

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 $\pi\text{-}\pi^*$ 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,

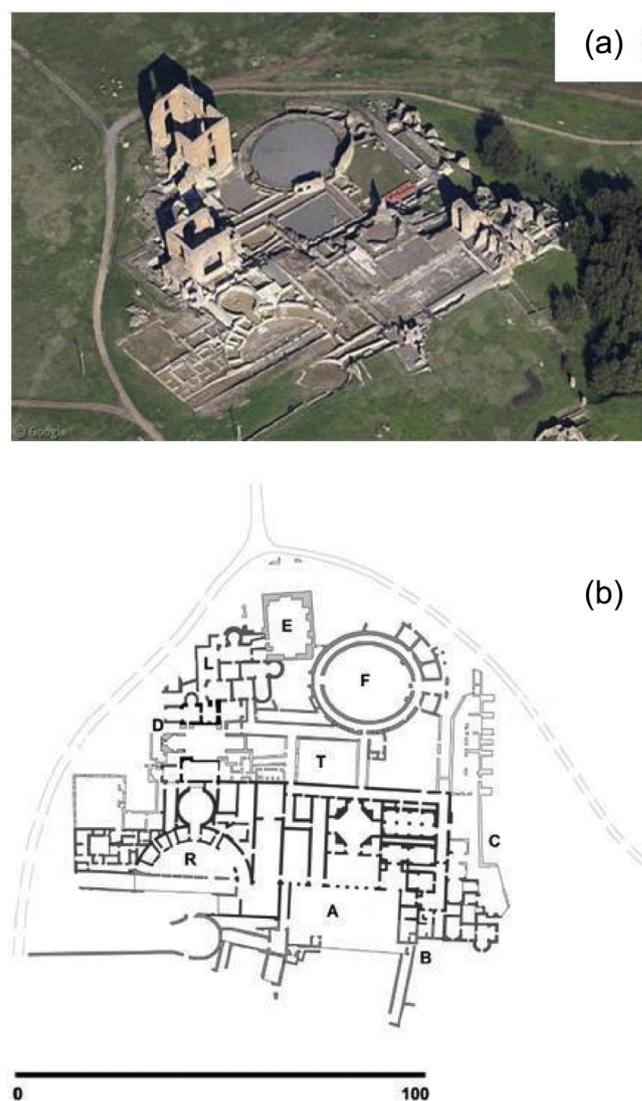


Fig. 1. Satellite view of *Villa dei Quintili* (a) and details of the sampled areas (b). Notes: A = representation area; B = private residences; C = Basis Villae; D = Frigidarium; E = Calidarium; F = Ludus-Viridarium; L = Tepidarium; R = Hippodrome; T = Arcades.

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

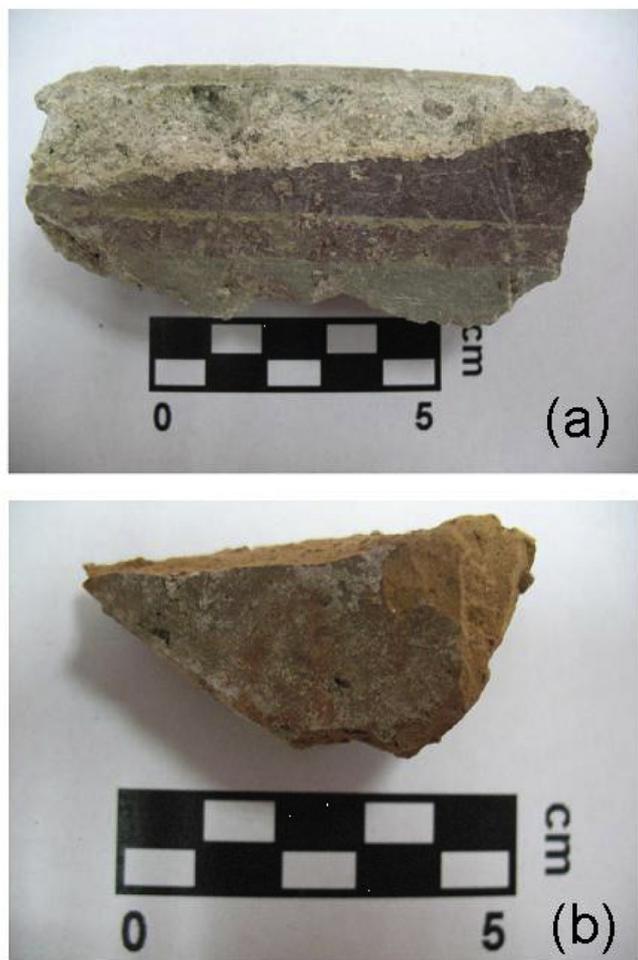


Fig. 2. Representative images of I2 (a) and MD1 (b) fragments.

assistance of archaeologists from the Archaeological Superintendence of Rome, in order to take samples representative of the different construction phases. The list of the analysed samples is reported in Table 1, together with a brief description of their macroscopic features, the indication of the sampling area, of the previously performed analyses [20], and of the methods of investigation applied in this work.

