OM, SEM-EDX, Micro-Raman and FT-IR investigation of Roman frescoes from Villa dei Quintili (Rome, Italy)

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Abstract

The present work reports a multi-analytical study, based on optical microscopy (OM), scanning electron microscopy equipped with an energy dispersive X-ray detector (SEM-EDX), micro-Raman and Fourier transform infrared spectroscopy (FT-IR) techniques, aimed at establishing the painting techniques and palettes used to decorate a variety of fragments of frescoes coming from Villa dei Quintili in Rome (Italy) and dated back II century A. D.. This combined methodological approach, covering different spatial scales extending from the macroscopic to the elemental domain, revealed successful for the unambiguous identification, in non-invasive or at least micro-destructive way, of pigments and binders. The used chromatic palette was identified as yellow ochre (goethite), carbon black (of vegetal origin), green earth, red ochre (haematite), lime white and Egyptian blue (cuprorivaite). Organic and inorganic binders were respectively identified as linseed oil and calcium carbonate. Plaster layer was mainly composed by calcite, feldspars and gypsum.

The obtained data revealed crucial for improving our knowledge of materials and preparation methods of pigmenting agents of these fragments, taken from the warehouse of the Villa and hence of unknown provenance area, in view of their right positioning in a specific area of the archaeological complex. In fact, the characterization of the different pigments could support the conservators to better identify the distribution of the frescos among the different rooms and to reconstruct the original aesthetic of the Villa during the Quintili age.

Keywords: micro-Raman spectroscopy; FT-IR spectroscopy; SEM-EDX; OM; Roman decorated plasters; pigments.

1. Introduction

Since long time, the investigation of Roman wall paintings has attracted the interest of researchers for many reasons. Frescos are, in fact, extended in a wide geographic area, in different architectural contexts, exhibiting a variety of vivid colours. At present, even if many studies have been performed from the artistic and archaeological points of view, we are still far from a comprehensive evaluation of the employed materials and techniques (Bakiler et al., 2016; Mazzocchin et al., 2003).

In this context, the identification of pigments as well as of the composition of the plaster layers used on the mural paintings represents one of the most important issue. As well known, it constitutes the starting point for the understanding of the particular technique used from Roman artists in a specific area (Barilaro et al., 2008). From that, the reconstruction of the possible communication and trade routes can be, in principle, attempted.

An archaeometric investigation has been conducted on Roman plasters at different archaeological sites, mainly in Italy, but not only (Aliatis et al., 2010; Amadori et al., 2015; Baraldi et al., 2007; Duran et al., 2011; Edwards et al., 2003; Mahmoud et al., 2012; Mateos et al., 2015; Weber et al., 2009). In all these cases, a multi-technique approach, involving both non-invasive and micro-destructive methods such as Raman micro-spectroscopy, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy equipped with an energy dispersive X-ray detector (SEM-EDX) and optical microscopy (OM), revealed successful in the determination of the plaster composition and the nature of pigments.

Hence, an investigation has been carried out on some ancient Roman frescoes coming from Villa dei Quintili (Rome, Italy) (Alberti et al., 2017; Crupi et al., 2015, 2016), in the framework of a wide

multi-technique archaeometric research performed on a variety of materials from this renowned archaeological site (Belfiore et al., 2015).

Villa dei Quintili (Fig. 1) is a monumental complex located on the fifth mile of the via Appia Antica, several kilometres far from the the center of Rome (Frontoni, 2000; Frontoni and Galli, 2010; Rotondi, 2012).

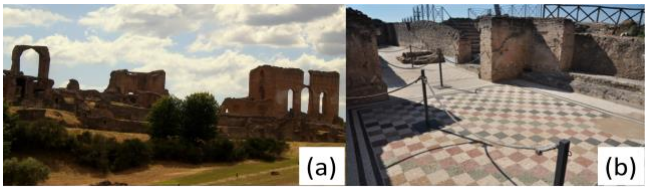


Fig. 1. (a) A view of the Villa dei Quintili (Rome, Italy). (b) Details of the archaeological site.

Built by the family of the Quintili brothers during the late Hadrian period (first half of the second century A. D.), it underwent a series of construction phases until the Middle and Modern Ages. The Villa assumes particular archaeological relevance in view of the high quality of the buildings and decorative materials. Opus sectile and polychrome mosaics generally constitute the ornamental elements of the floors, marbles, frescoes and mosaics those of the walls. Furthermore, in later times, this residential complex became a centre of recycling and production of a variety of materials, including glasses, marbles, frescoes and tuffs (Basso et al., 2014). This contributed to get complicated the case study of this site, since the most part of these materials, and in particular frescoes fragments, have been moved away from their original location and reused.

The six plasters under investigation in the present work are examples of this complex task. Taken from the warehouse of the Villa, and hence of unknown provenance area, they have been already subjected to an X-ray fluorescence (XRF) analysis in order to identify the elemental constituents of the pigmenting agents (Alberti et al., 2017). Nevertheless, at that time, the investigation of the molecular nature of pigments, necessary for their unambiguous identification, performed by means of a portable Raman spectrometer, gave unreliable results because of the organic layers that covered the samples, originating a high fluorescence that completely masked the signal coming from the pigment. This is, unfortunately, the main disadvantage of portable equipments, that don't have confocal attitude and micro-head.

Here, we have been able to overcome this difficulty by carrying out measurements using a micro-Raman set-up working with different wavelengths of excitation, in the visible and middleUV range, so increasing the signal-to-noise ratio and reducing the sample areas down to a few of μm^2.

