1 *Type of the Paper (Article)*

2 Pigments on Roman wall painting and stucco
3 fragments from the Monte d'Oro area (Rome): a
4 multi-techniques approach

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13 **Abstract:** This work concerns the characterisation of a samples set of wall painting and stucco
14 fragments collected during a rescue excavation carried out in 2013 by the Soprintendenza
15 Archeologica in the Monte d'Oro area (Rome). Due to the contextless archaeological situation,
16 analyses were performed to obtain more information about the collected materials. A multi-
17 analytical approach has been applied including spectroscopic (FTIR, Raman and visible reflectance
18 analyses) and elemental analysis (SEM-EDS) techniques. The chromatic palette has been in this way
19 disclosed evidencing the use of pigments such as cinnabar, Egyptian blue, red and yellow ochre and
20 green earth but also a simultaneous use of them. The presence of a decoration achieved by using a
21 gold leaf has been also highlighted indicating the preciousness of the decorations. The convenience
22 and advantages linked to the use of portable instrumentation have been also evidenced.

26 1. Introduction

27   One of the most important issues in the field of cultural heritage is the characterisation of the
28 materials employed for the realisation of paintings of historical and artistic value, since it can provide
29 information on old technological knowledge, for instance, the painting techniques or the capability
30 in the supply and production of pigments from raw materials, as well as ancient community
31 connections [1]. Moreover, the study of materials can also allow detecting possible restoration or
32 conservation works or in some cases, can even provide information on dating and/or authenticity of
33 the artwork [2-3].
34   In this context is of major relevance the application of suitable archaeometric methodologies,
35 aimed to the comprehensive characterisation of pigments and binders used for the realisation of the
36 wall paintings; indeed the chemical characterisation of the materials, joined with the information
37 gathered from historical and archaeological studies, can be both the starting point to reach a complete
38 understanding of the piece of art and, more in general, a precious tool available for the art
39 conservators in the hypothesis of restoration work.
40   In spite of the numerous studies having as a topic the characterisation of Roman pigments and
41 published up to now in the scientific literature (about 250 papers in the last 20 years), due to the
42 widespread presence of the Roman empire and also to the fact that new sites keep coming to light,
43 the investigation of the pigments and of the artists' palettes employed in Roman wallpaintings, is still

an issue of great interest as also witnessed by the papers published in particular during the last two years.

Aim of the present study was the identification of the pigments used to decorate some destroyed Roman building walls, discovered between the Claudio Marcello and the Porta Latina streets in Rome (Monte d'Oro) within a private property. The fragments were rescued in 2013 by the Soprintendenza Archeologica di Roma together with a great number of ceramic shards dating mainly between the 1st and 2nd centuries A.D. Unfortunately, the wall painting and stucco fragments, as well as the pottery, cannot be related to any visible ancient building (probably destroyed in the '50s of the last century) in the surroundings and are therefore to consider contextless. Also, for this information gap, the performed analyses were important to obtain some further data to confirm or disappoint the archaeological interpretation. In the present study, the investigation was carried out on twelve samples chosen within all recorded colour and painting/stucco types (listed in table 1), dating approximately between the 1st century B.C. and the 1st century A.D.

The combined use of elemental analysis techniques together with spectroscopic ones represents the methodological approach which is commonly applied to fulfil the comprehensive characterisation of samples such as Roman frescoes [4-14]. Scanning Electron Microscopy equipped with an Energy Dispersive X-ray detector (SEM-EDS), Raman spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) techniques have been employed aimed at establishing the painting technique used to decorate the fragments. Among the analytical techniques implemented during this measurement campaign, it is worth to notice that Raman spectroscopy has been successfully applied by means of both a benchtop device and a more versatile portable Raman spectrophotometer. Furthermore, the comparison of the considerable analytical results achieved from either the two pieces of equipment have been really encouraging in the perspective of an *in situ* application (i.e. directly on wall paintings) of this powerful and totally non-destructive technique. Among non-destructive measurements, visible reflectance analyses have also been performed.

Such a multi-technique approach allowed to define the chromatic palette of the fragments, that included red ochre, hematite, yellow ochre, cinnabar, litharge, green earth (celadonite), Egyptian blue, chalk, and carbon black.

2. Materials and Methods

2.1. Materials

The analysed samples consist in 10 wall painting shards and 2 stucco fragments (fig. 1) which to an optical overview appear as bright red, red, purple red, light red/orange, yellow, white, black, green and light blue. These samples, which were chosen among many others, carrying in some cases also fine decorations, synthesise the colour palette employed to decorate some vanished rooms belonging probably to one or more private roman buildings. Style and quality of some of the classified fragments suggest a rather high level of the walls' decoration, as also demonstrated by the great variety of stucco mouldings discovered among them. These types of mouldings (an example is reported in fig. 2) were generally used on walls to hide decoration transitions. They were realised on the wet plaster and then finally overpainted with brilliant and contrasting colours. Two small stucco fragments (samples 9 and 10 in fig. 1) presenting light blue and yellow overpainting traces were therefore also selected to compare the pigments used for their decoration to the wall painting ones.

The sampling phase was carried out with the support of the University of Trento, which was involved by the Soprintendenza Archeologica di Roma in the archaeological study of the decorated wall and stucco fragments.

