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Things come always in three: Non-invasive investigations of Alexander and Roxane's Wedding Room in Villa Farnesina

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Abstract: Non-invasive optical spectroscopical analyses were conducted on the three main walls of Alexander and Roxane's Wedding Room in Villa Farnesina, Rome. The north and the east wall were frescoed by Sodoma in 1519. The decoration of the third wall is subsequent and neither the author nor the period is known. The north and east walls underwent various restorations, some even very invasive. For these reasons the supposed left original parts of the two walls by Sodoma were studied and compared with the third one, aiming to obtain more information about its author and epoch. The results show the use of the same pigments for the three walls. In particular, the same yellow pigments including lead antimonate; the use of enamel blue with Bi impurities whose use is time-limited, and the use of a certain kind of purple hematite. The commonality in the pictorial technique also emerged, especially in the yellow parts, painted in the same way in each wall. This information, and documentary sources, reinforce the hypothesis that the third wall was decorated shortly after the death of Agostino Chigi by someone who was well acquainted with the materials and techniques used by Sodoma for the other two walls.

Keywords: non-invasive investigations; portable/reflectance spectroscopy; portable Raman spectroscopy; lead antimonate; enamel blue; caput mortuum.

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1. Introduction

Villa Farnesina, the Renaissance Roman villa built in 1506 by the Sienese banker Agostino Chigi, patron and close friend of Raphael, is currently the headquarter of the Accademia Nazionale dei Lincei. It is devoted to promote and protect its huge artistic heritage consisting in some of the most famous artworks of the Italian Renaissance Masters –Raphael included- which were summoned by Chigi for adorning its own private, suburban, relaxing place. Among the artists who left their sempiternal mark inside the residence, was also Giovanni Antonio Bazzi, better known as Sodoma (1477-1549) who frescoed the bridal suite of Agostino Chigi and his beloved Francesca Ordeaschi. The suite was decorated with scenes from the life of Alexander the Great,

included his marriage with Roxane, explicit reference to that of Chigi. Before the new restoration of the room began, some non-invasive analyses were carried out on the two walls painted by Sodoma and his workshop depicting *Alexander meeting his new bride-to-be Roxane* on the north wall (Fig.1), and the *Darius family before Alexander* on the east one (Fig.2). A third wall, the west one, depicts the *Taming of Bucephalus* by an unknown author (Fig.3). It was frescoed later than the other two walls because it hosted the double bed of Agostino Chigi and Francesca Ordeaschi. After the death of both the spouses the wall was decorated, but it is still uncertain how later this work was done and by whose hand.