Data have been integrated by FT-IR spectroscopy measurements for the characterization, at molecular level, of the painted surfaces (supporting Raman results) and the bulk, by optical microscopy (OM) observation, in order to gather information on the textural characteristics of sample layers, and Scanning Electron Microscopy/Energy Dispersive Using X-Ray (SEM-EDX) analysis for studying the morphology and the chemical composition of the samples.

2. Material and methods

2.1 Materials

Measurements have been performed on six fresco fragments, dated back II century A. D., referred as Cod. r19a, Cod. r19b, Cod. r19c, Cod. r19d, Cod. r19f, Cod. section. Their representative images are shown in Fig. 2.

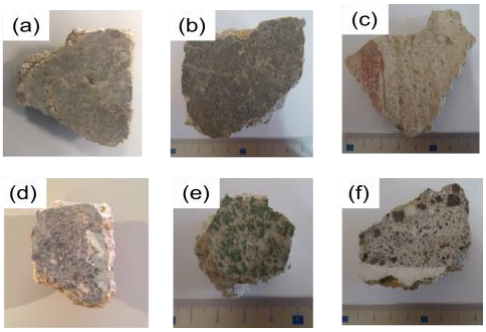


Fig. 2. Photographs of analysed fragments. (a) Fresco Cod. r19a, (b) Fresco Cod. r19b, (c) Fresco Cod. r19c, (d) Fresco Cod. r19d, (e) Fresco Cod. r19f, (f) Fresco Cod. section.

As already said in the Introduction, samples are taken from the warehouse of Villa dei Quintili, as a consequence their provenance is unknown. The sample selection was undertaken under the supervision of the archaeologists from the Archaeological Superintendence of Rome, in order to select representative fragments.

The mascroscopic features of the investigated frescoes are reported in Table 1, together with an indication of the previously (Alberti et al., 2017) and present performed analyses.

Table 1

Macroscopic features of investigated frescoes together with the employed analytical techniques.

Sample	Description	Employed techniques

Cod. r19a	Fragment of fresco with two pigmented areas: yellow and black	SEM-EDX, FT-IR, micro-Raman
Cod. r19b	Fragment of fresco with a green pigmented area	XRF (previously), SEM-EDX, FT-IR, micro-Raman
Cod. r19c	Fragment of fresco with two pigmented areas: red and white	XRF (previously), SEM-EDX, FT-IR, micro-Raman
Cod. r19d	Fragment of fresco with two pigmented areas: blue and white	XRF (previously), OM, SEM-EDX, FT-IR, microRaman
Cod. r19f	Fragment of fresco with a green pigmented area	XRF (previously), OM, SEM-EDX, FT-IR, microRaman
Cod. section	Fragment of fresco with three pigmented areas: brown, dark brown and white	XRF (previously), SEM-EDX Mapping, FT-IR, micro-Raman

2.2 Methods

2.2.1 OM and SEM-EDX analyses

Some micro-samples, bearing the characteristic of the whole stratigraphy, were collected by a scalpel from every fragment of fresco. Cross-sections were obtained by embedding the samples into epoxy resin (Epofix Struers and Epofix Hardener with ratio 15:2) and by polishing them with silicon carbide fine sandpaper (800-4000 mesh). The polished cross-sections were thus observed through a polarized light optical microscope Olympus BX51TF equipped with an Olympus TH4200 lamp (visible light) and an Olympus U-RFL-T (UV radiation). Imaging at higher magnifications and micro-analyses were performed by SEM-EDX using a FE-SEM Tescan Mira 3XMU-series (Brno, Czech Republic), set with an accelerating voltage of 15-20 kV in high vacuum and equipped with a Bruker Quantax 200 Energy-Dispersive X-ray spectrometer. Before the SEMEDX investigation, the samples were made conductive with a graphite coating obtained by a Cressington Carbon Coater 208C. Data were then processed using the Bruker Esprit 2 microanalysis software.

2.2.2 Micro-Raman analyses

Micro-Raman spectra were obtained, in non invasive way, by means of a LabRam HR800 Raman confocal Micro-Spectrometer (Horiba-Jobin Yvon) in the back-scattering configuration and making use of excitation wavelengths ranging from the near UV to the near infrared. Indeed, this setup allows for a multi-wavelength excitation being coupled to a He-Ne laser (633 nm), an argonion laser used to

produce the UV line at 364 nm, a solid state laser at 561 nm and a diode laser at 785 nm. The laser beams at l_{exc} = 633 nm, 561 nm and 785 nm were focused by means of a microscope objective 50X Long Working Distance (Olympus LM-Plan-Fl, NA = 0.5, power of 0.5 mW on samples) mounted on an Olympus BX41-microscope, while the UV line was used focused by means of a 60X fluorite objective microscope (Olympus UPlan FLN, NA = 0.9, power of 0.5 mW on samples). During the measurements the scattered radiation was dispersed by a 600 l/mm grating and collected by a silicon CCD as detector (Synapse, Horiba-Jobin Yvon). For each sample we chose the excitation wavelength which gave the best Raman response, in order to overcome problems arising from fluorescence contribution to the spectrum. For each spectrum reported in the Results and Discussions section, the chosen wavelength is indicated in the corresponding figure caption.

The obtained spectra were compared with those of various databases and literature (Bell et al., 1977; Buzgar et al., 2009; RRUFF Project, 2010).

