. At longer time intervals (between 1 and 8 h from the swabbing cleaning tests), the water content was slightly greater into the acrylic paints. In these latter, therefore, the process of water evaporation was found slower than that in the vinyl paints, as confirmed by the CPMG echo decay data.

Another important result achieved in this research is the observation that the penetration of water into both types of synthetic paint films was not significantly minimized by adopting an aqueous gel formulation based on Klucel® G compared with the use of the free solution applied by swabbing. This finding must be evaluated in the context of the specific controlled experimental conditions used in the present research. Moreover, the comparison with the findings from the limited number of NMR studies present in literature was hampered by the use of different cleaning protocols (sometimes unrealistic) and reagents as well as different experimental parameters that sometimes in the past provided discordant results (see for example ref. [15] vs ref. [16]) as discussed in the "Introduction" section. In the light of these considerations, we want to remark the need for a careful control of the comparability and reproducibility of results from this type of studies before achievement of misleading conclusions.

Potential and limits of NMR profilometry were, also, evaluated in preliminary experiments designed to non-invasively monitor the varnish removal from traditional model paints (oil and egg binders) to study solvent penetration and swelling effects of the paint using ligroin as organic solvent.

Interestingly, in the case of the oil paint, the swelling effect due to solvent penetration was found weaker than in the egg paint.

The encouraging results obtained in this research and in similar NMR studies should be evaluated considering the applicability of the NMR-MOUSE to assist research on the development of novel cleaning methodologies of paintings, with particular focus on the cleaning effects of aqueous systems. To this purpose, as here evidenced, the use of a robust analytical methodology based on thoroughly comparable NMR measurements at both short and long time intervals is strongly necessary. The perspective of development of future research is to extend the investigation to other water-based cleaning systems as well as to study different synthetic binding media. It will be also of fundamental importance to include the clearance step in testing the gel systems in order to have a closer simulation of the actual cleaning procedures.

Furthermore, in spite of the limited spatial resolution of the used instrumentation, the NMR-MOUSE showed to be useful also in monitoring varnish removal from traditional paints by an organic solvent, evidencing sensitivity of the technique to solvent penetration and swelling affects.

Overall, these results make the prospect of using the NMR-MOUSE for in situ non-invasive monitoring of cleaning treatments directly on real paintings very attractive. Nevertheless, the exact repositioning of the painted surface in front of the NMR probe after cleaning is still very problematic; therefore, much effort is needed to make possible this challenging application.

Funding information The authors received financial support from the IPERION-CH project (Integrated Platform for the European Research Infrastructure ON Cultural Heritage) funded by the European Commission, H2020-INFRAIA-2014-2015, under Grant No. 654028.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Stolow N. Solvent action. In: Feller RL, Stolow N, Jones EH, editors. On picture varnishes and their solvents. Washington D.C.: National Gallery of Art; 1985. p. 47–116.
2. Phenix A, Sutherland K. The cleaning of paintings: effects of organic solvents on oil paint films. Rev Conserv. 2001;2:47–60.
3. Stolow N. The measurement of film thickness and of solvent action on supported films. Stud Conserv. 1957;3:40–4.
4. Masschelein-Kleiner L, Deneyer J. Contribution à l'etude des solvants utilisés en conservation. In: ICOM Committee for Conservation. Ottawa: 6th Triennial Meeting; 1981. pp 1–10.
5. Phenix A. The swelling of artists' paints in organic solvents. Part 1, a simple method for measuring the in-plane swelling of unsupported paint films. JAIC. 2002;41:43–60.
6. Phenix A. The swelling of artists' paints in organic solvents. Part 2, comparative swelling powers of selected organic solvents and solvent mixtures. JAIC. 2002;41:61–90.
7. Kampasakali E, Ormsby B, Cosentino A, Miliani C, Learner T. A preliminary evaluation of the surfaces of acrylic emulsion paint films and the effects of wet-cleaning treatment by atomic force microscopy (AFM). Stud Conserv. 2011;56:216–30.
8. Goossens ELJ, van der Zanden AJJ, Wijen HLM, van der Spoel WH. The measurement of the diffusion coefficient of water in paints and polymers from their swelling by using an interferometric technique. Prog Org Coat. 2003;48:112–7.
9. Blümich B, Perlo J, Casanova F. Mobile single-sided NMR. Prog Nucl Magn Reson Spectrosc. 2008;52:197–269.
10. Blümich B, Casanova F, Perlo J, Presciutti F, Anselmi C, Doherty B. Noninvasive testing of art and cultural heritage by mobile NMR. Acc Chem Res. 2010;43:761–70.
11. Capitani D, Di Tullio V, Proietti N. Nuclear magnetic resonance to characterize and monitor cultural heritage. Prog Nucl Magn Reson Spectrosc. 2012;64:29–69.
12. Rehorn C, Blümich B. Cultural heritage studies with mobile NMR. Angew Chem Int Ed. 2018;57:7304–12.
13. Ulrich K, Centeno SA, Arslanoglu J, Del Federico E. Absorption and diffusion measurements of water in acrylic paint films by single-sided NMR. Prog Org Coat. 2011;71:283–9.
14. Jablonski E, Learner T, Hayes J, Golden M. Conservation concerns for acrylic emulsion paints. Rev Conserv. 2003;4:3–12.
15. Angelova LV, Ormsby B, Richardson E. Diffusion of water froma range of conservation treatment gels into paint films studied by unilateral NMR. Part I: acrylic emulsion paint. Microchem J. 2016;124:311–20.
16. Doménech-Carbó MT, Silva MF, Aura-Castro E, Doménech-Carbó A, Fuster-López L, Gimeno-Adelantado JV, et al. Multitechnique