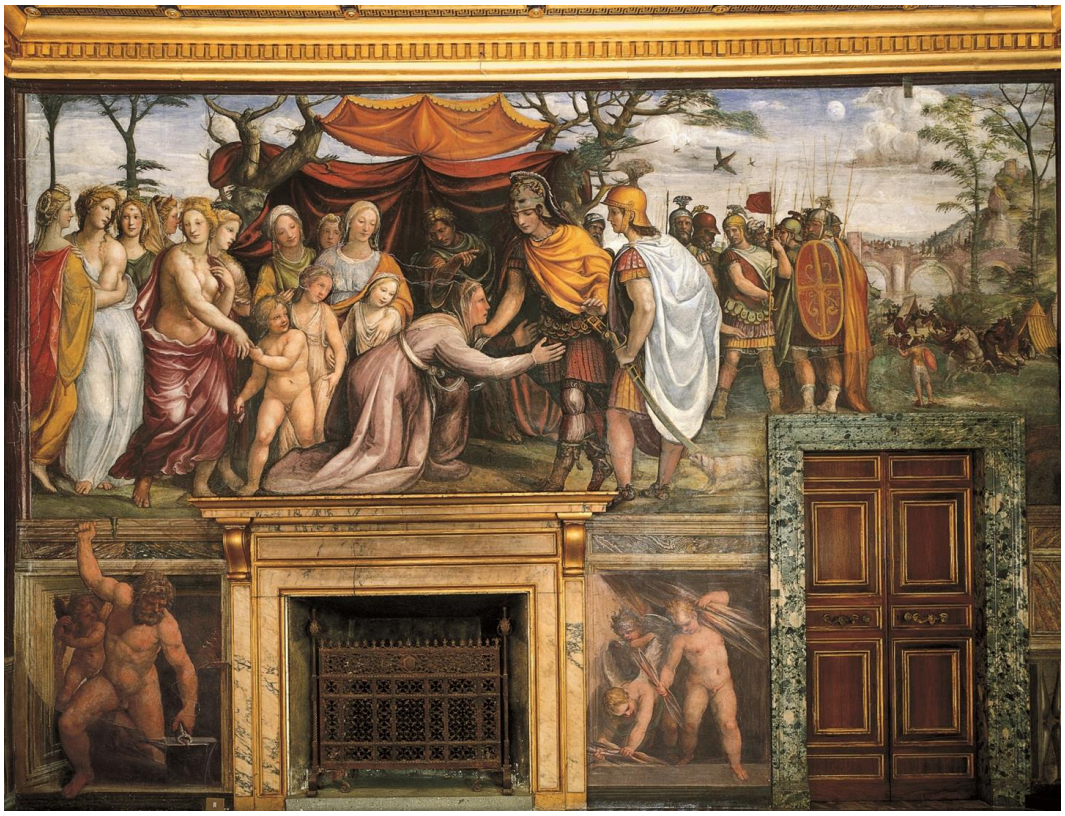

Figure 1. The *Darius family before Alexander.* Fresco by Giovanni Antonio Bazzi, called Sodoma, 1519. Alexander and Roxane's wedding room, east wall. Villa Farnesina, Rome. Courtesy of Archivio Villa Farnesina.

Taking advantage of the restoration involving the northern and eastern walls, the non-invasive analyses were extended also to the *Taming of Bucephalus*, the west wall, which was never investigated before, trying to collect information about its painting material to be compared with the other two walls of certain authorship in order to establish the epoch of this fresco. It is important to highlight that the both the north and the east wall underwent many restorations, three of them documented. The first restoration dates back to 1870 when the Duke of Ripalta, shortly after buying in emphyteusis the Villa [1], had these murals restored, adopting as a programmatic choice to "entrust the restoration of the frescoes by Sodoma, not to an illustrious artist - who no doubt would have hardly resisted the desire to redo as much as possible but, on the contrary, to a modest painter

- already elderly – whose action would be limited to the indispensable [2]." The second one, carried out at the beginning of the 20th century, is documented by an inscription on one of the walls of the room: "*Vito Mameli restored in May 1915*" whose work remained a "*thick dark mixture painted with glue*" to which the Istituto Centrale del Restauro (ICR) was called to remedy in the 1970s, as can be seen from the technical report attached to the cost report no. 4 of 1 February 1974 signed by the restorer Paolo Mora, which provided for "consolidation, cleaning and restoration of the frescoes by Sodoma and other 16th cen tury artists" and referred to the "implementation of the work plan prepared for the resto ration of the entire pictorial decoration of the Villa [3]."

