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Investigation of degradation mechanisms by portable Raman spectroscopy and thermodynamic speciation: The wall painting of Santa María de Lemoniz (Basque Country, North of Spain)

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Abstract

This article presents the "in situ" and totally non destructive investigation of a wall painting in Santa María de Lemoniz (Biscay, Basque Country, Spain) by Raman microprobe spectroscopy 14 years after its restoration. Although no sample was allowed to be taken, it has been possible to determine the original pigments in the artwork (vermilion, red iron oxide, yellow iron oxide, carbon black, lead white), as well as some degradation products (calcium oxalate dihydrate, anhydrite). For the first time, the mechanism for the transformation of malachite into copper basic sulphates has been ascertained by the integration of Raman data with thermodynamic speciation studies. Moreover, some remarks regarding the unsuitability of the past intervention procedure with regard to the chemical stability of the artwork are made.

Keywords: Portable Raman spectroscopy; Wall painting; Pigment/mortar identification; Pigment/mortar degradation; Thermodynamic speciation

1. Introduction

The systematic and thorough study of archaeological specimens and artworks allows to decide properly what methods and products should be used in the restoration taking into account the raw materials on the work and their degradation products [1]. For this purpose the number of analytical techniques available is in fact really large. Traditionally, the analysis of wall paintings has been tackled with a complex mixture of instrumental analytical approaches [2] such as optical microscopy, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), electron paramagnetic resonance spectroscopy (EPR), etc. In recent years Raman spectroscopy has been proved as a suitable methodology for the identification of pigments in several kinds of artefacts with artistic, historical and/or archaeological value: manuscripts [3,4], cantorals [5,6], wall paintings [7–11], polychromes [12], oil on canvas [13], papyri [14], Chinese paper [15], wallpapers [16,17] and so on. Furthermore, several authors have researched on the application of Raman spectroscopy to the study of weathering and biodeterioration processes in rock art and frescoes [18], outside artworks [19], wall paintings [20], and some ecclesiastical monuments in northern Spain [21].

The development of portable Raman equipment has promoted one of the most interesting applications of this vibrational spectroscopy. These devices make it possible to perform the analysis "in situ" with no need for sampling, that is to say, directly on the artwork and in the same location where it has appeared. It is the analysis of wall paintings and other large scale pieces that can benefit most from this innovation, as sampling from these artworks is rarely allowed. For example, gemstones adorning the Heinrich's Cross reliquary, dating from the late Middle Ages [22], and the XV century wall paintings in the chapel of St. Orso, Priory Palace (Aosta, Italy) [23] were analysed using these portable Raman devices.

Almost all references listed so far, and others in the literature, refer to scientific analysis with the aim of characterising the objects or diagnosing the state of conservation as a preliminary step before defining the intervention works. Only few references can be found regarding the assessment of the state of

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conservation of an artwork after its conservation and/or restoration [24]. A clear example of how an inadequate intervention may induce a decaying process is presented by Dei et al. [25]. They exposed how the application of ammonium carbonate and barium hydroxide to some wall paintings induced the degradation of azurite to paratacamite and copper hydroxide together with a remarkable colour change.

The mural painting of Santa María de Lemoniz, produced in 1587 as a temporary decorative artwork and found hidden behind a wooden altarpiece, was subjected to restoration in 1991. The original wall painting was established as a *false fresco*. In that restoration only three small samples (predominant colours and inner mortars) were taken to be analysed by destructive analytical techniques. The results stated that the mortar was composed by gypsum, clays, calcium carbonate and a proteinaceous binder. Unfortunately that chemical analysis turned out to be insufficient as it will be shown. Some repaintings probably from a XVII century recomposition were appereciable, specially a widely spread green coloured stain. The painting was consolidated with a plastic glue adhesive, seriously cleaned, reintegrated with the *Tratteggio* technique and consolidated with Paraloid. The general view of the wall painting can be seen in Fig. 1, and a more in depth description of the painting and the restoration can be found elsewhere [26]. Should the graphic documentation [26] is compared with the current state, it is easy to notice how the visual appearance has changed. There is a general blackening and yellowing of the surface and some colour changing in specific areas. The aim of the present work is the identification of the degrading compounds and the elucidation of the chemical processes involved in their formation. For this purpose, thermodynamic equilibrium models will be integrated with the instrumental response obtained by remote Raman spectroscopy. Moreover a description of all the materials employed both originally and during the intervention will be presented.

Fig. 1. Experimental set-up with the Raman instrument on the scaffolding.

2. Experimental

A Renishaw System 100 Raman spectrometer was used to collect the spectra. The spectrometer was equipped with a 785 nm diode laser connected with a fibre-optics cable to the measuring probe, and a CCD detector. The laser beam was focused onto the wall painting by a long working distance (12 mm) 20× microscope objective, resulting in an spot with a maximum lateral resolution of 5 μm. The probe mounted on a tripod was coupled to a TV microcamera (allowing a perfect location of the pigment grains to be analysed) and its positioning was controlled by a micrometric stage. The calibration of the instrument was carried out daily with the 520 cm^{-1} band of the Raman spectrum of a silicon chip. Each spectrum was recorded with exposition times from 5 to 100 s and 1–10 accumulations changing the spectral interval generally between 200 and 2200 cm^{-1} according to the type of compound.

The device together with the personal computer to control it was placed on top of a scaffolding (see Fig. 1), which made the analysis process more laborious due to the corrective actions taken to avoid the vibrations of the structure. Fig. 2 shows in detail the Raman probe during the analysis. For the proper identification of the compounds involved several spectra were recorded in each selected area. Neutral density filters were used giving 1% or 10% reduction of the laser power in order to avoid any thermal decomposition of the sampled areas. Our analytical

Fig. 2. Detail of the Raman probe at the working distance on the wall painting.