2.2. FT-IR spectroscopy measurements

Fourier transform infrared measurements were performed in the “micro-destructive” transmission configuration on all the

samples by means of a BOMEM DA8 FT-IR spectrometer, equipped with a Globar as light source, a KBr beamsplitter, and a DTGS/MIR detector. Spectra were collected from 500 to 4000 cm^{-1} , using a resolution of 4 cm^{-1} . The samples were prepared in pellets, using small quantities (~ 2 mg) of sample dispersed in ~ 200 mg of powdered CsI, that is, transparent in the investigated IR frequency range. 32 repetitive scans were automatically added to obtain a good signal-to-noise ratio and spectral reproducibility. The experimental absorbance profiles were compared with those of standard minerals and clays [25] and with data reported in different sources [26,27] for a reliable assignment of the bands.

2.3. Micro-Raman spectroscopy measurements

All micro-Raman measurements were carried out on samples deposited on a glass slide in air and at room temperature. The corresponding spectra were obtained in backscattering geometry and by using two different experimental setups to better explore different spectral features of the samples.

2.3.1. Raman mapping measurements

Raman maps were acquired by using a software-controlled motorized XY stage coupled to a Raman system (HORIBA Jobin Yvon LabRam HR800) consisting of an 80 cm focal length spectrograph using a 600 grooves/mm grating and a charge-coupled device (CCD) detector cryogenically cooled. The Raman spectra in the wavenumber range between 200 and 1200 cm^{-1} were collected by using an exciting radiation at 632.8 nm (He-Ne laser, power at the output ≈ 20 mW). The laser was focused onto the sample surface with a spot area of about 4 μm^2 through the 80 \times objective (NA=0.9) of the microprobe setup. The elastically scattered radiation was filtered by using a notch filter. In this configuration, the resolution was about 1 cm^{-1} /pixel. Raman mapping was achieved by collecting sets of spectra sequentially recorded step-by-step from sample points, 3 μm away from each other, within rectangular regions of interest. Repeated Raman maps were carried out from the same sample in order to assess the analysis reproducibility.

2.3.2. UV-Raman spectroscopy measurements

UV Micro Raman scattering measurements were carried out at the BL10.2-IUVS beamline at the Elettra Synchrotron laboratory in Trieste by exploiting the experimental set-up described in Ref [20]. Vertically polarized VV Raman spectra were excited at 266 nm. The inelastic scattered signal was collected in a back-scattering geometry by means of a reflective 40 \times objective. A triple stage spectrometer (Trivista, Princeton Instruments) and a back-thinned CCD detector were used to get the Raman spectra in the 200–1200 cm^{-1} wavenumber range. The experimental resolution was set to 5 cm^{-1} in order to ensure enough resolving power and count-

Table 1
List of investigated fragments of plasters, together with their macroscopic features, the indication of provenance area, of the previously performed analyses, and of the methods of investigation applied here.

Fragment	Macroscopic features	Provenance area	Previously performed analyses	Present performed analyses
I1A	Reddish finishing layer	R54	hXRF, pRaman	IR
I1B	Fragment of plaster with reddish finishing layer	R54	hXRF	IR, Micro- Raman
I2	Fragment of plaster with 3 finishing layers: reddish-brown, green and light yellow	R6	hXRF	IR, Micro- Raman, UV-Raman
I3	Fragment of plaster with two reddish-brown finishing layers	A5-A6	hXRF	IR, Micro- Raman
I4A	Fragment of plaster with whitish finishing layer	Basis Villae	hXRF, pRaman	IR
I4B	Fragment of plaster with reddish finishing layer	Basis Villae	hXRF, pRaman	IR, UV-Raman
MD1	Fragment of plaster with reddish finishing layer	E2	–	IR, Micro- Raman