2.2.3 FT-IR analyses

FT-IR spectra were collected, in micro-invasive way, in the 400 ÷ 4000 cm^{-1} wavenumber region with a resolution of 4 cm^{-1}, using a Bomem DA8 Fourier transform spectrometer, operating with a Globar source, combined with a KBr beamsplitter, and a DTGS/MIR detector. The IR spectra were recorded on the samples in the form of pellets, by taking ~ 2 mg of sample, that has been powdered and dispersed in ~ 200 mg of a powdered CsI matrix, transparent in the investigated range. The measurements were performed in transmission configuration and in dry atmosphere to avoid unwanted dirty contributions, automatically adding 32 repetitive scans in order to guarantee good signal-to-noise ratio and high spectral reproducibility.

No smoothing was applied, and Spectracalc software package GRAMS (Galactic Industries, Salem, NH, USA) was used for baseline correction.

The identification of pigments and accessory components has been achieved by comparison of the experimental profiles with those of various databases and literature (De Benedetto et al., 2002; Sadtler Database for FT-IR, BioRad Laboratories).

3. Results and Discussion

Generally, in most of the cross sections, the "intonachino" layer is absent below the pictorial film. The pigmenting phase is therefore in direct contact with the underlying "curl" level. In the "arriccio" layer are dispersed different deposits, with rounded and sub-rounded clasts and with a good

granulometric selection. In almost all the samples, except for r19c, the composition of the aggregate is rich in female minerals (amphiboles and pyroxenes associated with quartz and feldspars). The smaller sizes are absent, perhaps indicating a washing of the material before use and therefore suggesting a good level of preparation. The sediment seems to be rich in volcanic material. An estimate of the amount of aggregate averages between 40 and 60%.

Fresco Cod. r19a. The SEM visual examination performed on the cross section of fresco highlighted an homogeneous layer of pigments along the surface with a thickness of about 50 µm. The EDX analysis carried out the pictorial layer revealed the presence of low signal of Fe, probably ascribable to the yellow pigment, and stronger emission peaks of Ca, Si, Mg and Al, due probably to the presence of feldspars (Fig. 3). Raman spectrum collected on the yellow pigment (Fig. 4(a)) clearly evidenced the typical bands of goethite (a-FeOOH) at ~ 240 cm^{-1}, ~ 298 cm^{-1}, ~ 403 cm^{-1}, ~ 528 cm^{-1}. The identified pigment is then yellow ochre, whose use is largely documented in the case of Roman wall paintings (Aliatis et al., 2010). In the 1100 ÷ 1400 cm^{-1} region characteristic features of a fatty acid medium are well evident. The observed bands at ~ 1154 cm^{-1} and ~ 1266 cm^{-1} suggest, from comparison with literature data (Schönemann et al., 2011; Vandenabeele et al., 2000), the use of linseed oil. In the FT-IR spectrum (Fig. 4(b)), contributions attributed to calcite ($CaCO_3$, peaks at ~ 711 cm^{-1}, ~ 873 cm^{-1}, band centred at ~ 1440 cm^{-1}), feldspars (broad band between ~ 950 cm^{-1} and ~ 1270 cm^{-1}) and gypsum ($CaSO_4 \cdot 2H_2O$, broad band between ~ 950 cm^{-1} and ~ 1270 cm^{-1} and band centred at ~ 1440 cm^{-1}), have been recognized. In particular, the presence of the double peak at ~ 1003 cm^{-1} and ~ 1029 cm^{-1} deserves attention. These lines correspond to Si-O-Al and SiO-Si stretching vibrations and play an important role in identifying ochre components. Furthermore, as far as the high frequency range of the FT-IR spectrum is concerned (inset of Fig. 4(b)), the peaks in the 2800 ÷ 3000 cm^{-1} region are attributed to the C-H stretching mode of linseed oil, in agreement with Raman results, whereas those in the 3300 ÷ 3800 cm^{-1} range, indicative of the O-H stretching vibration, suggest that the feldspar present is kaolinite ($Al_2Si_2O_5(OH)_4$). The result of goethite is interesting because this kind of yellow ochre was used since the Paleolithic age, and researchers have recognized goethite in pigments from ancient Egyptian specimens and have characterized it in Roman wall paintings from England. Goethite in this case is the main constituent of the yellow ochre and this result will be compared with the fresco still conserved *in situ*.

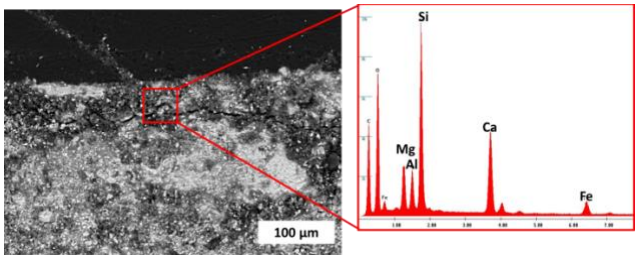


Fig. 3. (left) cross section of sample from r19a fresco, (right) EDX spectrum performed on the pictorial layer.

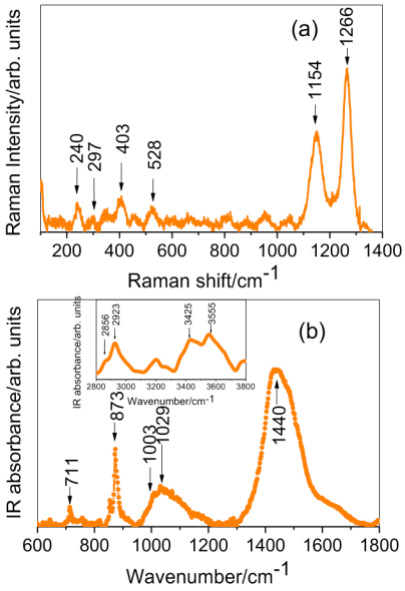


Fig. 4. (a) Raman spectrum recorded at l_{exc} = 785 nm on yellow pigment of fresco Cod. r19a. (b) FT-IR spectrum recorded on yellow pigment of fresco Cod. r19a. In the inset, the high frequency range of the FT-IR spectrum is shown.