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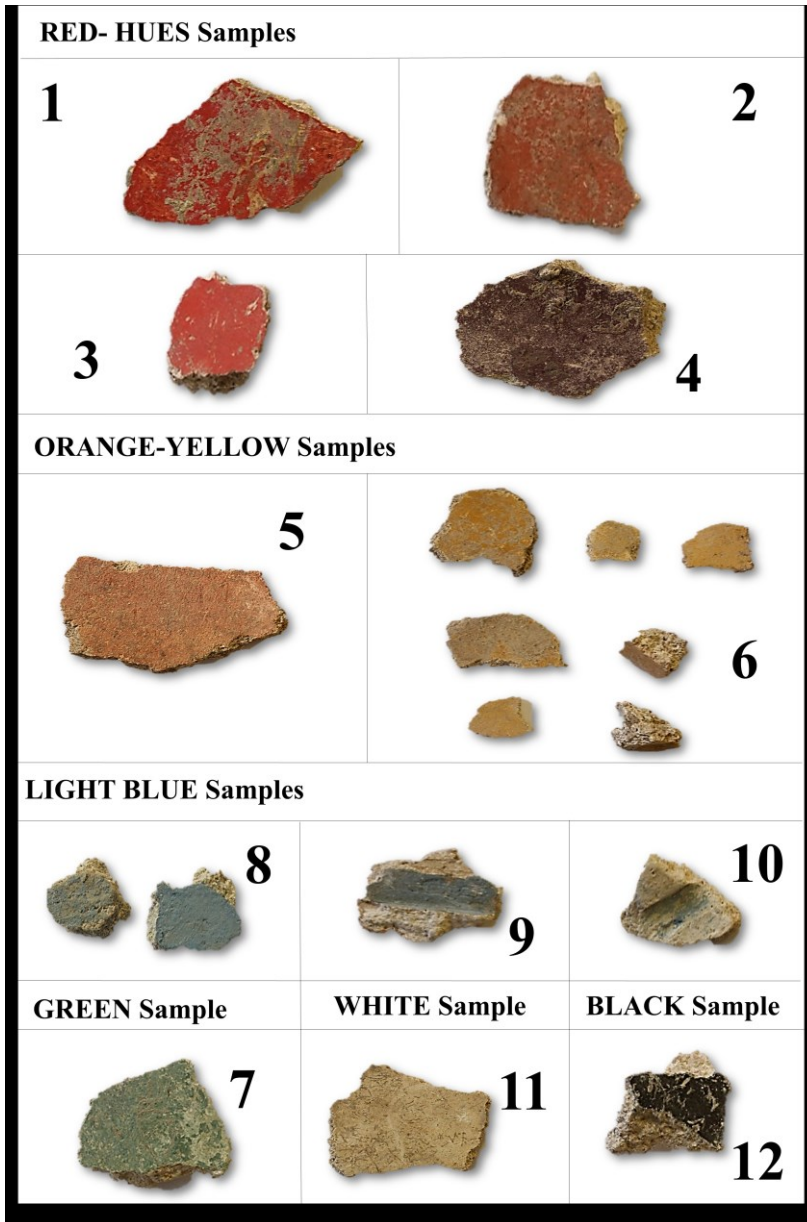**Eliminato:** gypsum,

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Figure 1. Photographs of the analysed painted fragments.

Figure 2. Example of a stucco moulding.

Table 1. Claudio Marcello Street. List of investigated fragments and colours.

SAMPLE	Colour	Description and provenance area
1	bright red	607354 (wallpainting)
2	red	608046 (wallpainting)
3	bright red	608043 (wallpainting)
4	purple red	608042 (wallpainting)
5	light red/orange	(wallpainting)
6	yellow	608054 (wallpainting)
7	green	608039 (wallpainting)
8	light blue	608040 (wallpainting)
9	light blue	Type 15 (stucco)
10	light blue	607286 (stucco)
11	white	608048 (wallpainting)
12	black	608050 (wallpainting)

2.2. Methods

The shards were analysed by SEM-EDS (scanning electron microscopy coupled with energy dispersive X-ray analysis) to obtain both qualitative and semi-quantitative information on the chemical composition, using a methodology already set up [15]. The instruments employed were a Hitachi TM-1000 equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED) and a JEOL 5500 LV equipped with an IXRD EDS 2000 microprobe.

In both cases the fragments were analysed as such, namely without any sampling from the surface and excluding any coating application as well, being the latter not required as the samples were analysed under low vacuum conditions. The shards were attached to the sample holder with double-sided tape or removable glue pads.

Basically, the Hitachi instrument was utilised to perform a preliminary morphological screening of the samples surfaces and the qualitative/semi-quantitative determinations as well, whereas the JEOL one, due to its higher spatial resolution, was employed to better investigate some details as in the case of samples 1 and 6 where some punctual analyses have been performed.

Eliminato: Table 1. List of investigated fragments, together with colour and the.¶
indication of provenance area.

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ATR-FTIR analyses were performed by a Nicolet 380 spectrophotometer coupled with an ATR accessory Smart Orbit equipped with a diamond crystal. The spectra have been acquired on the samples as such in the range 500–4000 cm^{-1} with a 4 cm^{-1} resolution. Each spectrum was obtained as the result of 64 accumulations.

Raman analyses were carried out by a Thermo Fisher Raman iXR spectrophotometer equipped with a microscope and a solid-state laser emitting at 785 nm as an excitation source, and a BWTek i-Raman EX device provided with a fibre optic probe and an Nd-YAG laser emitting at 1064 nm. All the measurements were performed directly on the fragments, without any sampling and the spectra were obtained as an average of 20 scans in the spectral range between 200 and 2000 cm^{-1}.

The identification of compounds was performed comparing the FTIR and Raman spectra recorded on the samples to those available in the literature.

Finally, visible reflectance analyses have been performed by means of a Konica Minolta CM 2300d portable spectrophotometer. The instrument was calibrated using its 100% reflective white reference and a 0% reflective calibration box in the 400–700 nm range. All the measurements were conducted straight on the samples surfaces.

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3. Results

The first step of the implemented methodological approach was a widespread study of the morphology and of the elemental chemical composition of the surfaces of the entire samples set by means of the SEM-EDS instrument having the lower resolution (Hitachi instrument). In fact, just from the simple observation of the images achieved with that microscope, it was possible to establish the necessity of further and deeper analyses to be performed with the other one allowing to reach a better resolution.

In table 2, the results of the semi-quantitative chemical analysis performed by means of the aforementioned SEM-EDS are reported. The values shown for each element as a percentage, are referred to the average of three measurements. Indeed, the analyses of X-ray fluorescence were carried out three times for each sample; more precisely every percentage value comes from an average of three X-ray measurements each realised on an about 2 mm^2 area, performed moving the probe on three different positions for each sample.

Table 2. SEM-EDS semi-quantitative analyses (wt%); for each element, the value for a sample has inferred from an average of three measurements on three different areas of the same sample.