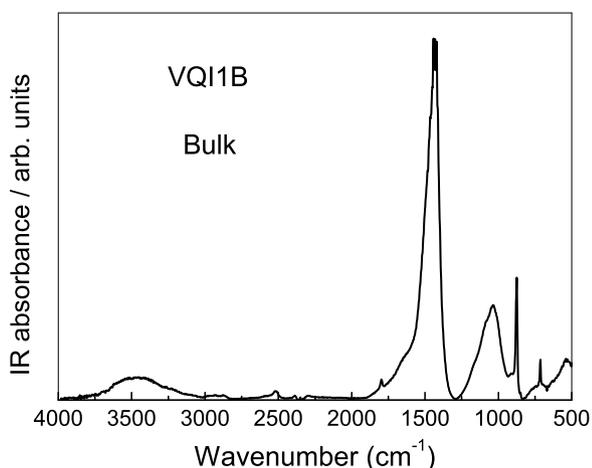


Fig. 3. FT-IR spectrum, in the 4000–500 cm^{-1} range, of the bulk of I1B sample.

rates. No baseline correction was performed to achieve the final spectra.

3. Results and discussion

3.1. FT-IR spectroscopy measurements

FT-IR analysis, performed for all samples in the 500–4000 cm^{-1} range, has been aimed at qualitative identification of the mineralogical composition of the bulk of the findings, and to the determination of the molecular nature of the pigmenting agents.

In Fig. 3 the FT-IR spectrum of the bulk of the sample I1B is reported as an example.

In spite of the complexity of the vibrational features in the investigated range, we have been able to assign spectra to specific materials. In particular, in Fig. 4, we plotted, as examples, the IR spectra of the findings I2, I3, MD1, and I4A relative to different sampling areas, amplified in the 500–2000 cm^{-1} region, where most of the vibrational contributions of the different mineralogical phases fall, together with the corresponding centre-frequencies of the main vibrational bands.

These IR spectra revealed the most relevant differences between the bulk and the corresponding painted surface, so hereinafter we will focus the discussion only on these samples. Table 2 summarizes the obtained results.

As far as sample I2 is concerned (Fig. 4(a)), the FT-IR profile of the bulk is dominated by the absorption bands of calcite (CaCO_3), centred, in particular, at $\sim 714 \text{ cm}^{-1}$, $\sim 874 \text{ cm}^{-1}$, $\sim 1440 \text{ cm}^{-1}$ and $\sim 1797 \text{ cm}^{-1}$. Furthermore, a broad band is clearly evident in the ~ 950 – 1268 cm^{-1} range that can be ascribed to the presence of feldspars. Considering the high H_2O content, as suggested by the observation, for all samples, between ~ 3000 and $\sim 3800 \text{ cm}^{-1}$ of the O–H stretching vibration (see Fig. 3), we can hypothesize that the present feldspar is kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2(\text{H}_2\text{O})$), product of a slow and complex hydrothermal alteration of feldspars, of feldspathoids and of other aluminiferous silicates, present as essential components in many rocks, mainly of granitic and gneissic type. The FT-IR profile of the red pigment clearly revealed the presence of iron oxides pigment based contributions centred at ~ 544 and 910 cm^{-1} . Furthermore, the large band between ~ 950 and $\sim 1268 \text{ cm}^{-1}$ includes, other than the contribution of feldspar, also those of iron oxide centred at ~ 1011 and $\sim 1052 \text{ cm}^{-1}$. It is interesting to note how very similar the FT-IR spectra of green