As far as the black pigment is concerned, FT-IR spectrum evidenced only the absorption peaks of calcite. This allowed us to hypothesize the presence of carbon black (Bakiler et al., 2016; Mahmoud et al., 2000), used as decorative pigment since the earliest times. The vegetal origin of the pigment is also confirmed by Raman analysis, that detected no band at ~ 960 cm^{-1}, associated to the stretching of the phosphate ion $[PO_4]^{3-}$, and revealed the characteristic two-band feature at ~ 1335 cm^{-1} and ~ 1565 cm^{-1}.

Fresco Cod. r19b. The SEM study of the cross section reveals a structure of the mortar ground with grains different in size and crystal habit, that is typical of roman fresco grounds. In this case, the painting layer shows a low thickness and a not homogeneous coat along the surface, maybe due to a strong alteration process of the pigment. The presence of typical elements of feldspars (Ca, Si, Mg

and Al) has been detected by EDX analysis (Fig. 5), associated to a characteristic emission of Cu, probably due to the use of a green earth as pigment.

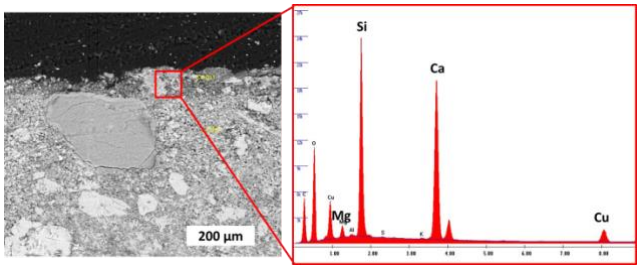


Fig. 5. (left) SEM image of cross section sample from r19b fresco, (right) EDX spectrum performed on the pictorial layer.

Previous XRF analysis on the green pigment (Alberti et al., 2017) didn't provide enough information for the identification of the pigment, probably because of a too low concentration of the pigment itself or a too limited thickness of the paint layer. Raman analysis in this case, probably for the aforementioned reasons, didn't furnish reliable results. Nevertheless, FT-IR spectra evidenced, other than the characteristic peaks of the base, a peak at ~ 798 cm^{-1}, that seems to confirm the use of a green earth, in agreement with SEM-EDX results.

Fresco Cod. r19c. As the r19b sample, SEM-EDX analysis performed on the red layer of the cross section (Fig. 6) highlight signals related to the presence of feldspars ascribable to the mortar of the ground. A strong Fe signal has been detected in the same layer, probably due to the presence of a red earth. It's interesting to highlight in the same layer the presence of a weak Pb signal: this element seems to be related to the use of white lead just under the pictorial film or mixed with pigment, maybe in order to obtain a brighter red color. The presence of lead in this cross section could be used as a possible marker to recognize other frescos from the several fragments reveled during the archeological site. Moreover, in this sample, a different structure of the ground mortar is detected, that appears in section more homogeneous than r19a and r19b samples without the grains typical of the aggregate deposits.

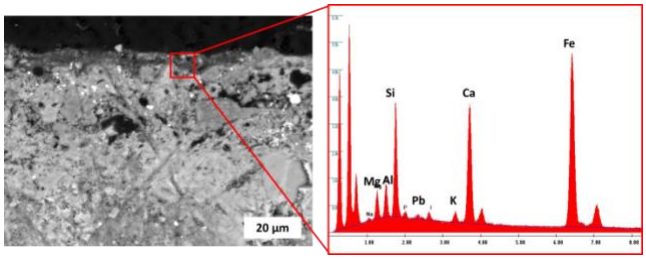


Fig. 6. (left) SEM image of cross section sample from r19b fresco, (right) EDX spectrum performed on the pictorial layer.

The Raman spectrum collected for the red pigment (Fig. 7(a)) confirmed the SEM-EDX results and allowed, from the characteristic vibration modes at ~ 225 cm^{-1}, ~ 294 cm^{-1}, ~ 410 cm^{-1}, and ~

607 cm^{-1}, for the identification of hematite (a-Fe_2O_3), as usually found in red ochres. This result is in agreement with previous XRF measurements (Alberti et al., 2017), that revealed the presence of iron as major element. Hematite belongs to the crystal space group of D_6^{3d} symmetry, that has seven Raman-active vibrational modes, i.e. two A_{1g} modes and five E_g modes (De Faria et al., 1997). In

particular, the strong band at ~ 410 cm^{-1} indicates that a well-crystallized hematite was used. The use of a red ochre is also confirmed by looking at the FT-IR spectrum (red line of Fig. 8), that showed, other than bands attributed to calcite (~ 715 cm^{-1}, ~ 874 cm^{-1}, ~ 1437 cm^{-1}), features centered at ~ 537 cm^{-1} and ~ 910 cm^{-1}, assigned to iron oxides. In addition, in the large band between ~ 940 cm^{-1} and ~ 1280 cm^{-1}, mainly associated to feldspars and gypsum, contributions of iron oxides at ~ 1011 cm^{-1} and ~ 1050 cm^{-1} also appear.