Sample	Al	Au	Ba	Ca	Cl	Cu	Fe	Hg	K	Mg	Na	P	Pb	S	Si
1	2,2	-	-	83,1	0,4	-	2,2	5,1	1,4	-	-	-	-	1	4,5
1$_P$	-	95,4	-	4,7	-	-	-	-	-	-	-	-	-	-	-
2	2,1	-	-	72,1	-	-	13,7	-	0,7	-	-	-	4,7	-	6,8
3	2,2	-	-	54,7	-	-	3,9	27,6	1	-	-	-	-	6,03	4,6
4	1,8	-	-	61,6	-	-	28,6	-	0,8	0,1	0,3	-	-	-	6,7
5	11,2	-	-	31,6	-	-	22,0	-	6,4	1	-	-	-	-	27,8
6	2,5	-	3,3	78,7	-	-	7,3	-	1,0	-	-	-	-	-	7,2
6$_P$	1,1	-	64,2	13,2	-	-	1,2	-	0,4	-	-	-	-	17,1	2,8
7	2,4	-	-	75,3	-	-	7,2	-	3,1	0,7	-	-	-	-	11,4
8	2	-	-	66,5	-	2,3	5,5	-	1,5	-	-	-	-	-	22,3
9	4,5	-	-	50,8	0,5	1,8	10,5	-	3,0	0,4	0,5	-	-	-	27,9
10	4,1	-	-	66,8	-	1,5	0,8	-	0,7	0,1	0,2	-	-	0,2	25,5
11	2,9	-	-	80,4	1,2	-	4,7	-	2	0,2	-	-	-	-	8,7
12	1,1	-	-	94,4	-	-	-	-	0,9	-	-	-	-	-	3,6

Except for samples 1 and 6, no punctual analyses were needed, as all the surfaces, with the exclusion of the two just mentioned and named 1$_P$ and 6$_P$ for clarity (p=punctual), were quite homogeneous (figure X).

165   All the sample surfaces are characterised by a high content of calcium, whose percentage stands
166   quite often over the 50%, and then by silicon, aluminium and potassium, ubiquitous as well. Since
167   the painted coat lay on a conspicuous preparatory layer, it is likely that the signals of those elements
168   came both from the coloured surface and from the plaster too.

169   It is worth to stress that also iron was quite widespread, although in this case, the outcome is
170   due preponderantly to the presence onto the samples of pigments based on that element, as it will be
171   deeper explained in the next paragraphs.

172   The other elements that immediately leap out are undoubtedly mercury and sulphur (samples
173   1 and 3), lead (sample 2), copper (sample 8, 9, 10), but it also worth to notice the presence of a large
174   percentage of gold in sample 1p and of barium and sulphur in sample 6p, keeping in mind that the
175   latter are the outcomes of the punctual EDS analysis. The presence of barium was due to a tiny grain
176   of BaSO4, that could be ascribed to modern building fragments in contact with the ancient ones in
177   the same waste trench. It is worth noting that the presence of barium was highlighted only in one
178   fragment.

179   These results allowed to be fairly sure that in samples 1 and 3, which are red samples, were
180   mainly composed of cinnabar (HgS), because of the contemporary presence of mercury and sulphur.

181   In all the other cases, the actual nature of the pigment on the surfaces could be only
182   hypothesised, since numerous might be the reasons to find iron, lead and copper in a painted layer.
183   In fact, matching the information coming from the colour and the iron content, it seemed quite
184   probable the presence of red ochre or hematite on the red samples 2 and 4, and of yellow ochre on
185   sample 6; the same could not be stated for the light red/orange pigment, where the coexistence of
186   such minerals could be hypothesised. An analogous argument can be proposed for the blue copper-
187   based pigments 8, 9 and 10; in fact, it is well known that a lot of green and blue shades in painting,
188   especially in ancient artifacts, are due to copper compounds, and that is rather impossible to
189   determine their actual nature by means of elemental analysis [16-17].

190   As regard samples 7, since on the basis of its EDS spectrum the presence of copper and/or other
191   elements that might be undeniably associated with green, blue and yellow pigments has been
192   excluded, it was supposed it could be a not better identified green earth; on this purpose it is worth
193   to recall that sometimes a green hue can be the result of a mix of blue and yellow matters [18].

194   As regard samples 11 and 12, the presence of almost nothing but calcium, led to hypothesise the
195   presence of calcite in the white sample and to exclude the presence of iron or manganese-based
196   pigments in the black one; as a consequence, it has been supposed the presence of a carbon-based
197   pigment, but of course without true evidence only on the basis of elemental analysis.

198   It is evident that even the outcomes of SEM-EDS analyses were quite significant, there were some
199   residual doubts on the actual nature of almost all the pigments so that the samples were undergone
200   to FTIR and Raman spectroscopic analyses. Depending on the sample, the Raman spectrum has been
201   acquired with the bench tool (Thermo Fisher instrument), with the portable one (BW Tek instrument)
202   or with both of them. At this purpose in each figure, the excitation line is indicated.

203   The results inferred from the study of the vibrational spectra were synthetically reported for
204   each sample in Table 3 and discussed in detail in the following paragraphs, depending on the hues.
205   It is worth to note that no band ascribable to the presence of organic materials was detected.

3.1. Bright red, red, purple red, light red/orange and yellow

207   Samples 1, 2, 3 and 4 showed various and evidently different red hues even under a simple
208   naked-eye examination; in particular, the main chromatic dissimilarities were observed between the
209   red and purple red colour group, namely samples 2, and 4, and the bright red couple of samples 1
210   and 3.

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221 **Table 3.** SEM-EDS, ATR-FTIR and Raman results.

Sample	Colour	SEM-EDS analysis (elements)	FTIR peaks (cm⁻¹)	Raman peaks (cm⁻¹)
1	bright red	Ca, Hg, Si, Fe, Al, K, S, Cl, Au	1403, 1032, 1007, 871, 712, 532, 472	253, 284, 343, 1086
2	red	Ca, Fe, Si, Pb, Al, K	1409, 1032, 1009, 913, 872, 712, 533, 468	147, 223, 253, 291, 406, 494, 605, 1086
3	bright red	Ca, Hg, S, Si, Fe, Al, K	1404, 1024, 872, 712, 670, 467	253, 284, 343, 1086
4	purple red	Ca, Fe, Si, Al, K, Na, Mg	1409, 1090, 872, 794, 712, 540, 472	223, 288, 404, 490, 604
5	light red/orange	Ca, Si, Fe, Al, K, Mg	1421, 1032, 1007, 913, 873, 797, 779, 712, 693, 526, 466	143, 284, 405, 463, 710, 1086
6	yellow	Ca, Fe, Si, Ba, Al, K, S	1406, 1032, 1009, 913, 873, 797, 712, 532, 468	284, 391, 712, 1086
7	green	Ca, Si, Fe, K, Al, Mg	1414, 970, 873, 798, 712, 679, 490, 452	-
8	light blue	Ca, Si, Fe, Cu, Al, K	1430, 1160, 1048, 1008, 874, 795, 778, 754, 712, 663, 593, 519, 472	-
9	light blue	Ca, Si, Fe, Al, K, Cu, Cl, Mg, Na	1412, 1160, 1045, 1008, 874, 793, 754, 712, 663, 593, 519, 467	-
10	light blue	Ca, Si, Al, Cu, Fe, K, Na, S, Mg	-	-
11	white	Ca, Si, Fe, Al, K, Cl, Mg	1403,1033, 872, 712	285, 391, 712, 1086
12	black	Ca, Si, Al, K	1403, 1033, 872, 712	1300, 1580

222   Sample 1 and sample 3 were characterised by a highly saturated bright red colour, that was
223 attributed by SEM-EDS analyses (see table 2) mostly to the presence of cinnabar [5], although iron
224 was also contained in both fragments. As regards sample 2, the elemental analysis suggested the
225 contemporary presence of iron-based and lead-based pigments, whereas in sample 4 the SEM-EDS
226 results led to think that it was basically composed of iron oxide (see table 2).