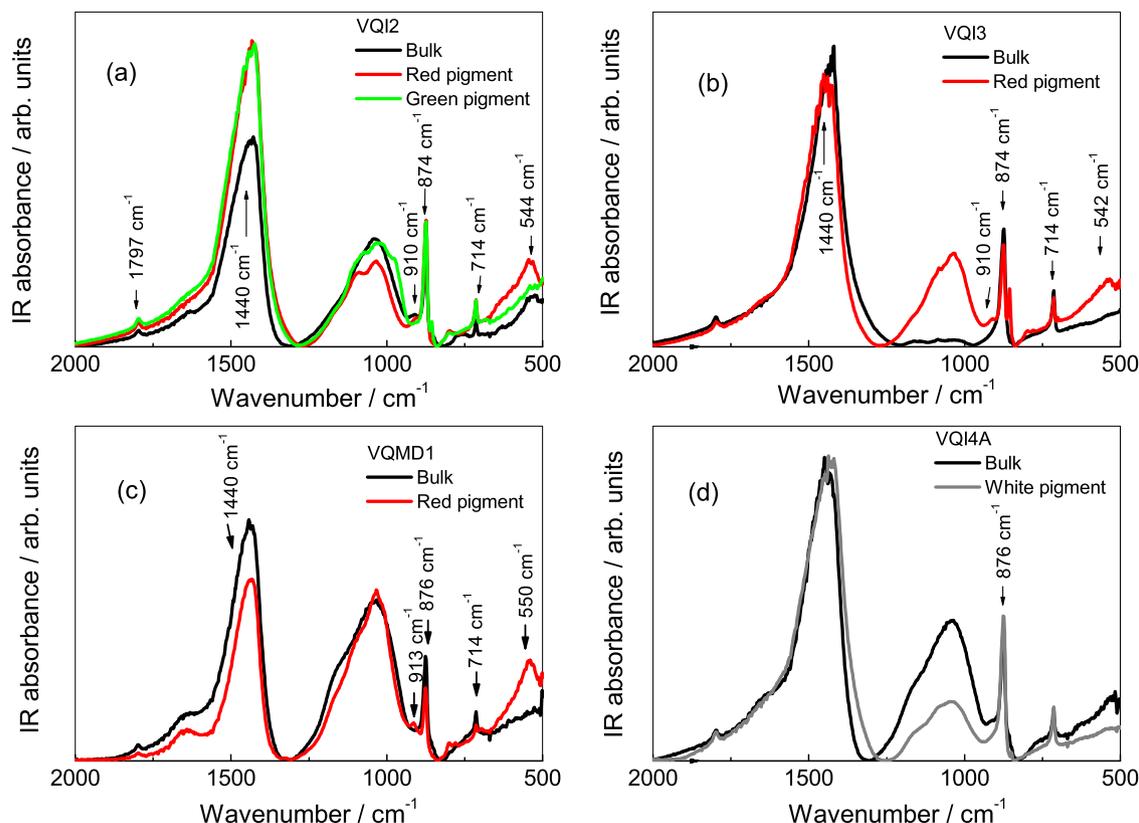


Fig. 4. FT-IR spectrum, in the 2000–500 cm^{-1} range, of the I2 (a), I3 (b), MD1 (c), and I4A (d) samples, relative to the different analysed zones. Dark line: bulk, red line: red pigment, green line: green pigment, grey line: white pigment. The main centre-frequencies are also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Results of IR, micro-Raman and UV-Raman analyses performed on the investigated fragments of plasters.

Performed analyses	Analyzed fragment	Bulk	Red layer	Green layer	White layer
IR	I2	Calcite Kaolinite	Iron oxides	Iron oxides	–
	I3	Calcite	Iron oxides	–	–
	MD1	Calcite Kaolinite	Iron oxides	–	–
	I4A	Calcite	–	–	Calcite
			Red layer	Green layer	White layer
Micro-Raman	I1B	–	Hematite Magnetite	–	–
	I2	–	Hematite Magnetite	Hematite Magnetite	–
			Red layer	Green layer	White layer
UV-Raman	I2	–	Calcite	Calcite	–
	I4B	–	Cinnabar Calcite	–	–

and red pigments appear. Consequently, we can guess that, with good probability, the same agents act to colour the sample both green and red.

In the case of I3 fragment (Fig. 4(b)), the FT-IR spectrum of the bulk presents, as for I2 sample, the same absorption bands of calcite. The absence of feldspars can be ascribed to the different sampling area of the two findings. In the spectrum of the red pigment we reveal, once again, the presence of the characteristic peaks of the bulk with, in addition, those of pigments based on iron oxides, centred at ~ 542 , ~ 910 , ~ 1011 , and ~ 1052 cm^{-1} (these latter two, in particular, give rise to the broad band observed between ~ 950 and ~ 1268 cm^{-1}).

Calcite is always present in the FT-IR profile of the bulk of MD1 sample (Fig. 4(c)). The observation of the spectrum in the whole analysed wavenumber range suggests us that the sample is strongly hydrated, as appears evident from the intense O–H stretching band between ~ 3000 and ~ 3800 cm^{-1} . The band between ~ 950 and ~ 1268 cm^{-1} is in part attributable to kaolinite that contributes, in particular, with peaks centred at ~ 1002 and ~ 1118 cm^{-1} . In the spectrum of the red pigment it is possible to recognize, similarly to the sample I2, the characteristic contributions of the pigment based on iron oxide, at ~ 550 and ~ 913 cm^{-1} . The broad band between ~ 950 and ~ 1268 cm^{-1} is due, other than to feldspars, also to the presence of iron oxide, with peaks at ~ 1011 and ~ 1052 cm^{-1} .

