Microchemical Journal 141 (2018) 40–50

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

^{1}H NMR depth profiles combined with portable and micro-analytical techniques for evaluating cleaning methods and identifying original, non-original, and degraded materials of a 16th century Italian wall painting

Valeria Di Tullio[a,b,*], Giorgia Sciutto[c], Noemi Proietti[a], Silvia Prati[c], Rocco Mazzeo[c], Chiara Colombo[d], Emma Cantisani[d], Valentina Romè[e], Davide Rigaglia[e], Donatella Capitani[a]

[a] Magnetic Resonance Laboratory "Annalaura Segre", Institute of Chemical Methodologies (IMC), CNR, Via Salaria km. 29,300, 00015 Monterotondo (RM), Italy
[b] Metropolitan Museum of Art, 1000 5th Ave, New York 10028, NY, USA
[c] University of Bologna, Department of Chemistry "G. Ciamician" Via Guaccimanni 42, 48121 Ravenna, Italy
[d] Institute for the Conservation and Valorization of Cultural Heritage (ICVBC), CNR, Via Madonna del Piano, 10, 50019, Sesto Fiorentino (FI), Italy
[e] Restorer, Impresa individuale, Italy

ARTICLE INFO

Keywords:
Unilateral NMR
Infrared spectroscopy
Wall painting
Cleaning treatments
Carboxylates

ABSTRACT

In this study, portable NMR was applied to monitor and evaluate cleaning treatments on the surface of a 16th century Italian wall painting.

Due to the complexity of the state of degradation of the wall painting, a campaign of measurements was carried in situ to evaluate the performance of traditional and innovative eco-friendly cleaning systems such as sulphate-reducing bacteria *D. vulgaris* confined in hydrogels, and to compare two different cleaning systems used to remove a degraded hydrophobic organic layer.

Specifically, NMR stratigraphy allowed to determine the thickness of the organic layer covering the surface of the wall painting, its distribution in the wall painting, the presence of residues after applying the cleaning treatment, and to evaluate and compare the effectiveness of applied treatments. A new analytical parameter here named *the solubilization degree of the cleaning system* permitted the selection of the most performing treatment. ^{1}H NMR depth profiles allowed to evaluate changes in the permeability of the wall painting caused by the presence of organic substances during the application of water-based cleaning systems, and to evaluate the water content and its depth of penetration in the wall painting. Changes in permeability were estimated calculating another new analytical parameter, i.e. *the percentage of water saturation* before and after the application of the cleaning treatment. Depth profiles also permitted the evaluation of the degree of wettability of the wall painting surface as a function of the time of application, and the obtainment of a detailed information about the interaction between water molecules, the gel network and the surface of the wall painting. Finally, to obtain the chemical characterization of the artefact surface a multi analytical approach was applied using both portable and micro-invasive analytical methodologies.

1. Introduction

Among restoration procedures, the cleaning of artefacts is one of the most delicate and potentially damaging operation. It is well known that a cleaning treatment is aimed at removing different type of undesired layers of degradation (i.e. crusts, salts efflorescence, metal stains) and it has to respect diverse requirements. High performing cleaning systems should have high physico-chemical stability, weak aggressiveness to the material. In addition, cleaning systems should be environmental friendly, and not toxic to the operator, and should be able to control the evaporation and penetration of solvents into the porous structure without leaving residual materials on the surface of the artefact. Furthermore, if the artefact experienced a number of retouching, a cleaning system should provide high selectivity between the materials to be removed and those to be preserved [1–3]. The monitoring of cleaning treatments, the characterization of the constitutive materials and the knowledge of interactions among these materials and cleaning treatments are a fundamental step in a restoration project as well as in research projects focused on the development of new cleaning systems.

Efficacy, suitability of products and procedures should be subjected

* Corresponding author at: Magnetic Resonance Laboratory "Annalaura Segre", Institute of Chemical Methodologies (IMC), CNR, Via Salaria km. 29,300, 00015 Monterotondo (RM), Italy.
E-mail address: valeria.ditullio@cnr.it (V. Di Tullio).

https://doi.org/10.1016/j.microc.2018.04.034
Received 30 August 2017; Received in revised form 2 April 2018; Accepted 30 April 2018
Available online 01 May 2018
0026-265X/ © 2018 Elsevier B.V. All rights reserved.

to a preliminary evaluation on selected area of the surface artefact or on specimens prepared in laboratory. The aim of cleaning trial area should be to determine the suitably of the cleaning method for the object and the degree of cleaning that can be achieved. Nevertheless, the simultaneous presence of ancient, non-original, and degraded materials makes both the analytical characterization and the study of interactions very challenging. Due to the difficulty to collect samples from precious artefacts and the complexity of simulating a surface of an ancient naturally degraded artefact, the use of portable instrumentation is highly advisable to monitor and evaluate cleaning treatments directly on the surface of the artefact.

Several analytical methodologies, such as GC/MS, Raman and FT-IR spectroscopy, have been applied to evaluate the performance of cleaning products and to chemically characterize the presence of organic residual materials on the surface of artefacts such as paintings, papers and lapideous materials [4–8]. Although these analytical methodologies are very powerful techniques to obtain a chemical characterization of materials, they have been rarely applied to monitor and to evaluate the thickness reduction and the degree of removal of layers subjected to a cleaning treatment.

