Sensors and Actuators A 281 (2018) 15–23

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

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

Micro-Raman analysis of mortars and wallpaintings in the Roman villa of Fuente Alamo (Puente Genil, Spain) and identification of the application technique

Laura D. Mateos, Dolores Esquivel, Daniel Cosano, César Jiménez-Sanchidrián, José Rafael Ruiz*

Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, Carretera Nal. IV-A km. 396, 14071 Córdoba, Spain

ARTICLE INFO

Article history:
Received 18 May 2018
Received in revised form 19 July 2018
Accepted 22 August 2018
Available online 23 August 2018

Keywords:
X-ray diffraction
Micro-Raman spectroscopy
Roman pigments
Roman wallpaintings

ABSTRACT

This paper reports results of ongoing research on wallpaintings in the Roman villa of Fuente Alamo (Puente Genil, Southern Spain). Wall decoration vestiges from an older building stage and a newer one subsequently erected on it were examined. The lack of information about wallpaintings in this villa led us to study the materials constituting the mortars and pigments, and to elucidate the painting technique used in order to facilitate optimal restoration. Paint layers exhibited a wide variety of colours but mainly red, ochre, blue, green, black and white. Pigments included high-quality materials such as Egyptian blue and other, more common elements of the Roman palette such as red and yellow earths, and lime white. The materials were characterized by X-ray diffraction and Raman microspectroscopy.

1. Introduction

This work was part of a broader, more ambitious project aimed at characterizing wallpaintings from the Roman Baetic region south of Cordoba in Southwestern Spain. Previous studies in the region had focused on the Roman villas of Almedinilla [1] and Priego de Cordoba, as well as on Cerro de las Cabezas in Fuente Tojar [2]. Identifying pigments and mortars is important in these archaeological investigations. In fact, the archaeometric characterization of materials often allows serious archaeological and conservation problems to be efficiently solved. Such problems often include identifying the origin of the materials present in mortars and pigments, the painting technique used and any conservation or restauration procedures applied.

Ever since the earliest Vesuvian villages were unearthed, there has been strong debate over the particular application techniques used in Roman wall paintings, which were described long ago by classic historians. There is usually no debate, however, over the materials used to prepare the pigments and mortars since, as shown here, they can be unequivocally identified by using various instrumental techniques. For example, Mora et al. [3] have provided a detailed description of the dry and wet procedures potentially used to make Roman wallpaintings. In the wet procedures, pigments were applied to fresh mortar, to which they adhered by carbonation; in the dry procedures, pigments were mixed with a binder prior to application to dry mortar. The binders typically used were either organic such as gum Arabic, oil, egg, milk or casein, or inorganic such as lime. In some wall paintings, pigments were applied by using a mixed technique involving painting on fresh mortar and subsequently applying motifs by using the dry procedure. Characterizing the fresh painting technique allowed Mora et al. [3] to develop specific conservation procedures for Roman wall paintings.

Excavations in the Roman villa of Fuente Alamo over the period 2005–2009 unearthed an area approximately 4000 m2 in size housing a Roman sequence with two well-defined stages as regards structure, orientation and purpose [4]. Stage I was a public balneum finished in the first century A.D. that remained in use until the middle of the second. Next to the balneum was a thermal building with easily recognized hypocastum remains; the other rooms, however, were either erased by subsequent construction or had disappeared altogether. The site was abandoned for some time but later re-occupied with a rather different architectural layout and use. Thus, a new building in the form of a villa was built atop part of the balneum framework and using some of its rooms in the second half of the third century.

Wallpainting fragments from the Roman villa of Fuente Alamo were characterized in two steps. The first step involved analysing the paint layer (namely, the pigment and primer) and the sec-

* Corresponding author.
E-mail address: qo1ruarj@uco.es (J.R. Ruiz).

https://doi.org/10.1016/j.sna.2018.08.038
0924-4247/

Fig. 1. Photographs of the fragments from Stage I.

ond elucidating the composition of the wall mortar. The chemical composition and structure of mortar provides useful information about its ingredients and how they were applied. In this work, we examined wallpainting fragments by using various instrumental techniques including optical microscopy, X-ray diffraction and Raman microspectroscopy. In recent years, Raman microspectroscopy has been widely used to characterize pigments decorating walls, floors and ceilings [5–8]. Other techniques such as X-ray fluorescence spectroscopy and X-ray diffraction spectroscopy have also been used for more thorough characterization [9,10]. Identifying the mineral pigments present, and their composition and uses, can be highly useful with a view to exposing the history behind artwork and facilitating its dating, preservation and restoration.

2. Materials and methods

A total of 15 paint layer and mortar fragments from Stage I and 11 from Stage II were examined. Figs. 1 and 2 show their photographs and names. The fragments from Stage I could be assigned to no specific *balneum* room because the original building was completely erased at Stage II. On the other hand, Stage II fragments were clearly from the house's office or library.

Raman spectra for the specimens were recorded with an InVia Raman microscope from Renishaw equipped with a Leica microscope fitted with several lenses —and used for optical microscopy observations as well— in addition to monochromators, filters and a CCD. A silicon standard sample was used as reference for calibration (520 cm^{-1}). Spectra were obtained by excitation with green laser light (532 nm) over the wavenumber range 150–1700 cm^{-1}. The laser has a maximum output power of 100 mW at the source. In order to avoid thermal decomposition of the samples, laser powers between 5 and 0,2 mW at source are usually set. The time of acquisitions and number of accumulations per spectrum differed with the particular spectral acquisition conditions. In any case, it was chosen in such a way as to maximize the signal/noise ratio. All spectral treatments (viz., baseline correction, smoothing, etc.) were done with the software Wire 3.4 from Renishaw. The assignment of the spectra has been carried out by comparing them with the spectra described in the databases [11,12]. Subsequently, the exact assignment of the different Raman bands has been made by comparison with the spectra described in the literature.