

Spectroscopic investigation of Roman decorated plasters by combining FT-IR, micro-Raman and UV-Raman analyses



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ABSTRACT

In this work, the complementary use of Fourier transform infrared (FT-IR) spectroscopy, conventional micro-Raman spectroscopy and UV-Raman scattering proved successful for the characterization of bulk minerals and of a variety of pigments from decorated finishing layers of plasters from a Roman archaeological site known as *Villa dei Quintili*, a monumental residence located in the south-eastern part of Rome (Italy).

The used multi-technique approach provided insights on the pictorial technique, giving information that could be useful for proper restoration.

It is worth underlining that the present study represents the first attempt of carrying out UV resonance Raman measurements for analysing cultural heritage materials.

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1. Introduction

The knowledge of bulk and pigment minerals, their composition and methods of utilization is very important for understanding the history of a work of art and the resolution of problems related to conservation, restoration, dating and author attribution [1,2]. As well known, when dealing with archaeological materials, even the fragments sampled from the artwork, whatever it is, can be precious and the preservation of their integrity is often required. Hence, the use of non-destructive or at most micro-destructive analytical techniques such as the vibrational spectroscopies, have been extensively used for the identification of archaeological source materials [3,4], especially ancient pigments [5–8]. In particular, the combined application of Fourier transform infrared (FT-IR), Raman and micro-Raman spectroscopies [9–11] has shown to yield valuable complementary [9] information for the analysis of pigments on wall paintings. As well known, in fact, although both

FT-IR and Raman spectroscopy provide information about characteristic vibrational levels of molecular systems [12–15], nevertheless, according to selection rules, some transitions may turn out IR-allowed and Raman-forbidden, or vice versa. Furthermore, some of them are detected in both IR and Raman profiles at coincidental frequencies and, others can be observed in neither of these two kinds of spectra. Again, if the molecule has a low symmetry, most of the vibrational modes appear in both its IR and Raman spectra, but, usually, with very different intensities. It occurs because the polarizability change (which provides the required selection rule for Raman scattering) associated to a specific vibration differs from the dipole moment change (i.e.: the required selection rule for IR absorption) associated to the same vibration [16,17]. The simultaneous use of the two techniques, then, will be helpful for the complete identification of the various possible materials characterizing the pigments, such as the minerals, the oxides and the sulphides, as examples. Finally, the incorporation of micro-Raman spectroscopy into the study allows us to achieve more detailed results with high spatial resolution by means of a rapid, non-destructive spectroscopic tool.

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In the present work, we carried out an archaeometric characterization, at molecular level, by using FT-IR spectroscopy, micro-Raman and UV-Raman spectroscopy, of the bulk and of different painted surfaces of plasters, sampled from various areas of an important Roman monumental complex, known as *Villa dei Quintili* (Rome, Italy), dated back to the first half of the 2nd century CE [18]. In the frame of a wider research project aimed at the reconstruction of this attractive archaeological site, up to now little explored, the study of these archaeological findings through the investigation of any changes in the composition of the materials is assessed in order to understand variations in the artistic methodology, styles, or production processes. The obtainable information can strongly contribute, on the one hand to the studies of the archaeologists for the full knowledge of the history of the site, and on the other hand to restoration aims.

Thin-sections of samples have been already classified from the petrographic point of view into three different groups based on the type/sorting of the aggregate and on the main features of the cluster [19]. Preliminary measurements performed by scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) revealed the presence of two layers, identified as the preparation layer and the painted layer. Moreover, two portable instruments (XRF and Raman) have been already used in order to achieve information, in non-invasive way, on the surface of some of these samples [20]. In particular, a handheld energy-dispersive X-ray fluorescence (hXRF) analyser was employed in order to obtain, starting from the elemental composition, an indirect identification of pigments through the detection of their key elements. For example, in the case of some plasters with reddish layer, the simultaneous presence of Hg and S allowed us to hypothesize the use of cinnabar (HgS). However, XRF is insensitive to the chemical state and/or the molecular environment in which the elements are present. Consequently, it cannot provide information of the specific kind of pigment present in the sample. For this reason, the analysis was integrated with conventional Raman measurements performed with a portable spectrometer (pRaman) working in the visible light region. The collected data evidenced the typical peaks of cinnabar for those samples for which XRF revealed the simultaneous presence of Hg and S [20].

Here, we performed the analysis of pigments with the use of a micro-Raman set-up working in the visible light range, in order to obtain an increased signal-to-noise ratio and a reduction in of the sample areas down to a few μm^2 .