227   ATR-FTIR and Raman measurements were applied both to confirm the presence of cinnabar in
228 samples 1 and 3 and to investigate the possible presence of some red iron-based and/or lead-based
229 pigments.

230   Figure 3 shows the ATR-FTIR spectra of red samples. All of them are characterised by the strong
231 bands of calcium carbonate at 1403-1430, 871 e 712 cm⁻¹ [19-22] and by a wide band around 1000 cm⁻¹,
232 due to the presence of silicate minerals [23-24], that is perfectly aligned with the elemental analysis
233 results. It is to note that in the following discussion, ubiquitous and well-known bands of calcite at
234 1403-1430, 871 and 712 cm⁻¹ will be not taken into account.

235   Actually, the most diagnostic zone of these spectra is the one from about 1200 to 450 cm⁻¹,
236 especially the wavenumber range below 700 cm⁻¹, where the differences among the spectra are even
237 more emphasised.

238   Sample 1, whose main bands stand at 1032, 1007, 532, 472 cm⁻¹ (figure 3a), shows the features of
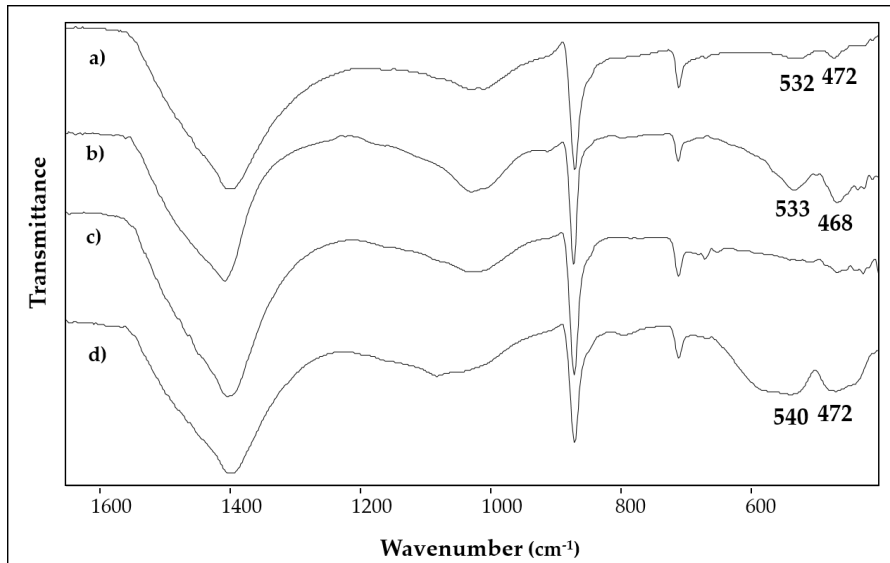239 a red ochre containing kaolinite [24, 25-27]; in sample 3 the band at 1024 cm⁻¹ (figure 3c) suggests the

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presence of another silicate, possibly illite [28], whereas the bands of red ochre are barely detectable. This difference from the point of view of the composition could seemingly be due to a different provenance of the raw material, but this would deserve a further study.

The presence of cinnabar, hypothesised on the basis of the elemental analysis, was then confirmed by the results of Raman spectroscopy; the spectra of samples 1 (figure 4d) and 3 (figure 4e) have in fact its unmistakable features characterised by very strong bands at 253, 284 (sh) and 343 cm^{-1} [19]; the weak peak at 1086 cm^{-1} is due to calcite [30].

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Figure 3. ATR-FTIR spectra of: a) sample 1; b) sample 2; c) sample 3; d) sample 4.

In sample 2 (figure 3b) the peaks at 1032, 1009, 913, 533 and 468 cm^{-1} are once again attributable to red ochre containing kaolinite [23,24-27,30,32].

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Raman analysis confirmed the outcomes of FTIR analysis on the previously discussed samples; the spectra of red ochre characterised by peaks at 291, 406, 605 cm^{-1} were obtained (figure 4a and 4b) [33]. Also in this case, the peak at 1086 cm^{-1} is due to calcite, whereas the band at 147 cm^{-1} can be ascribed to lead oxide in its tetragonal form known as litharge [34]. The weak peak at 254 cm^{-1} could be associated to the presence of a low percentage of cinnabar, even though mercury does not appear in the EDS spectrum; as this concerns, it is to underline that the Raman spectrum in figure 4b was acquired by means of a punctual analysis performed by micro-Raman (whereas no spot analysis was performed with SEM-EDS on that sample) which infers that cinnabar was probably not uniformly distributed on the painting layer; furthermore, the relative intensity of EDS peaks associated with Hg for samples 1 and 3, where cinnabar has been clearly detected, is quite small, so it seems plausible that the Hg signals were not detectable through SEM-EDS in sample 2.