Approach to evaluate cleaning treatments for acrylic and polyvinyl acetate paints. In: Mecklenburg MF, Charola AE, Koestler RJ, editors. New insights into the cleaning of paintings. Proceedings from the Cleaning 2010 International conference. Universidad Politecnica de Valencia and Museum Conservation Institute. Washington, D.C.: Smithsonian Institution Scholarly Press; 2013. p. 125–34.

17. Hendrickx R, Ferreira ESB, Boon JJ, Desmarais G, Derome D, Angelova L, et al. Distribution of moisture in reconstructed oil paintings on canvas during absorption and drying: a neutron radiography and NMR study. Stud Conserv. 2016;62:1–7.
18. Fife GR, Stabik B, Kelley AE, King JN, Blümich B, Hoppenbrouwersa R, et al. Characterization of aging and solvent treatments of painted surfaces using single-sided NMR. Magn Reson Chem. 2015;53:58–63.
19. Kehlet C, Nunberg S, Alcala S, Dittmer J. Nuclear magnetic resonance analysis for treatment decisions: the case of a white sculptural environment by Louise Nevelson. Microchem J. 2018;137:480–4.
20. Prati S, Sciutto G, Volpi F, Rehorn C, Vurro R, Blümich B, et al. Cleaning oil paintings: NMR relaxometry and SPME to evaluate the effects of green solvents and innovative green gels. New J Chem. 2019;43:8229–38.
21. Cremonesi P. L'uso di tensioattivi e chelanti nella pulitura di opere policrome. Collana I Talenti. Padova:Il Prato; 2004.
22. Cremonesi P. L'ambiente acquoso per il trattamento di opere policrome. Collana I Talenti Padova:Il Prato; 2011.
23. Cremonesi P. L'uso dei solventi organici nella pulitura di opere policrome. Collana I Talenti. Padova:Il Prato; 2004.
24. Perlo J, Casanova F, Blümich B. Profiles with microscopic resolution by single-sided NMR. J Magn Reson. 2005;176:64–70.
25. Carr HY, Purcell EM. Effects of diffusion on free precession in nuclear magnetic resonance experiments. Phys Rev. 1954;94:630–8.
26. Whitmore PM, Morris HR, Colaluca VG. Penetration of liquid water through waterborne acrylic coatings, in Modern paints uncovered. In: Learner T, Smithen P, Krueger J, Schilling M, editors. Proceedings from the Modern Paints Uncovered Symposium. London: Tate Modern, May 16–19, 2006, Los Angeles: Getty Conservation Institute; 2007. pp. 217–223.
27. Rosi F, Legan L, Miliani C, Ropret P. Micro transflection on a metallic stick: an innovative approach of reflection infrared spectroscopy for minimally invasive investigation of painting varnishes. Anal Bioanal Chem. 2017;4098:3187–97.
28. Iwanicka M, Moretti P, van Oudheusden S, Sylwestrzak M, Cartechini L, van den Berg K, et al. Complementary use of optical coherence tomography (OCT) and reflection FTIR spectroscopy for in-situ non-invasive monitoring of varnish removal from easel paintings. Microchem J. 2018;138:7–18.
29. Rosi F, Daveri A, Moretti P, Brunetti BG, Miliani C. Interpretation of mid and near-infrared reflection properties of synthetic polymer paints for the non-invasive assessment of binding media in twentieth-century pictorial artworks. Microchem J. 2016;124: 898–908.