Furthermore, the depth of penetration of solvents used in cleaning treatments and the distribution of residues inside the artefact are important parameters to be evaluated during a cleaning treatment. The capability of solvents to diffuse through a porous material affects the performance of a cleaning system that has to guarantee a high selectivity and provide a superficial action of solubilization. To remove undesired materials distributed in a porous network and obtain a swelling action on thick materials that are difficult to solubilize, some degree of penetration of solvent can be desirable. On the contrary, a high degree of penetration of solvents can cause a dispersion of residual materials in deeper layers of the artefact triggering off, over time, serious and often irreversible processes of alteration. Evaluating the depth of penetration of solvents during a cleaning treatment can help at modulating the solubilization degree of the cleaning system and at controlling an excessive or inadequate penetration within the artefact.

Portable nuclear magnetic resonance (NMR) allows measurements to be performed in situ without any sampling. The magnetic field is applied to one side of the object, thus the integrity and the dimension of the object under investigation are fully preserved [9,10]. Although the magnetic field of this sensor is inhomogeneous, it is possible to measure NMR parameters such as proton density, relaxation times, self-diffusion coefficients, and even to collect correlation maps [11]. Due to the capability to measure the hydrogen content as a function of depth of measurement, unilateral NMR is a very powerful tool to scan layers constituted by organic substances as well as to measure the water content absorbed by porous materials [11–13]. In recent years, unilateral NMR has been previously used to evaluate restoration treatments applied on porous stones and painted surfaces [14–19], to explore the interaction between lead white and collagen-based binders in a medieval-illuminated manuscript [20], and to study new and artificially aged vegetable leathers [21].

In this study, portable NMR was used to investigate the possibility of establishing an analytical protocol to evaluate the action of cleaning products based on micro-emulsion and solvent gels, and to detect the possible presence of residual materials on the surface of the artefact. Because the reduction of thickness of layers under removal is strictly correlated with the power of cleaning system, hydrogen depth profiles were collected by unilateral NMR on the surface of the painting before and after the cleaning treatment to evaluate the solubilization degree of the cleaning system applied.

Unilateral NMR was applied to compare and monitor the penetration depth, and the mobility and diffusivity of water in two types of hydrogel/bacteria systems applied on the surface of a degraded wall painting. Since the penetration of a solvent also depends on the duration of the application of the treatment itself, different regions of the wall painting treated for varying lengths of time were investigated. In fact, the possibility of optimizing the length of time of the treatment application would also be of help during restoration and maintenance.

Finally, to obtain the chemical characterization of the artefact surface before and after the cleaning treatment a multi analytical approach was applied using both portable and micro-invasive analytical methodologies.

2. Materials and methods

The cleaning procedure was planned with the dual purpose of removing both the degraded non-original translucent layer and the very thick salt efflorescences.

A micro-emulsion and a solvent gel were used to remove the non-original translucent substance, and their efficiency was compared. Poultices of sulphate-reducing bacteria entrapped in two different type of hydrogels were applied to remove salt efflorescences affecting the wall painting surface.

In order to investigate the performance of these cleaning treatments as well as to obtain chemical characterizations of the surface before and after the cleaning, a multi-analytical study was carried out in two successive steps. During the first step, a full characterization of the materials of the wall painting was carried out by portable infrared spectroscopy (FTIR), and a set of micro-invasive techniques such as ^{13}C Cross Polarization Magic Angle Spinning NMR spectroscopy (^{13}C CPMAS NMR), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), μFTIR in attenuated total reflection (ATR), and X-ray diffraction (XRD), was applied. To investigate the distribution of elemental and molecular components of original and non-original materials, ATR-FTIR and EDS mappings on cross-sections were carried out.

During the second step areas M1-M4 on the surface of the wall painting surface were selected to monitor the effect of cleaning treatments by unilateral NMR and portable FTIR, see Fig. 1. Eight samples, S1-S8 were collected from the wall paintings to perform analyses in laboratory.

2.1. The wall painting

The pictorial cycle garnishing the Vitelleschi's chapel of the Tarquinia cathedral was painted by Antonio da Viterbo nicknamed *Il Pastura* (1450–1516) who was most likely a Perugino's scholar [22] and worked with Pinturicchio to decorate the Borgia Apartment in Vatican City, Rome, Italy. The chapel decoration represents the *Prophets and Sybils* and *Coronation of the Virgin* on the vault, the *Marriage of the Virgin* on the right side of the chapel, *Birth of the Virgin Mary*, *the /Pietà, the Meeting of Joachim and Anna* and *the Virgin and Child* on the left side. In 1642 a fire destroyed the bottom of the chapel and damaged the painted surface of the vault. Restoration works were carried out in 1877, 1939, 1979, and 2013. The latest restoration was aimed at the renovation of the roof in order to avoid rainwater infiltration that had previously affected the wall painting causing salt efflorescences on the painted surface. Repeated crystallization cycles had caused loss of cohesion and detachment of the pictorial layers from the plaster and compromised the appearance and the chromatics of the painting. A thick translucent layer and darkened areas were also observable on the painted surface along with several pictorial reintegrations due to previous restorations.

2.2. Cleaning products and application

An oil-in-water micro-emulsion containing an anionic surfactant was used to remove the translucent layer from the wall painting [23,24]. The oil-in-water micro-emulsion (Nanorestore Cleaning Apolar Coating, CSGI Firenze, Italy) entraps 1-pentanol, an anionic surfactant, namely sodium-dodecyl-sulphate, and p-xylene. The micro-emulsion was daubed on paper pulp and applied on the surface of the wall painting for 1 h and then it was washed by water.

Download English Version:

https://daneshyari.com/en/article/7640051

Download Persian Version:

https://daneshyari.com/article/7640051

Daneshyari.com