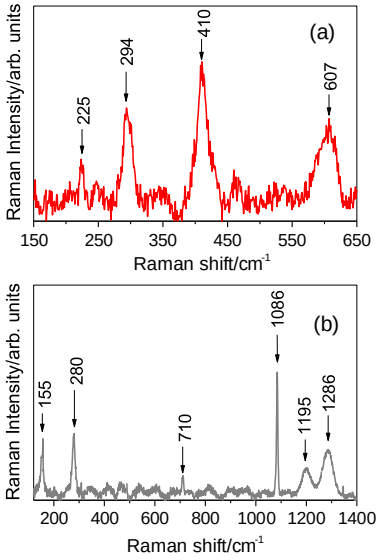


Fig. 7. (a) Raman spectrum recorded at l_{exc} = 785 nm on red pigment of fresco Cod. r19c. (b) Raman spectrum recorded at l_{exc} = 785 nm on white pigment of fresco Cod. r19c.

White paint layer of fresco Cod. r19c contained lime white, based on the Raman bands (Fig. 7(b)) at ~ 155 cm^{-1}, ~ 280 cm^{-1}, ~ 710 cm^{-1}, and ~ 1086 cm^{-1}, corresponding to calcite. The well evident profiles in the amide III region (1100 ÷ 1400 cm^{-1}) reveal the use of a proteinaceous binder, probably linseed oil, as suggested by comparison with literature data (Schönemann et al., 2011; Vandenabeele et al., 2000). FT-IR technique gave evidence of calcite, gypsum and feldspars (white line of Fig. 8). It is worth of note that, comparing the FT-IR spectrum of white pigment with that of the bulk of the same sample (black line of Fig. 8), contributions due to calcite appears much more intense with respect to those due to gypsum and feldspars. This occurrence supports the hypothesis of the use of lime white as white pigment, as evidenced by Raman spectroscopy. Nevertheless, this enhancement can also be due to the preparatory layers of lime plaster. Finally, the use of the organic binder in the

white painted surface is also testified by the presence, in the high frequency region of the FT-IR spectrum, not reported here, of several bands in the 2800 ÷ 3000 cm^{-1} interval.

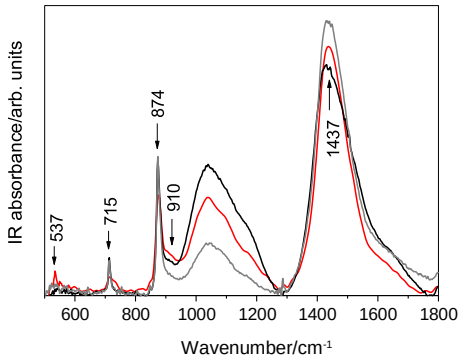


Fig. 8. FT-IR spectra recorded on the bulk (black line), red pigment (red line) and white pigment (white line) of fresco Cod. r19c.

Traces of blue pigment were also present on the painted surface of the fresco. Nevertheless, unfortunately, the micro-Raman spectrum, collected using an excitation wavelength of 785 nm, was completely covered by a very strong fluorescence. Also FT-IR measurements, because of the too small amount of sample, resulted unreliable.

Fresco Cod. r19d. The study of the cross section under optical microscopy (Fig. 9) shows a painted layer with a brown binder and different grains in colour and shapes. The blue particles appear, under OM, grey and shiny, mixed with orange and white grains. The SEM-EDX analysis performed on this area (Fig. 10) highlights some intense emission peaks related to the presence of Si, Ca and Cu, with some weak peak due to Mg, Al, K and S. The presence of Cu suggests the presence of a copper based mineral used as blue pigment. The presence of Si and Ca could be ascribed to quartz and calcium carbonate ($CaCO_3$). Finally, the observation of Mg, Al and K together with Ca and Si allows to hypothesize the presence of aluminium silicates (feldspar). Even in this case the mortar shows the same aggregate compositions in grains with different size and shape.

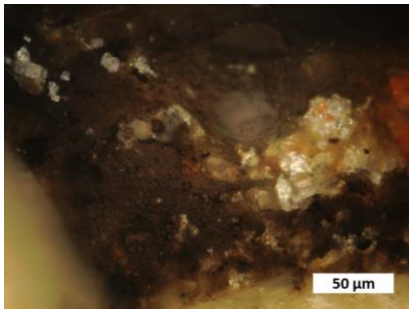


Fig. 9. OM image of the painting film with magnification of grains.

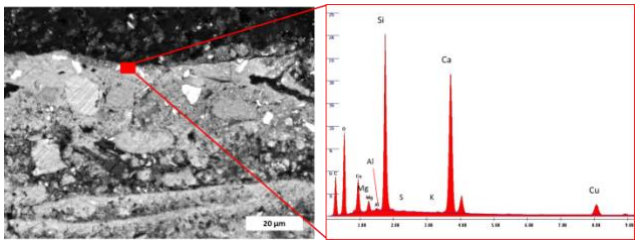
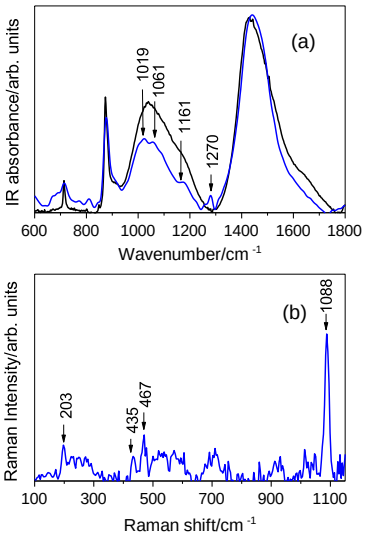


Fig. 10. (left) SEM image of cross section sample from r19d fresco, (right) EDX spectrum performed on the pictorial layer.