Finally, in sample I4A (Fig. 4(d)), vibrational bands of calcite can be noticed for the bulk, and for the white pigment as well. Nevertheless, in the case of the white surface layer, the contribution of calcite (peak at ~ 876 cm^{-1}) appears much more intense with respect to the broad band observed between ~ 950 and ~ 1268 cm^{-1} due to feldspars. This occurrence indicates calcite as main constituent of the white pigment, in agreement with our previous portable Raman measurements. It is probably produced by the calcium oxide (CaO) also used for the preparatory layer.

To conclude, the predominant presence of Ca in all the investigated samples can be attributed to the fact that IR absorption does not allow to distinguish the surface layer from the ceramic bulk that inevitably remained as a result of micro-sampling. Nevertheless, it is also true that, as well known, Roman frescoes were generally made by applying pigments on dry plaster, which reacted with the atmospheric CO_2 producing an external layer of CaCO_3 . A mixture based on water and lime was often used for fixing pigments and getting the desired shade.

3.2. Micro-Raman spectroscopy measurements

Micro-Raman analysis has been performed on the finishing layer of those fragments reported in Table 1, and we discuss here those spectra for which fluorescence did not mask meaningful information. Again, the results obtained for the analysed fragments are reported in Table 2.

In Fig. 5, some optical microscopy images, taken on the I1B fragment, as detected by Raman mapping, (a) and the related typical spectra (b), are shown.

Several clearly contrasted peaks are observed in the region between 200 and 700 cm^{-1} , associated to hematite and magnetite (red arrow) [28–30], thus suggesting the presence of red ochre, an inorganic substance which was known and largely used since antiquity. The spectra collected on the several investigated areas appear to be more similar to each other, therefore we can hypothesize that magnetite is widely distributed in the pigment layer.

It is worth noting that, although I1A and I1B are fragments of plasters both collected from the R54 area, different pigments (cinnabar [20] and red ochre) are revealed. This latter result could be indicative of a different manufacturing technique related to the occurrence that the monumental complex of *Villa dei Quintili* was the residence of emperors belonging to different times, or more probably related to the various restoration works incurred.

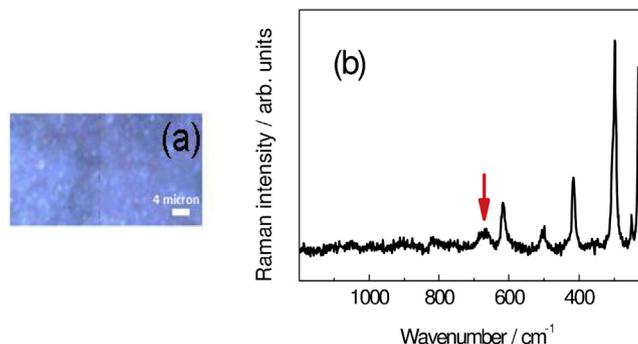


Fig. 5. Optical microscopy image of the sample region investigated by Raman mapping (a) and a related typical spectrum (b) of I1B sample, fragment of plaster with reddish finishing layer. The red arrow indicates the main contribution of magnetite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

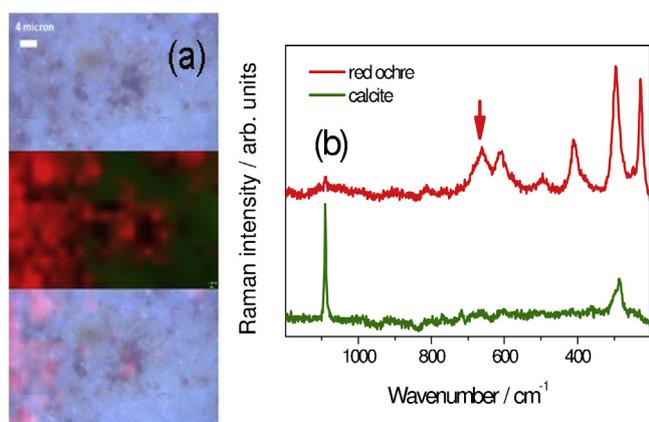


Fig. 6. Optical microscopy image of a sample region ((a), top panel) together with two Raman maps of this region ((a), middle and bottom panels) and two related typical (b) recorded from reddish-brown finishing layer of I2 fragment of plaster. Red line: ochre, Green line: calcite. The red arrow indicates the main contribution of magnetite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Fig. 6, we show the optical microscopy image of a sample region ((a), top panel) together with two Raman maps of this region ((a), middle and bottom panels) and two related typical spectra (b) recorded from reddish-brown finishing layer of I2 sample.