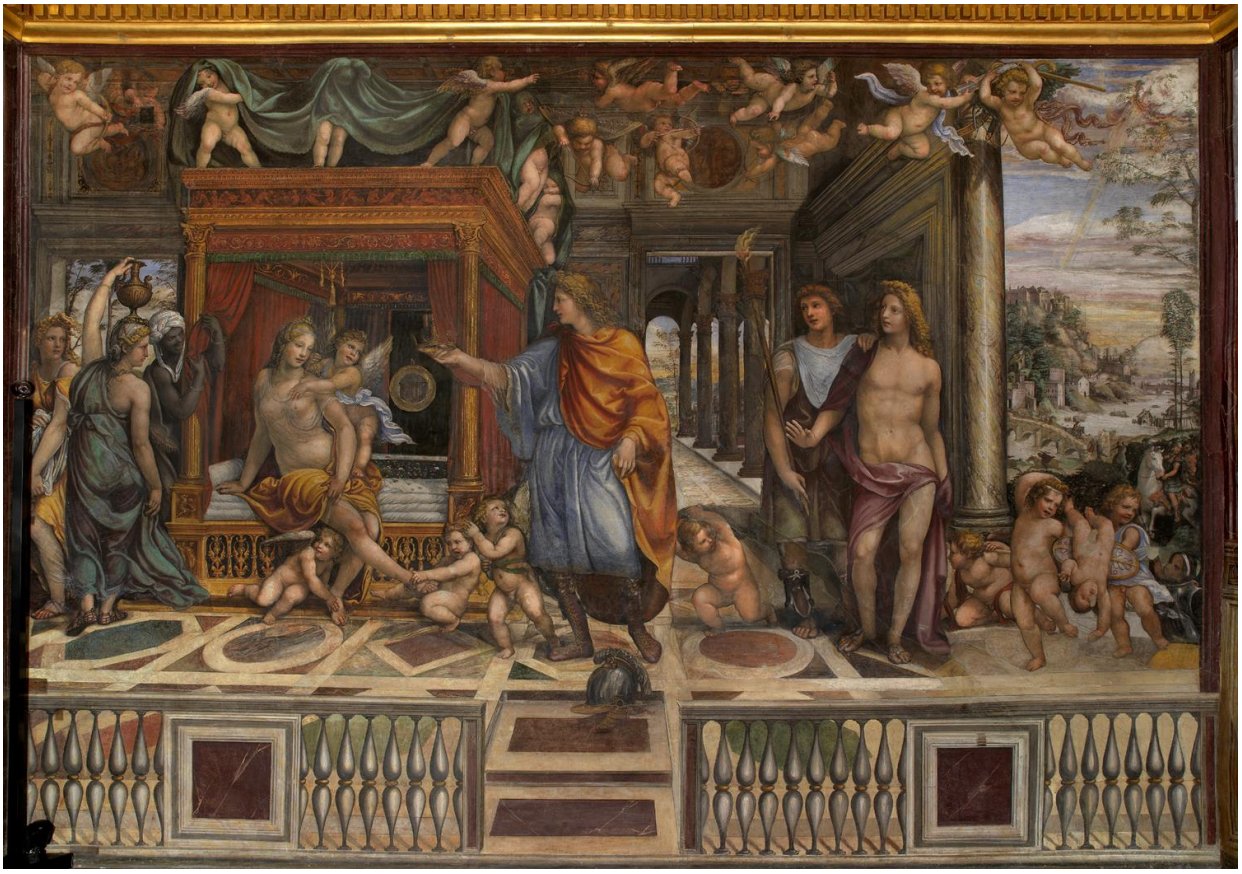

Figure 2. *Alexander meeting his new bride-to-be Roxane.* Fresco by Giovanni Antonio Bazzi, called Sodoma, 1519. Alexander and Roxane's wedding room, north wall. Villa Farnesina, Rome. Courtesy of Archivio Villa Farnesina.

For this reason the non-invasive investigations of the north wall depicting *Alexander meeting his new bride-to-be Roxane,* and the east wall depicting *Darius family before Alex ander* were limited to the supposed original parts and were compared with the results emerged from the third wall, the west one, showing the *Taming of Bucephalus* by un known artist, trying to chronologically define such fresco, in order to establish whether it was coeval to the other two. A set of non-invasive optical spectroscopic analyses including, Visible Reflectance (R-Vis), portable Raman and Reflectance In frared Spectroscopy (MIR) have been used in a multi-technique approach, widely used and well-established in the last decade [4,5] for the individuation of painting

materials by refining and unraveling the elemental information from X-Ray Fluores cence (XRF), making possible the comparison among the pigments of the three walls and even disclosing some peculiarities of the execution technique.

Figure 3. *Taming of Bucephalus.* Unknown author, unknown year. Alexander and Roxane's wedding room, west wall. Villa Farnesina, Rome. Courtesy of Archivio Villa Farnesina.

2. Materials and Methods

2.1. X-ray Fluorescence Spectrometer (XRF)

The portable XRF instrument Tracer III-SD (Bruker AXS) consists of an X-ray tube equipped with a Rh target, and a Peltier cooled Si drift XFlash detector having a resolution of 130 eV FWHM at 5.9 keV. The source was operated at 40 kV and 0.030 mA, with a data acquisition time of 30 s. This instrumental setup allows for the analysis of elements with atomic number (Z) greater than 10. The X-rays emitted by the tube are collimated on the analyzed surface with a spot diameter of 4 mm. The spectra, corrected for the effificiency of the detector, were expressed as counts per second (cps).