Raman spectrum of the blue painted layer of this sample was first of all collected by using an excitation wavelength of 785 nm, and no bands were recorded. Nevertheless, SEM-EDX analysis allowed us to hypothesize that the used blue pigment consisted mainly of copper, and FT-IR analysis (Fig. 11(a)) indicates the presence of cuprorivaite ($CaCuSi_4O_{10}$), whose characteristic features are centred at ~ 1019 cm^{-1}, ~ 1061 cm^{-1}, ~ 1161 cm^{-1} and ~ 1270 cm^{-1}. Now, since it has been reported (Westlake et al., 2012) that Egyptian blue, when excited in the visible and NIR range, exhibits strong fluorescence emission with a maximum at ~ 890 nm, the use of a laser line in the UV range (364 nm) became mandatory. The recorded spectrum is reported in Fig. 11(b). By the typical peaks at ~ 435 cm^{-1} and ~ 1088 cm^{-1}, the blue pigment was identified as Egyptian blue, in agreement with a variety of studies on wall paintings of Roman period (Aliatis et al., 2010; Mahmoud et al., 2000; Mateos et al., 2015; Mazzocchin et al., 2010). Quartz (SiO_2) is also detected by the observation of the typical features at ~ 203 cm^{-1} and ~ 467 cm^{-1}.


IR absorbance/arb. units
(a)
1019
1061
1161
1270
600
800
1000
1200
1400
1600
1800
Wavenumber/cm -1
Raman Intensity/arb. units
(b)
1088
203
435
467
100
300
500
700
900
1100
Raman shift/cm -1

68

Fig. 11. (a) FT-IR spectrum recorded on blue pigment (blue line) of fresco Cod. r19d. The FT-IR spectrum recorded on the bulk (black line) of the same sample is reported for comparison. (b) Raman spectrum recorded at l_{exc} = 364 nm on blue pigment of fresco Cod. r19d.

As far as the white pigment is concerned, Raman and FT-IR measurements (spectra not reported) gave evidence of calcite, gypsum and feldspars, probably also due to the preparation layer and plaster. In the FT-IR spectrum, in particular, characteristic contributions of Egyptian blue were recognized, in agreement with previous XRF results (Alberti et al., 2017) that revealed, other than Ca, also the presence of Cu in some amount. This occurrence can indicate that the artist wanted a different shade for this specific part of the decoration.

Fresco Cod. r19f. The cross section studied under optical microscopy (Fig. 12) shows a clear homogeneous green layer well preserved applied directly on a typical roman lime ground, with grains of different diameter and shapes. Even in this case, the "intonachino" layer is absent below the pictorial film and the pigmenting phase is in direct contact with the underlying "curl" level, confirming this procedure as a construction marker of the frescos of the Villa.

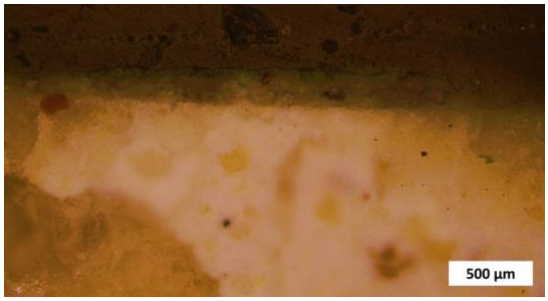


Fig. 12. OM image of the r19f cross section with green pictorial film.

The SEM-EDX analysis (Fig. 13) performed on the coloured layer highlighted an intense peak related to Fe, probably ascribable to the presence of an earth pigment, and the absence of the Cu peak, as expected. The presence of Si, Mg, Al and K emissions could be ascribable to the earth too,
and this seems to be confirmed by the presence of a weak peak of Ti. Ca is present in the spectrum with a strong peak probably due to the inorganic binder of the fresco ($CaCO_3$).

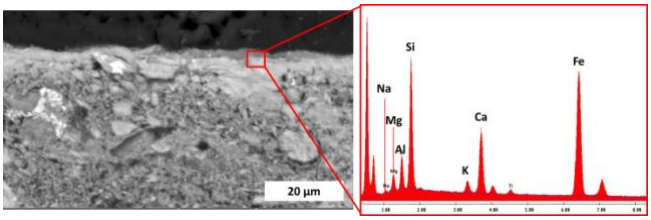


Fig. 13. (left) SEM image of cross section sample from r19f fresco, (right) EDX spectrum performed on the pictorial layer.

Raman spectrum of the green painted layer (Fig. 14) clearly shows typical peaks of calcite (~ 152 cm^{-1} and ~ 1086 cm^{-1}), probably due to lime present in the wall preparatory layer, and green earth of celadonite ($K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$) nature (~ 203 cm^{-1}), commonly identified in Roman wall paintings from different localities (Aliatis et al., 2009; Béarat and Fuchs, 1996; Mazzocchin et al., 2003; Villar and Edwards, 2005).

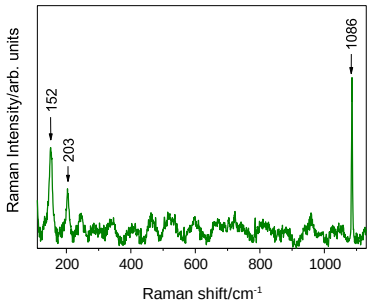


Fig. 14. Raman spectrum recorded at l_{exc} = 785 nm on green pigment of fresco Cod. r19f.

In order to gain information on the composition of the plaster layers, FT-IR and Raman measurements have been also performed on a point at the base without any pigment and on the bulk of this sample. The comparison of the FT-IR spectra obtained in these two cases, reported in Fig. 15, looks particularly interesting.