Again, Fig. 7 reports the optical microscopy image of a sample region ((a), top panel) together with two Raman maps of this region ((a), middle and bottom panels) and two related typical (b), this time recorded from greenish and light yellowish finishing layers of I2 fragment.

In both cases, the pigmented layer shows two different regions: one is characterized by the presence of ochre (red line), constituted by hematite and magnetite (red arrow), widely distributed as indicated by the homogeneity of the spectra in all the analysed area, and the other region shows the presence of calcite (green line), with its typical fingerprints occurring at 283, 714 and especially, 1088 cm^{-1} [31].

For this sample, micro-Raman spectral mapping, other than confirming the results obtained by FT-IR measurements, furnished useful information on the composition of the ochre. We can

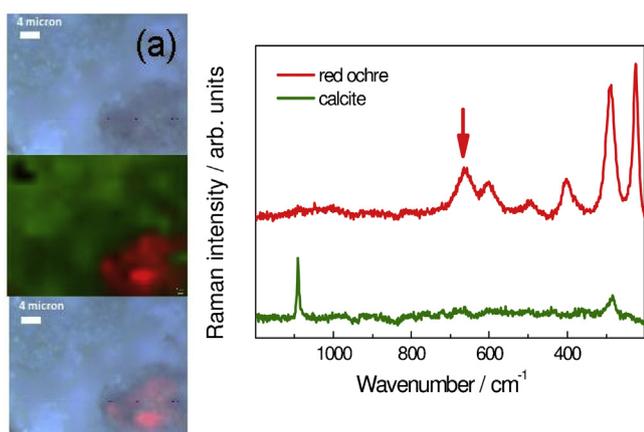


Fig. 7. Optical microscopy image of a sample region ((a), top panel) together with two Raman maps of this region ((a), middle and bottom panels) and two related typical (b) collected from greenish and light yellowish finishing layers of I2 fragment of plaster. Red line: ochre, Green line: calcite. The red arrow indicates the main contribution of magnetite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

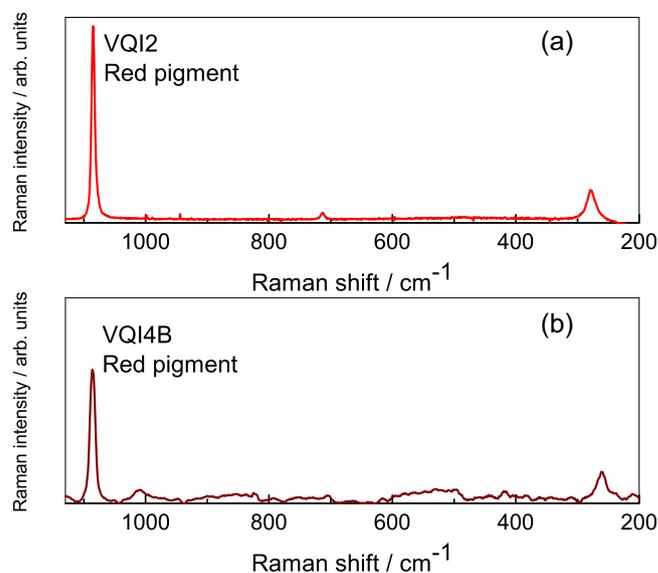


Fig. 8. UV-Raman spectrum, in the $1130\text{--}200\text{ cm}^{-1}$ range, recorded from the reddish finishing layer of I2 (a) and I4B (b) samples, relative to the different analysed zones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

associate the presence of CaCO_3 to the technique of Roman frescoes or consider it as accessory mineral that contributes to a particular nuance of red ochre.

Finally, the noticeable similarity of these two spectra confirms the hypothesis for the use of the same agents for obtaining the wanted colouration.

3.3. UV-Raman spectroscopy measurements

As first attempt in the cultural heritage field, UV-Raman measurements have been carried out for samples I2 and I4B, in the aim to compare them with, micro-Raman and portable Raman results, respectively.

UV-Raman spectrum of the red pigment of I2 (see Fig. 8(a) and Table 2) sample gave clear evidence of calcite peaks centred at ~ 283 , ~ 713 and $\sim 1088\text{ cm}^{-1}$ (main peak).