Finally, we have carried out, for the first time in the cultural heritage filed, complementary resonance Raman measurements employing the UV radiation available at the IUVS beamline at the Elettra facility [21]. The use of UV radiation instead of the conventional visible or near-IR ones takes several advantages: (a) it increases of order of magnitude the Raman signal coming from molecular groups having π - π^* electronic transitions in the UV range, e.g. such as aromatic rings and/or oxygen composites; (b) it allows to get a significant reduction of the unwanted fluorescence background, thus permitting a more accurate spectral lineshape analysis; (c) it allows to analyse also excitation modes occurring in the low-energy region, which is not easily accessible to a conventional Raman set-up.

2. Experimental

2.1. Materials and sampling

A detailed description of the archaeological site of the *Villa dei Quintili* has been already reported in Ref [19]; we recall here only the main points.

The Roman archaeological site of *Villa dei Quintili* is a monumental residence located in the south-eastern part of Rome,

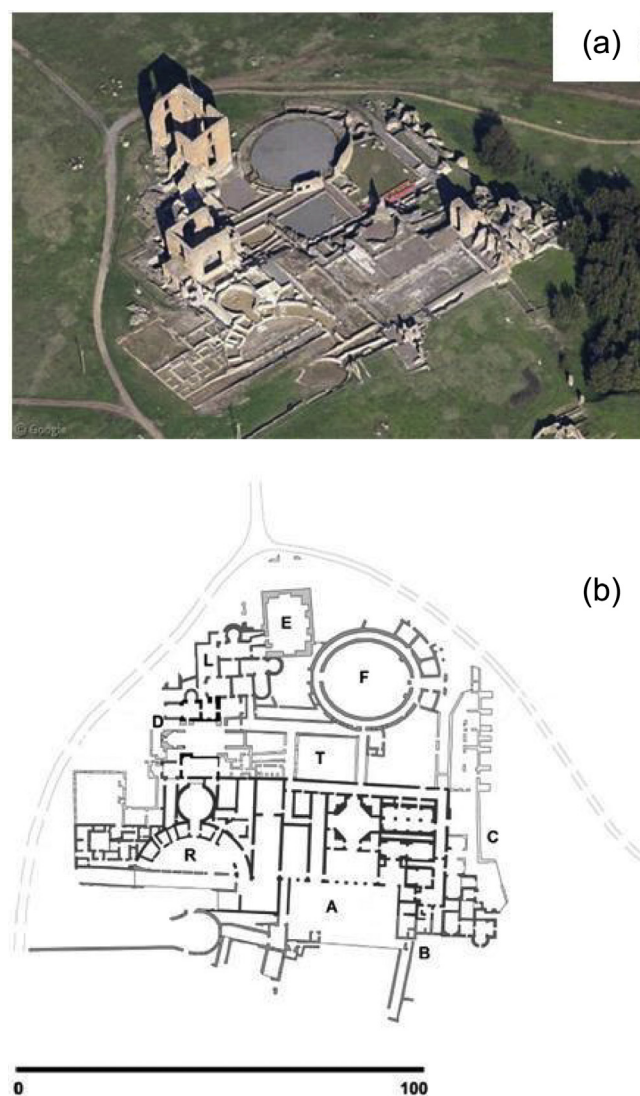


Fig. 1. Satellite view of *Villa dei Quintili* (a) and details of the sampled areas (b). Notes: A = representation area; B = private residences; C = Basis Villae; D = Frigidarium; E = Calidarium; F = Ludus-Viridarium; L = Tepidarium; R = Hippodrome; T = Arcades.

Italy (Fig. 1(a)). It was built in the first half of the second century by the family of the Quintili brothers, on the promontory formed by the ‘Capo di Bove’ lava flow, erupted during the volcanic activity of the Alban Hills [22]. The monumental complex, which belonged to several emperors, consists of many structures expanded around various centres and characterized by different building techniques ascribable to nine construction phases ranging from 98–138CE (Trajan-Hadrian) up to Middle and Modern Ages [23]. The archaeological importance of the residence is mainly related to the high quality of the building and decorative materials, particularly fine marble from around the world. The ornamental elements of the floors generally consist of opus sectile and polychrome mosaics, whereas marble, frescoes, and mosaics were used for the walls.

The samples under investigation are seven fragments of plasters coming from an extensive sampling performed on several edifices of the monumental complex of *Villa dei Quintili* (Fig. 1(b)).

Some images of the analysed archaeological fragments are reported in Fig. 2.

The sampling was carried out at full respect of the integrity of the monument according to the Italian regulations [24], with the

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