157 **2.2 Portable Raman spectrometer**

158 The BRAVO spectrometer uses a new patented technology called SSE™ (Sequentially
159 Shifted Excitation, patent number US8570507B1) in order to mitigate flfluorescence [6,7].
160 The laser is slightly wavelength shifted during the acquisition for three times and three
161 raw Raman spectra are recorded. A proper algorithm recognizes all the peak that shift at
162 different laser wavelength as good Raman peaks, and other peaks, non-shifting, as
163 fluorescence (or absorbance) peaks, removing them. Moreover, the BRAVO use two
164 different lasers (DuoLaser™), ranging from 700 to 1100 nm, during the acquisition. The
165 use of the second laser is not intended as in usual commercial handheld or portable Raman
166 spectrometer as a tool to try to mitigate the fluorescence, but as a way to collect Raman
167 spectra up to 3.200 cm−1 and hence to access the CH stretching region also. The fifirst laser
168 is dedicated to the acquisition of the Raman spectra in the first range (called fifingerprint
169 region), the second one in the second range (called CH region). The BRAVO acquired
170 spectrum is fifinally a Raman spectrum free from flfluorescence on a whole spectral range
171 from 3.200 cm^{-1} to 300 cm^{-1} . The applied laser power is always less than 100 mW for both
172 lasers. Obviously, using the BRAVO two lasers ranging from 700 to 1100 nm, the sensitivity
173 to inorganic green and blue is really reduced if compared to the use of a 532 nm laser. The
174 spectral information from the enhanced spectral range are useful for identifification, for
175 example, of resins and waxes. The spectra were acquired with acquisition time ranging
176 from 500 ms to 2 s and accumulation ranging from 5 to 100. For all the measurements
177 OPUS™ software (Version 7.7) has been used in order to select the appropriate acquisition
178 parameters.
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180
181 **2.3 Visible Reflectance**

182 The visible reflflectance measurements have been carried out by a portable spectrometer
183 CM-700d produced by Konika Minolta. The spectrometer is equipped with an UV
184 radiation filter Xenon lamp and a silicon photodiodes array detector. The analysis range
185 is 400 - 700 nm with a slit of 10 nm.
186
187
188 **2.4 Reflection Infrared Spectroscopy**

189 The portable infrared spectrophotometer ALPHA-R (Bruker Optik GmbH) is equipped
190 with a Globar IR source, a patented interferometer (RockSolid)™, insensitive to external
191 vibrations and able to work in any spatial orientation) and a DLaTGS room temperature
192 detector. The working optical layout for reflflection measurements is 22°/22° (specular
193 optics) with about 15 mm of working distance. The infrared spectra have been acquired
194 in the spectral range 7500–375 cm−1 with a spectral resolution of 4 cm^{-1} and 200
195 interferograms. The sampling area was 28 mm^2. A background correction using a
196 reference spectrum from a gold flat mirror was applied for representing the reflflectance
197 profile (R) expressed in the graphs as pseudo absorbance, log (1/R).
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199

3. Results

Non-invasive analyses were carried out on the supposed unrestored parts of the north and east walls of the Alexander and Roxane's wedding room in Villa Farnesina, both attributed to Sodoma and his workshop. Further analyses were carried out also on the third wall, the west one, of an unknown period and author. The XRF analysis indicates Fe and Co as the most abundant elements. Fe, which often characterizes most of the pigments used for fresco technique because of their stability and coverage, is found in red, orange, yellow and purple areas. Cobalt is present instead as the main constituent of blue areas, widely used in all the walls studied both alone and in a mixture with other pigments.

3.1 Red

In the red areas the presence of Fe-based pigments prevails. In the darker shades, Raman spectroscopy identified red ochre, with few addition of hematite as illustrated in Figure 4. The bright red of Dario's daughter's dress at the left end of the east wall is characterized by Fe (XRF, Fig.4), but Raman individuates only calcium carbonate with its typical band at 1085 cm^{-1} [8] while hematite results instead in the dark red areas, as the skirt of Alexander. Indeed in Figure 4 are highlighted the characteristic Raman bands of hematite at 498and 610cm^{-1}, and the LO Eu peak at 660cm^{-1} [9].