As expected, in this case these peaks are strongly enhanced, since we are working in resonant conditions with the functional groups of CaCO_3 , which occur just at UV wavelengths. Moreover, for the same fragment, the green pigment exhibited an UV-Raman spectrum (not reported here) very similar to that of the red pigment, in agreement with what has already been hypothesized according to the analysis of the FT-IR and micro-Raman spectra.

Concerning I4B fragment (Fig. 8(b)), the well evident peak centred at $\sim 262\text{ cm}^{-1}$ can be ascribed to cinnabar [28–31], confirming the portable-Raman results. In addition, the most prominent peak at $\sim 1080\text{ cm}^{-1}$ testifies once again the presence of calcite already associated to the painting technique of Roman frescoes.

The agreement of the obtained results with those coming from conventional Raman methodologies encourages us on possible future application of UV-Raman techniques in the cultural heritage field. We would like to further stress that, in principle, the tunability of the synchrotron radiation source, offered by IUVS set-up, will allow us to work in resonant conditions between the excitation wavelength and the wavelength of UV-absorption for specific functional groups of the investigated samples, which is not accessible to conventional laser Raman systems. Finally, it could also be considered as an alternative spectroscopic approach with

respect to synchrotron radiation X-ray absorption spectroscopy (SR-XAS) techniques, recently successfully exploited in some cultural heritage studies, in which the non-destructive identification of the main pigments of coloured coatings was indirectly achieved by means of structural information.

4. Conclusions

The plaster making technique used in the Roman archaeological site of *Villa dei Quintili* wall paintings is here explored by a multi-methodological characterization of seven fragments of plasters with coloured finishing layers.

The FT-IR profiles of the bulk of all the investigated samples revealed a strong hydration and are dominated by the presence of calcite. In addition, kaolinite is recognized for I2 and MD1 fragments.

Concerning the decorated layers, the combined use of FT-IR and micro-Raman spectroscopies allowed, as main result, for the unambiguous identification of red ochre as red pigment. This occurrence suggests the use of locally available materials in the paintings of *Villa dei Quintili*.

Finally, we attempted for the first time to test and validate the UV-Raman technique as a non-destructive powerful tool for obtaining a detailed compositional characterization of the decorated surfaces of artworks of historical-artistic interest. For the two samples investigated, the results are in agreement with those obtained by conventional Raman techniques, encouraging us on possible future application of UV-Raman techniques in the cultural heritage field whenever the conventional Raman set-up is not able to detect Raman scattering.