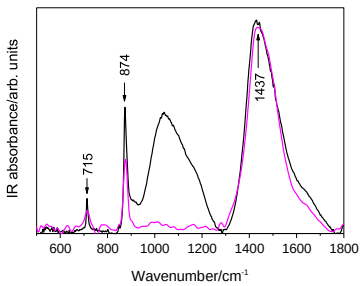


Fig. 15. FT-IR spectrum recorded on a point at the base without any pigment (magenta line) and on the bulk (black line) of fresco Cod. r19f.

The two spectra appears similar, both of them contain the main characteristic peaks of calcite. Nevertheless, these are the only contributions in the case of the point at the base without any pigment (magenta line of Fig. 15). This was confirmed also by Raman technique that evidenced, for the point at the base without any pigment, only peaks attributable to calcite (spectrum not reported). On the contrary, in the FT-IR spectrum of the bulk (black line of Fig. 15), the large band between ~ 940 cm^{-1} and ~ 1280 cm^{-1} due to feldspars and gypsum is also well evident. We can then argue that the fine plaster "intonaco" is mainly based on calcite. As Vitrivius reported in his work *De Architectura* (I century B. C.) (Vitrivius, 1914), limewash was very commonly used in Roman walls before painting, and the result of this practice was calcium carbonate obtained by reaction of lime (calcium hydroxide) with atmospheric carbon dioxide. As far as the second layer "arriccio" is concerned, it is mainly composed by calcite, feldspars and gypsum.

Fresco Cod. section. Due to the not homogeneous painted layer of the fresco and in order to better consider the distribution of the different elements and, consequently, of the mineral grains, a SEM-EDX mapping analysis has been performed on the cross section of this sample. As can be seen from an inspection of Fig. 16, Ca is well dispersed out among the section, confirming the presence of $CaCO_3$ as the inorganic binder of the fresco. Al, Si, K and Fe are concentrated in the same area of the cross section and therefore ascribable to the same mineral phase, probably an earth. The S element, that could be ascribed to gypsum, seems to be distributed in the area where Ca is not present. This result seems to confirm the degradation process of chemical transformation from carbonate to sulphate.

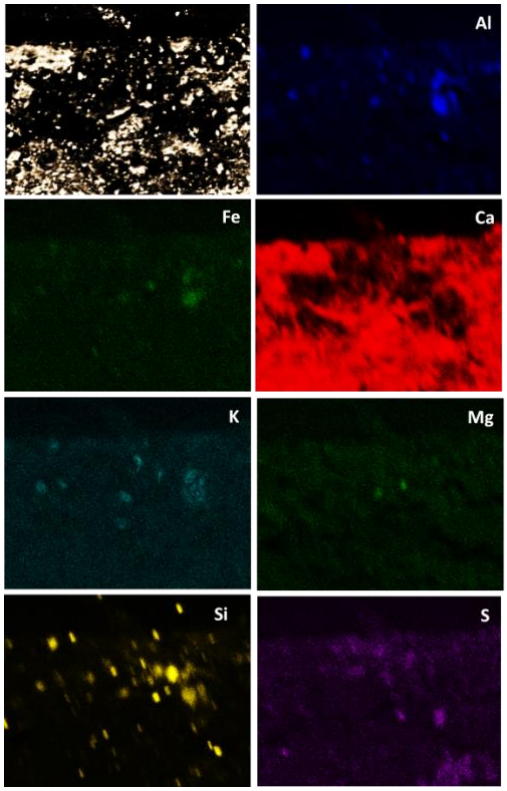


Fig. 16. SEM-EDX mapping of Cod. section.

The Raman spectrum collected on the brown pigment is reported in Fig. 17. All peaks relative to haematite, centered at ~ 225 cm^{-1}, ~ 249 cm^{-1}, ~ 293 cm^{-1}, ~ 410 cm^{-1}, ~ 609 cm^{-1}, ~ 661 cm^{-1}, have been identified. In addition, the features at ~ 497 cm^{-1} and ~ 722 cm^{-1} are associated to maghemite (g-Fe_2O_3).

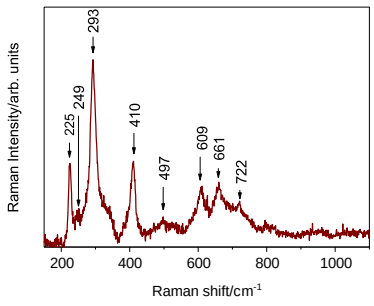


Fig. 17. Raman spectrum recorded at l_{exc} = 785 nm on brown pigment of fresco Cod. section.

Fig. 18 shows the Raman spectrum for the dark brown pigmented area of the sample.

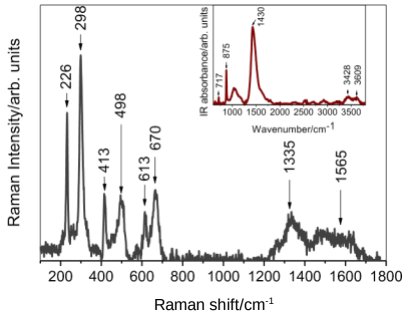


Fig. 18. Raman spectrum recorded at l_{exc} = 633 nm on dark brown pigmented area of fresco Cod. section. In the inset, FT-IR spectrum of the same specimen is depicted.

The spectrum contains a series of bands in the region between 200 cm^{-1} and 800 cm^{-1}, that are all those identified in the Raman spectrum of red ochre, which consists of a mixture of silica, clay and iron oxide (Bikiaris et al., 1999). In particular, the Raman peak at ~ 670 cm^{-1} is attributed to Al-OSi bond of kaolinite (Frost et al., 1993). Kaolinite has a weak white colour, that lends luminance to red ochre.