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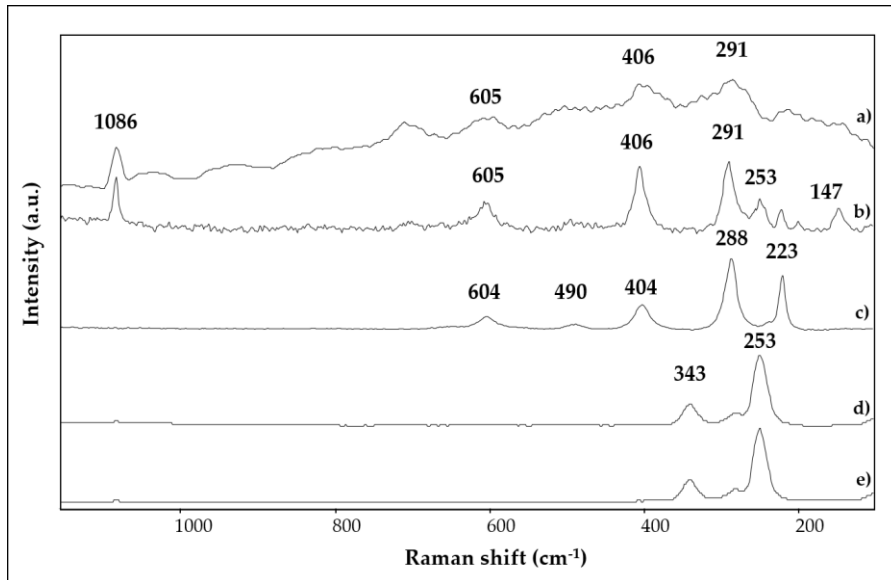
Figure 4. Raman spectra of a) red sample 2 (λexc=1064 nm); b) red sample 2 (λexc=785 nm); c) purple red sample 4 (λexc=785 nm); d) bright red sample 3 (λexc=1064 nm); e) bright red sample 1 (λexc=1064 nm);.

The spectrum reported in figure 3d for sample 4 shows a trend that is rather associable to Fe_2O_3 (haematite) than to red ochre, because of the wavenumber and especially the shape of the bands at 540 and 472 cm^{-1} is [26-27,32]; the broad bands at 1090 and 794 cm^{-1} are once again ascribable to silicate minerals, but not, as typically in ochres, to kaolinite, giving strength to the hypothesis that pure haematite was present in this sample. It must be remarked that also in this case Raman spectroscopy was really helpful since the spectrum shown in figure 4c is practically identical to the one of haematite, showing peaks at 223, 288, 404, 490 and 604 cm^{-1} [30]; that definitively made it possible to assign the nature of the purple red pigment in sample 4.

ATR-FTIR spectra shown in figure 5a and 5b are referred respectively to light red/orange sample 5 and to yellow sample 6.
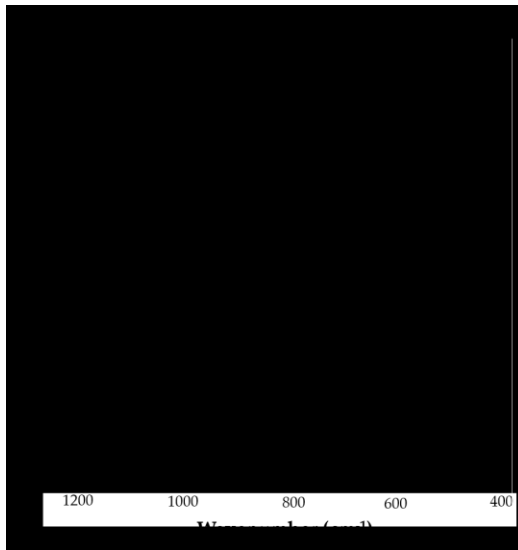
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Figure 5. ATR-FTIR spectra of: a) light red-/orange sample 5; b) yellow sample 6.

Among the strong bands at 873 and 712 cm⁻¹ due to calcite and those at 1032, 1009 cm⁻¹ of silica [24,27], there are the main peaks of yellow ochre at 913 e 797, 532, 468 cm⁻¹ [26].

Raman analysis confirmed the presence of yellow ochre in sample 6 (figure 6c), particularly because of the peak at 391 cm⁻¹ attributed to goethite [33], whereas in sample 5 (figure 6b) the peak at 405 cm⁻¹ is attributable to red ochre [25], as well as in the already discussed sample 2 and included in figure 6 for comparison (figure 6a). It must be noted that the micro-Raman analysis performed on sample 5 (figure 6b), gave also the strong band at 143 cm⁻¹ of lead oxide, probably present in this case in its yellow orthorhombic form called massicot [35], and the peak at 463 cm⁻¹ of quartz [26]. As in the case of sample 2, also in sample 5 micro-Raman spectroscopy revealed a composition that was slightly different from the one evinced by SEM-EDS measurements, where no lead has been found; however, it must be stressed that no punctual SEM-EDS analyses were performed on sample 5 and also that the sample had quite big dimensions, so it seems probable that the measurements were not performed exactly on the same area by Raman and SEM-EDS technique.

The ubiquitous peak at 710 cm⁻¹ belongs to calcite, whose presence was even confirmed by the peak at 1086 cm⁻¹ (not included in the figure).
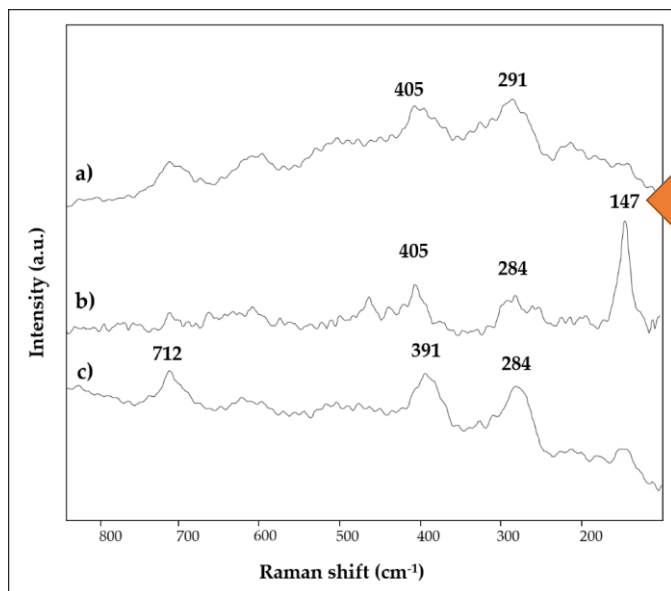
Finally, the peak at 284 cm⁻¹ achieved from each measurements presented in figure 6, could be most likely assigned to calcite [30], but it is not to exclude that it might be the result of the superimposition of that band of calcite with the one in the 290-300 cm⁻¹ range of red and yellow earth spectra [25-26], so in this case, it was not that diagnostic.

Figure 6. Raman spectra of a) red sample 2 (λexc=1064 nm); b) light red/orange sample 5 (λexc=785 nm); c) yellow sample 6 (λexc=1064 nm).

Summing up the results of vibrational spectra analysis, it can be stated the presence of yellow ochre on sample 6. The light red/orange hue of sample 5 was instead probably intentionally obtained either as the overlapping of yellow and red painting or as a mixture of pigments with different yellow and red shades; more precisely yellow ochre, red ochre and massicot were employed in this case [36].