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References

- [1] F. Bardelli, G. Barone, V. Crupi, F. Longo, G. Maisano, D. Majolino, P. Mazzoleni, V. Venuti, Iron speciation in ancient Attic pottery pigments: a non-destructive SR-XAS investigation, *J. Synchrotron Radiat.* 19 (2012) 782–788.
- [2] G. Barone, V. Crupi, F. Longo, D. Majolino, P. Mazzoleni, G. Spagnolo, V. Venuti, E. Aquilia, Potentiality of non-destructive XRF analysis for the determination of Corinthian B amphorae provenance, *X-ray Spectrom.* 40 (2011) 333–337.
- [3] V.C. Farmer, *Infrared Spectra of Minerals*, Mineralogical Society, London, 1974.
- [4] G.A. Hope, R. Woods, C.G. Munce, Raman microprobe mineral identification, *Miner. Eng.* 14 (2001) 1565–1577.
- [5] H.G.M. Edwards, E.M. Newton, J. Russ, Raman spectroscopic analysis of pigments and substrata in prehistoric rock art, *J. Mol. Struct.* 550–551 (2000) 245–256.
- [6] M. Bouchard, D.C. Smith, Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 59 (2003) 2247–2266.
- [7] P. Vandenberghe, H.G.M. Edwards, L. Moens, A decade of Raman spectroscopy in art and archaeology, *Chem. Rev.* 107 (2007) 675–686.
- [8] K. Eremin, J. Stenger, J. Huang, A. Aspuru-Guzik, T. Betley, L. Vogt, I. Kassal, S. Speakman, N. Khandekar, Examination of pigments on Thai manuscripts: the first identification of copper citrate, *J. Raman Spectrosc.* 39 (2008) 1057–1065.
- [9] M.C. Edreira, M.J. Feliu, C. Fernandez-Lorenzo, J. Martin, Spectroscopic analysis of roman wall paintings from Casa del Mitreo in Emerita Augusta, Merida, Spain, *Talanta* 59 (2003) 1117–1139.
- [10] L.M. Moretto, E.F. Orsega, G.A. Mazzocchin, Spectroscopic methods for the analysis of celadonite and glauconite in Roman green wall paintings, *J. Cult. Herit.* 12 (2011) 384–391.
- [11] I. Aliatis, D. Bersani, E. Campani, A. Casoli, P.P. Lottici, S. Mantovana, I.G. Marino, F. Ospitali, Green pigments of the Pompeian artists' palette: *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 73 (2009) 532–538.
- [12] R.J.H. Clark, S. Mirabaud, Identification of the pigments on a sixteenth century Persian book of poetry by Raman microscopy, *J. Raman Spectrosc.* 37 (2006) 235–239.
- [13] B. Schrader, *Infrared and Raman Spectroscopy: Methods and Applications*, VCH publishers, Weinheim, 1995.
- [14] J.R. Ferraro, K. Nakamoto, *Introductory Raman Spectroscopy*, Academic Press, Boston, 1994.
- [15] E. Smith, G. Dent, *Modern Raman Spectroscopy—A Practical Approach*, J. Wiley & Sons, Hoboken, 2005.
- [16] I.N. Levine, *Molecular Spectroscopy*, John Wiley and Sons, New York, 1975.
- [17] R.S. Czernuszewicz, T.G. Spiro, IR raman and resonance raman spectroscopy, in: E.I. Solomon, A.B.P. Lever (Eds.), *Inorganic Electronic Structure and Spectroscopy; Volume I: Methodology*, John Wiley and Sons, New York, 1999, pp. 353–441.
- [18] A. Rotondi, *Forma Urbis-Itinerari Nascosti Di Roma Antica*, ANNO XVII(2), Roma, 2012.
- [19] C.M. Belfiore, G.V. Fichera, M.F. La Russa, A. Pezzino, S.A. Ruffolo, G. Galli, D. Barca, A multidisciplinary approach for the archaeometric study of Pozzolan aggregates in Roman mortars: the case of Villa dei Quintili (Rome Italy), *Archaeometry* 57 (2015) 269–296.
- [20] V. Crupi, G. Galli, M.F. La Russa, F. Longo, G. Maisano, D. Majolino, M. Malagodi, A. Pezzino, M. Ricca, B. Rossi, S.A. Ruffolo, V. Venuti, Multi-technique investigation of roman decorated plasters from villa dei quintili (Rome, Italy), *Appl. Surf. Sci.* 349 (2015) 924–930.
- [21] F. D'Amico, M. Saito, F. Bencivenga, M. Marsi, A. Gessini, G. Camisasca, E. Principi, R. Cucini, S. Di Fonzo, A. Battistoni, *Nucl. Instrum. Methods Phys. Res., Sect. A* 703 (2013) 33–37.
- [22] A. Rotondi, *La Villa dei Quintili e i suoi antichi proprietari*, *Forma Urbis-Itinerari nascosti di Roma Antica ANNO XVII(2)* (2012) 6–8.
- [23] G.V. Fichera, D. Barca, C.M. Belfiore, M.F. La Russa, A. Pezzino, *Rendiconti Online Società Geologica Italiana* 21 (2012) 659–660.
- [24] *NORMAL 3/80. Materiali lapidei: campionamento e conservazione dei campioni*, 1980, Roma.
- [25] *Sadtler Database for FT-IR*, BioRad Laboratories.
- [26] W.P. Griffith, *Advances in Raman and infrared spectroscopy of minerals*, in: R.J. H. Clark, R.E. Hester (Eds.), *Spectroscopy of Inorganic-Based Materials*, John Wiley & Sons, Chichester, UK, 1987, pp. 119–186.
- [27] G.E. De Benedetto, R. Laviano, L. Sabbatini, P.G. Zamboni, *Infrared spectroscopy in the mineralogical characterization of ancient pottery*, *J. Cult. Herit.* 3 (2002) 177–186.
- [28] I.M. Bell, R.J.H. Clark, P.J. Gibbs, *Raman Spectroscopic Library of Natural and Synthetic Pigments*, <http://www.chem.ucl.ac.uk/resources/raman/>.
- [29] RRUFF Project, 2010, Department of Geosciences, University of Arizona, Tucson, USA. <http://rruff.info/>.
- [30] *Handbook of Raman spectra*, <http://ens-lyon.fr/LST/Raman>.
- [31] S.P.S. Porto, J.A. Giordmaine, T.C. Damen, Depolarization of Raman scattering in calcite, *Phys. Rev.* 147 (1966) 608–611.