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Original article

An innovative combination of non-invasive UV–Visible-FORS, XRD and XRF techniques to study Roman wall paintings from Seville, Spain

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ABSTRACT

This study attempts to establish the advantages and limitations of the combined use of portable UV–Vis-FORS and XRF-XRD portable equipment for the non-invasive characterisation of pigments from Roman wall paintings from Seville, Spain, dated to the first and second century AD. XRD revealed the presence of calcite, dolomite and aragonite, indicating the colour white. Egyptian blue was identified using FORS and XRF, and additional information was obtained with XRD. For the colour green, FORS and mainly FTIR and colorimetry enabled the distinction between glauconite and celadonite, although other techniques were necessary to classify all components of the green areas by determining the presence of cuprorivaite, chlorite and chromium. For the colours yellow and red, the presence of goethite, yellow ochre, cinnabar and haematite was confirmed using FORS and XRF in some cases; the results were corroborated by XRD. Chromatic characterisation and the values of inflection points of FORS spectra enabled a better differentiation between reddish colours (orange, brown, purple and pink). The XRD and XRF techniques revealed that violet was created by mixing red haematite and Egyptian blue and slight variations in FORS spectra confirmed this.

1. Introduction

A multi-technique analytical approach for the identification of pigments used to create wall paintings is crucial for a deeper knowledge of raw materials, manufacturing techniques and preservation methodology. Several works have been recently published on the characterisation of pigments from cultural heritage artefacts using Fibre Optics Reflectance Spectroscopy (FORS) and Raman and X-Ray Fluorescence (XRF) portable equipment [1–6], which are applied together in some cases. The imaging spectroscopy techniques can be effectively used for the identification of materials in artwork. The recent advances in the spectro-imaging field in addition to the demand for non-invasive techniques in the study of cultural heritage materials offer a favourable condition for the development of these methods.

However, these techniques are usually not conclusive for identifying pigments; thus, confirmation of the composition through other experimental techniques is required. The inadequacies of FORS are observed when mixtures of pigments or organic binders are present [1,3]. XRF is an elemental analytical technique that only yields information about key chemical elements. The employment of Raman equipment is only reliable when absolute stability is reached, and analysis using this technique takes a long time [1,3]. In addition, the sensitivity and lateral resolution does not typically allow for the obtaining of information about all layers of the polychrome painting [7]. Some pigments also fail to produce an identifiable Raman spectrum, and others do not even produce a detectable signal [8]. To overcome these difficulties, we have employed X-Ray Diffraction (XRD) in this work using a portable system, together with FORS and XRF. Only a few XRD portable systems are available at present [9–12]. XRD is the most consistent technique for the identification of crystalline materials, allowing for the identification of each component in a mixture.

The aim of the present work is to analyse several fragments of Roman wall paintings from an archaeological excavation of the Reales Alcazares Palace in Seville, dated between the first and second century AD The chemical composition of pigments is responsible for the colour of the paintings [13,14]. This study attempts to establish an appropriate methodology for the complete characterisation of the pigments by combining portable UV–Visible-FORS and XRF-XRD portable equipment. As far as we

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know, this is the first study to combine the use of UV–Visible-FORS and XRD portable equipment to analyse mural paintings.

2. Materials and methods

2.1. Materials

Since 2012, an archaeological campaign in the *Patio de Banderas* of Reales Alcazares in Seville has resulted in the recovery of fragments from a large number of wall paintings from the Roman period [15]. These fragments provide an opportunity to acquire more in-depth knowledge about the colour palette used in Roman wall paintings at this site in southern Spain. The set of mural paintings feature simple settings decorated with plant and geometric motifs, characteristic of the third Pompeian style. All date to the first and second century AD, and they were well preserved and not in any need of restoration. The 29 wall painting fragments used in this work were chosen for their colour variety. Non-homogeneous fragments with several motifs and colours were selected (Fig. 1).

2.2. Methods

In the experiments, we employed mainly portable and non-invasive techniques, which were applied directly on the surface of the fragments. The experiments were performed using the equipment available in the Laboratoire d'Archéologie Moléculaire et Structurale (Université Paris 06 - CNRS). The order of the description and discussion of the results from the various techniques was designed for the best comprehension of the readers.