Finally, on red, light red/-orange and yellow samples, the feasibility of visible reflectance analysis was evaluated. In figure 7a the reflectance spectra of samples 1 (bright red), 4 (purple red), 5 (light red/orange) and 6 (yellow) are shown.

The reflectance spectrum of sample 1 (the cinnabar-based sample) exhibited the typical semiconductor sigmoidal shape, characterised by a drastic rise around the inflexion point positioned in this case at 600 nm [37].

The features of red sample 4 (the haematite-based one) were instead mainly characterised by a positive slope at 590 nm, whereas a second positive slope is evident at around 700 nm. That shape matches what it is reported in the literature for red iron-based pigments [37-39]

As regards the yellow sample 6, it showed a profile that appeared very similar to that of the red sample, but in its case, the most pronounced slope stands at 540 nm; two absorbance bands at about 485 and 640 nm (readable as minima in the spectrum) were also detected. Once more the spectral trend resulting from the measurements here discussed conforms to the spectra of iron-based yellow pigments founded in the literature [37-39].

Actually, the spectrum of sample 5 (that basically resulted in a red and yellow overlapped painting) shown a trend quite similar to that obtained from the iron-based pigments; however, in this case, the rapid slope is positioned almost between the red and the yellow samples, namely at about 575 nm; no trace of massicot was revealed by visible reflectance measurements on sample 5.

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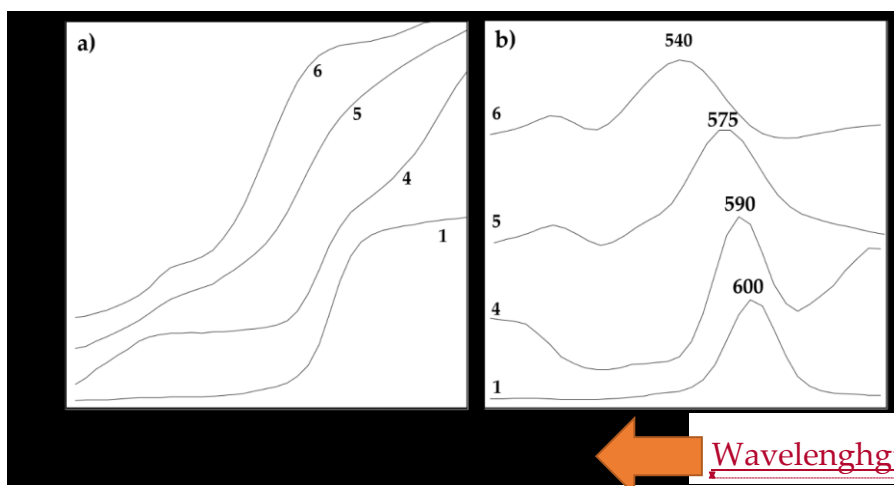
Figure 7. in 7a): visible reflectance spectra of samples 1, 4, 5 and 6; in 7b): first derivatives of the spectra presented in 7a).

The precise determination of the point of flex for each spectrum was performed reading the maximum of the corresponding first derivative curve (figure 7b).

All those observations are perfectly in accordance both with the literature [37-39] and with the previously discussed results concerning red and yellow pigments.

3.2. Green

ATR-FTIR spectrum of pale green sample 7, reported in figure 8a, shows the characteristic bands at 970, 798, 679, 490, 452 cm^{-1} ascribable to green earth and more likely to celadonite [23,29]; the bands at 1414, 873, 712 cm^{-1} are ascribable once more to calcite. This result matches perfectly with the previous SEM-EDS findings, since the detection of iron, silicon, potassium and aluminium is consistent with the composition of the green earth pigment [40].
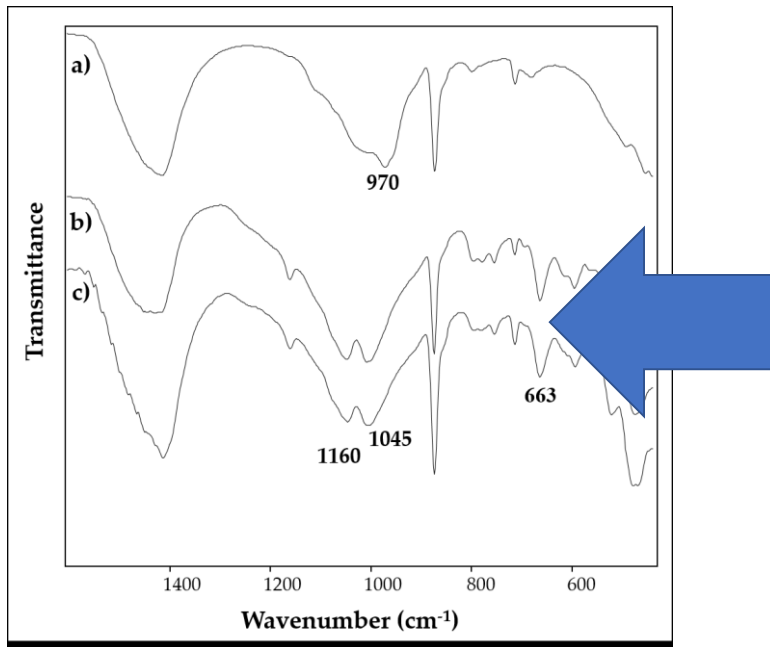
Figure 8. ATR-FTIR spectra of a) sample7, b) sample 8, c) sample 9.

3.3. Light blue

ATR-FTIR spectra of blue samples 8 and 9 are reported in figure 8b and 8c and they both present the unequivocal features of Egyptian blue, being them characterised by peaks at 1160, 1048, 1008, 754, 663, 593 and 519 cm^{-1} [4,41-43], whereas the band at about 470 cm^{-1} might belong to red ochre [35]. No decipherable Raman spectrum was obtained on blue samples, because of the presence of an extremely strong fluorescence background.

The SEM-EDS analyses clearly hind towards Egyptian blue for all the blue samples (see Table 2).

It is worth to note that from the chemical point of view the two stucco fragments didn't show differences from the other samples, indeed mouldings and wall paintings were generally prepared with similar plasters.