The two bands at ~ 1335 cm^{-1} and ~ 1565 cm^{-1} reveals the presence of carbon, probably used to darken the red colour.

It is worth remarking that the obtained results are, once again, supported by previous XRF analysis (Alberti et al., 2017). From that, Fe, K and Sr were identified for brown and dark brown points, suggesting the presence of clays in their composition, also present in the materials used for the preparation of the base. As a matter of fact, IR spectra collected on these two pigments (the case of dark brown pigmented area is plotted in the inset of Fig. 18) evidenced the presence of clayey minerals, such as calcite (peaks at ~ 717 cm^{-1}, ~ 875 cm^{-1}, ~ 1430 cm^{-1}), kaolinite and montmorillonite (peaks in the 3300 ÷ 3800 cm^{-1} range).

Finally, as far as the white pigmented area is concerned, characteristic peaks of calcite are clearly evident in the Raman spectrum, indicating calcite as the compound responsible for the white pigment. IR profile showed bands attributed to calcite, gypsum, silicates and feldspars (spectra not reported).

4. Conclusions

In the present paper, we used a combined methodological approach, performed through optical microscopy (OM), scanning electron microscopy equipped with an energy dispersive X-ray detector (SEM-EDX), micro-Raman and Fourier transform infrared spectroscopy (FT-IR) techniques, in order

to identify the palette of pigments found in Roman wall paintings from the archaeological context of Villa dei Quintili (Rome, Italy), dated back II century A. D..

From the results, the yellow pigment was identified as yellow ochre, the black pigment as carbon black of vegetal origin, the red pigment as red ochre (haematite), the white pigment as lime white and maybe lead white pigment, the blue pigment as Egyptian blue, the green pigment as green earth of celadonite nature and, finally, the brown pigment as red ochre (haematite and maghemite) brightened by kaolinite.

The fine plaster "intonaco" turned out to be mainly based on calcite, whereas calcite, feldspars and gypsum resulted the main constituents of the second layer "arriccio".

Linseed oil and calcium carbonate have been respectively recognized as organic and inorganic binders, even if it's not possible to exclude an application of those materials as protectives of the fresco surfaces. Some compositional marker to classify the frescos on the basis of their properties and to find a qualitative correlation with other fresco fragments extracted from other areas of the Villa, have been characterized.

Acknowledgments

The authors acknowledge Dr. Rita Paris, Archaeologist Director of the Soprintendenza Speciale per I Beni Archeologici di Roma, for supplying the investigated fragments of painted plasters, withdrawn from the archaeological site of Villa dei Quintili (Rome, Italy).

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204

205 **Figure captions**

206

207 **Fig. 1.** (a) A view of the Villa dei Quintili (Rome, Italy). (b) Details of the archaeological site.

208

209 **Fig. 2.** Photographs of analysed fragments. (a) Fresco Cod. r19a, (b) Fresco Cod. r19b, (c) Fresco
210 Cod. r19c, (d) Fresco Cod. r19d, (e) Fresco Cod. r19f, (f) Fresco Cod. section.

211

212 **Fig. 3.** (left) cross section of sample from r19a fresco, (right) EDX spectrum performed on the
213 pictorial layer.

214

215 **Fig. 4.** (a) Raman spectrum recorded at l_{exc} = 785 nm on yellow pigment of fresco Cod. r19a. (b)
216 FT-IR spectrum recorded on yellow pigment of fresco Cod. r19a. In the inset, the high frequency
217 range of the FT-IR spectrum is shown.

218

219 **Fig. 5.** (left) SEM image of cross section sample from r19b fresco, (right) EDX spectrum
220 performed on the pictorial layer.

221

222 **Fig. 6.** (left) SEM image of cross section sample from r19b fresco, (right) EDX spectrum
223 performed on the pictorial layer.

224

225 **Fig. 7.** (a) Raman spectrum recorded at l_{exc} = 785 nm on red pigment of fresco Cod. r19c. (b)
226 Raman spectrum recorded at l_{exc} = 785 nm on white pigment of fresco Cod. r19c.

227

228 **Fig. 8.** FT-IR spectra recorded on the bulk (black line), red pigment (red line) and white pigment
229 (white line) of fresco Cod. r19c.

230

231 **Fig. 9.** OM image of the painting film with magnification of grains.

232

233 **Fig. 10.** (left) SEM image of cross section sample from r19d fresco, (right) EDX spectrum
234 performed on the pictorial layer.

235

Fig. 11. (a) FT-IR spectrum recorded on blue pigment (blue line) of fresco Cod. r19d. The FTIR spectrum recorded on the bulk (black line) of the same sample is reported for comparison. (b) Raman spectrum recorded at l_{exc} = 364 nm on blue pigment of fresco Cod. r19d.

Fig. 12. OM image of the r19f cross section with green pictorial film.

Fig. 13. (left) SEM image of cross section sample from r19f fresco, (right) EDX spectrum performed on the pictorial layer.

Fig. 14. Raman spectrum recorded at l_{exc} = 785 nm on green pigment of fresco Cod. r19f.

Fig. 15. FT-IR spectrum recorded on a point at the base without any pigment (magenta line) and on the bulk (black line) of fresco Cod. r19f.

Fig. 16. SEM-EDX mapping of Cod. section.

Fig. 17. Raman spectrum recorded at l_{exc} = 785 nm on brown pigment of fresco Cod. section.

Fig. 18. Raman spectrum recorded at l_{exc} = 633 nm on dark brown pigmented area of fresco Cod. section. In the inset, FT-IR spectrum of the same specimen is depicted.

Table 1 Macroscopic features of investigated frescoes together with the employed analytical techniques.