FORS analyses were carried out with a portable Ocean Optics model USB 4000–Vis-NIR Fibre Optic Reflectance (FORS) spectrophotometer. The instrument was equipped with a couple of optic fibres (Ocean Optics RS monocoil), a halogen source lamp (Ocean Optics model HL-2000) and a high performance 3648-element linear CCD-array detector, covering the 200-1100 nm wavelength range with an optical resolution of 1.5 nm FWHM. To properly position the fibres on the samples, a device head was used with a 45° configuration to avoid specular reflectance. A constant sample-to-probe distance (ca. 4 mm) was preserved on the surface to be analysed. The diameter of the analysed area was 2 mm. The behaviour of the reflectance is influenced by the in-homogeneity of the surface or by the presence of underneath layers. Diffuse reflectance spectra were measured against a white standard with guaranteed reflectance at 98% or more in the range studied. The dispositive was also capable of providing colorimetric data (experiments in triplicate), following the CIEL*a*b* chromatic space as defined by the International Commission on Illumination (CIE). L* defines lightness and its values range from 0 to 100, a* and b*

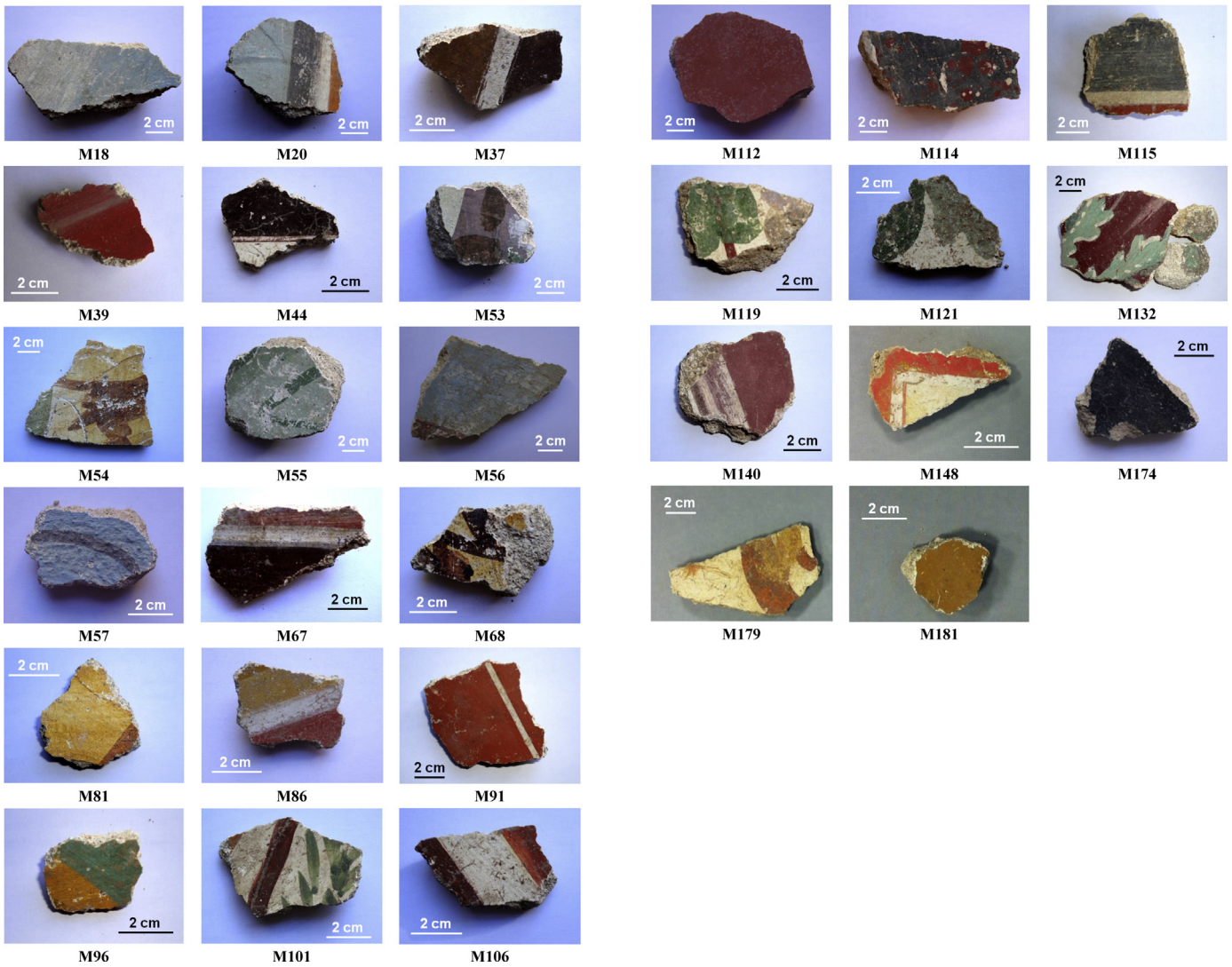

Fig. 1. Photographs of the fragments of the wall paintings studied in this work.

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