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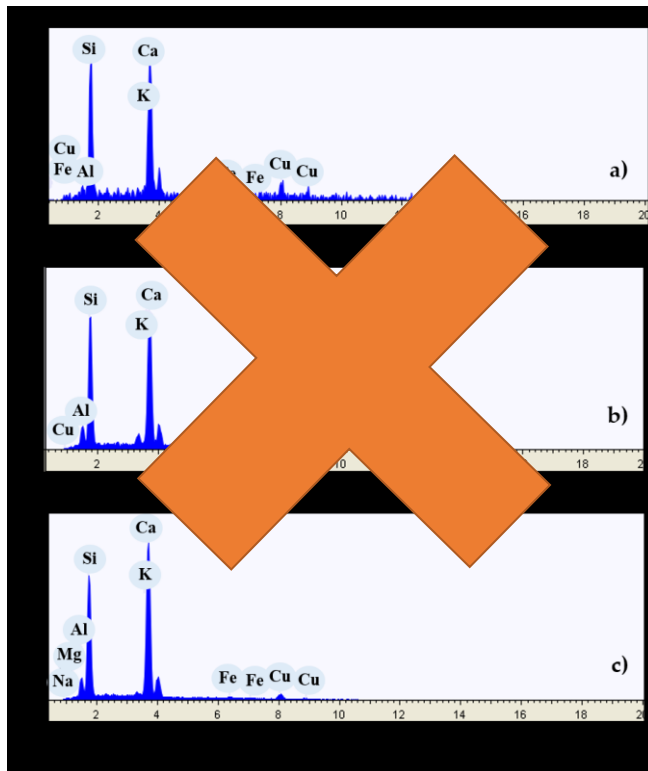
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Figure 9. EDS spectra of a) sample 8; b) sample 9; c) sample10.

3.4. White and black

Both ATR-FTIR spectra of white and black samples were just characterised by the bands of calcite at 1403, 872 e 712 cm^{-1} and of silicate minerals at 1033 cm^{-1}.

Those results allowed to hypothesise that calcium carbonate, that is the main component of the substrate in all samples, might have also been used as a pigment in sample 11.

Raman spectrum of sample 11 (figure 10a) shows, above a huge fluorescence background, the peaks at 1086, 712 and 285 cm^{-1} associate to calcite [30], and a band at 391 cm^{-1} ascribable to goethite [44 il 44 e il 33 sono lo stesso articolo] whose presence may be due to some impurity of the white pigment or even to an intentional addition made to obtain that pale yellowish hue of sample 11.

As regards the black pigment, nothing but calcite came from FTIR analysis and it was only possible to exclude the use of several compounds, as well as already stated in the SEM-EDS analysis paragraph.

Employing Raman spectroscopy, the black pigment was identified as carbon; in figure 10b it is shown the spectrum acquired on sample 12, that is characterised by the very broad bands at 1300 and 1580 cm^{-1} of black carbon [21,45].

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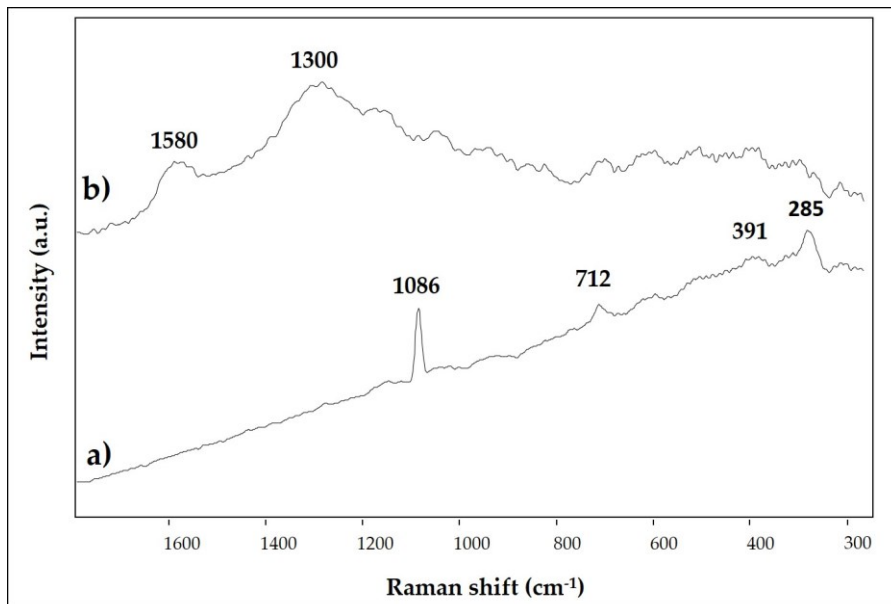Eliminato: 26,

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395   **Figure 10.** Raman spectra of a) white sample 11 (λ_{exc} = 1064 nm).; b) black sample 12 (λ_{exc} = 1064 nm).

396   *3.5. Golden area on sample 1*

397   The study of sample 1 was particularly interesting because it showed macroscopically small
398 iridescent areas of gold colour. To confirm the hypothesis of the presence of gold on the pictorial
399 surface, the study using SEM-EDS was fundamental. In fact, the morphological analysis has
400 highlighted, on the surface, the presence of a patina, as shown in figure 11.
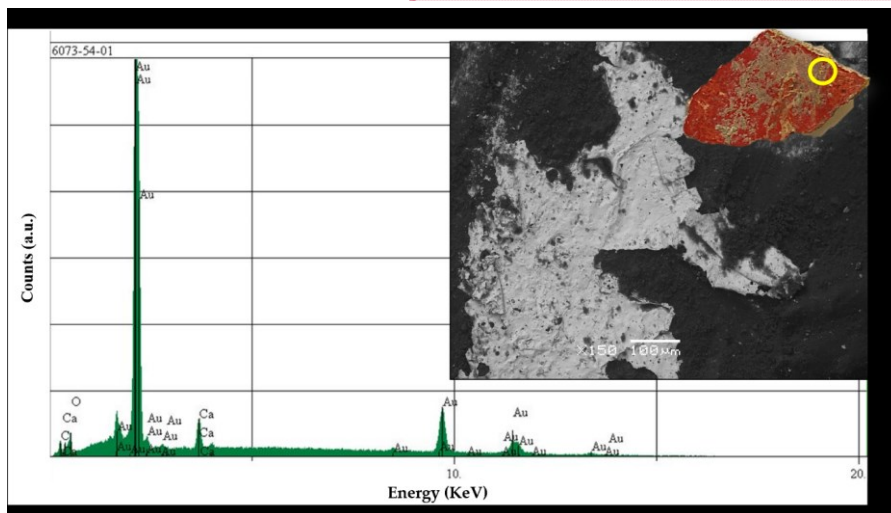

401

402   **Figure 11.** EDS spectrum acquired on sample 1 and the corresponding SEM image.

The chemical investigation carried out punctually on this patina (figure 11) showed the following composition: Au (95.4%) and Ca (4.7%). This composition has made it possible to hypothesise the use of gold leaf on this pictorial surface suggesting that the fragment could be part of some precious decoration probably commissioned by an illustrious and wealthy person since the use of gold leaf as decorative component on the pictorial surfaces of wallpaintings is not so common in the surviving roman wall paintings. Among the most important and well-known examples at Rome are the decorated walls of the Aula Isiaca [46] and the Domus Aurea. The use of this technique is also evidenced by some fragments of Julio-Claudian painting fragments collected during the excavations of Vigna Barberini (Palatino, Rome) [47].

4. Discussion

Table 4 provides a summary of all the identified elements/compounds responsible for the colours for each analytical technique employed and for each sample, together with the proposed identification of the palette. The components belonging to the substrate, i.e. calcite and silicates, are not included.

Table 4. Synthesis of the main results obtained by means of the different instrumental techniques.

Sample	SEM-EDS	ATR-FTIR	Raman	Pigments
1	Hg + S + Fe + Au	red ochre	cinnabar	cinnabar + gold leaf + red ochre
2	Fe + Pb	red ochre	red ochre + litharge + cinnabar	red ochre + litharge + cinnabar
3	Hg + S + Fe	red ochre	cinnabar	cinnabar + red ochre
4	Fe	haematite	haematite	haematite
5	Fe	red + yellow ochre	red ochre + massicot	red ochre + massicot + yellow ochre
6	Fe	yellow ochre	yellow ochre	yellow ochre
7	Fe	celadonite	-	green earth
8	Cu	Egyptian blue	-	Egyptian blue
9	Cu	Egyptian blue	-	Egyptian blue
10	Cu	-	-	Egyptian blue
11	Ca	calcite	calcite + yellow ochre	calcite + yellow ochre
12	-	-	amorphous carbon	carbon black

On the basis of the results obtained it can be stated that the palette employed for the decorations involves the use of numerous pigments and sometimes a simultaneous application of them to indicate a certain skill of the artists. In particular, the presence of a pigment such as cinnabar, much more precious than red ochre, and the use of gold leaf, could indicate an important commission.

The absence of organic binders and the possibility to differentiate specific spectral features infer the use of a fresco technique [48].

Thanks to the synergic use of both a portable Raman spectrophotometer and a conventional instrument such as a bench tool, the potentiality of these two systems have been exploited.

In particular, the use of the portable facility might allow us, in the future, to perform chemical analysis in a non-destructive way, i.e. without the necessity to withdraw some samples. It is absolutely true that the low spatial resolution achievable with the use of the portable tool equipped with a fibre optic probe might not match that of a Raman spectrometer equipped with a microscope, as proved in several of the performed analyses (for example results obtained on sample 2). Nevertheless, in this case completely not-destructive analyses can be performed.

Furthermore, it must be stressed that in the case of wallpainting samples the aforementioned portable Raman instrument could be the actual goal, most of all in the hypothesis of its application in the field, i.e. directly on painted surfaces.

449 From this point of view another important tool that could be successfully applied thanks to its
450 great versatility and the low cost of the instrumentation, is represented by the colourimetric
451 investigation.
452 At the moment these kind of measurements presented in this study have been acquired only on
453 red and yellow samples and only the visible reflectance results were investigated but, since the
454 technique seems really promising, the investigation might be extended to other fragments.
455 It is worth to notice that in case of pigmented surfaces, in particular in the case of great
456 dimension ones, both portable Raman spectroscopy and colourimetric analysis can be employed to
457 carry out a preliminary survey useful to identify where also an in-depth study with destructive
458 techniques could be useful.

5. Conclusions

460 In this paper, a multi-analytical approach has been applied to study some pigmented fragments
461 coming from Roman wallpaintings. In particular, the combined use of the different techniques has
462 allowed disclosing the entire palette employed by the artists and including not only single pigments
463 (such as cinnabar, red and yellow ochre, Egyptian blue and green earth) but also different painting
464 layers or possible mixtures.
465 Some interesting aspects, which could only be hypothesised archeologically, have now been
466 successfully confirmed, such as, for example, the presence of gold leaf decoration for a few collected
467 painting fragments (sample 1; another example on a cinnabar layer is actually preserved at Rome).
468 Regarding the pigments, as well, some worth mentioning features can be highlighted. First of all the
469 presence of a red ochre layer beyond the analysed cinnabar wall painting fragments (samples 1 and
470 3). As we well know from ancient literature and from surviving Roman wall paintings, cinnabar was
471 an expensive pigment imported to Rome and distinguished by a high risk of chemical transformation
472 (blackening). Former analyses of cinnabar fresco fragments have already demonstrated that this
473 pigment was often applied upon an aragonite or yellow ochre coat [49], as well as on a red ochre
474 layer [50] as detected in this study.
475 It is also interesting that in red sample 2 a different red pigment, derived from lead, was
476 observed. In this case, the result might be related to diachronic painting fragments and/or their
477 pertinence to different roman buildings.
478 The presence of some unusual chemical elements as for example barium is probably to relate to
479 the nature of the archaeological discovery. As mentioned above, the ancient shards were collected in
480 a modern waste trench, which could have caused contamination with modern building rests.
481 Finally, the white sample 10, on which yellow ochre traces were noticed, has probably to be
482 considered a fragment with yellow overpainted motifs, as verified on better conserved shards
483 belonging to the same assemblage.
484 Furthermore, from the point of view of the analytical approach applied, it has been
485 demonstrated that the portable instrumentation (Raman spectroscopy and reflectance spectroscopy
486 investigations) can successfully be applied for highlighting the nature of the pigment without to
487 invoke more expensive tools. The employment of portable devices might provide a rapid and
488 effective overview directly on vast wall painting giving the opportunity of performing either totally
489 non-destructive analysis (without any sampling from the artwork itself) or at least targeting the
490 sampling in order to do it as fewer as possible.

491 **Author Contributions:** Conceptualisation, P.F, M.A.; methodology, V.C. and V.G.; formal analysis, V.C.; C.A.L.;
492 V.G., F.D.; investigation, V.C.; C.A.L.; and V.G.; data curation, V.C. and V.G.; writing—original draft
493 preparation, P. F, V.G. and V.C; writing—review and editing, P.F, M.A; F.D; supervision, P.F. and M.A.

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