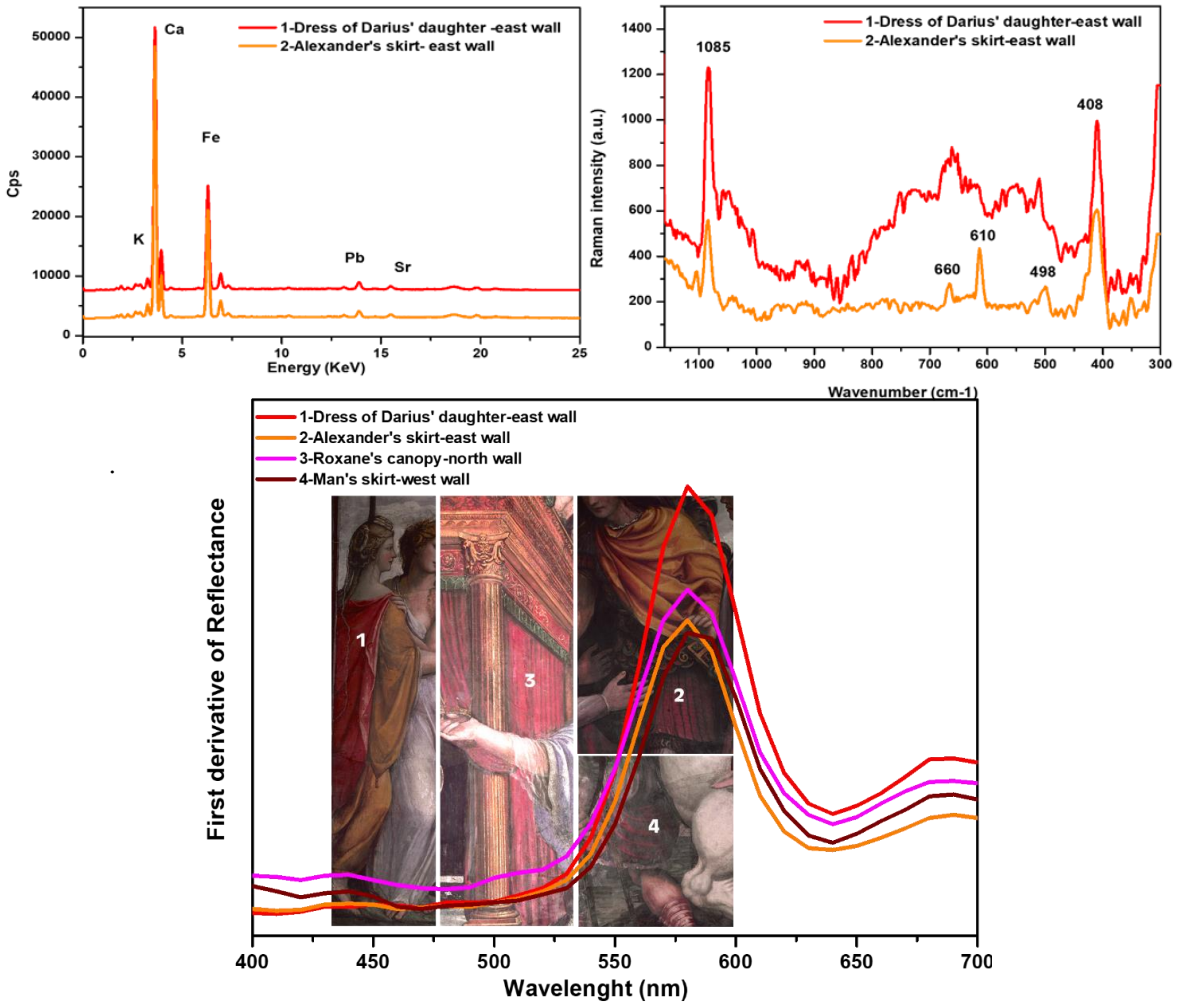

Figure 4. **Above from left to right:** XRF and Raman spectra of points 1 and 2 on the east wall. **Below**: Comparison of the first derivative reflectance spectra of selected red areas.

The same mixture of generic Fe-based red with hematite can be found in the north wall on the red curtains of Roxane's canopy bed and in the dress of the putto on the right end. The first derivative reflectance spectra of such dark red areas do not show differences respect with the bright red ones, and in each analysed point the spectrum follows the trend of a generic iron oxide (Fig.4).

It is worth to note the presence of traces of cinnabar on the north wall, on Roxane's canopy curtains confirmed by Hg at XRF and by Raman. Since from the reflectance spectrum it is not possible to individuate the characteristics of the cinnabar it is likely that it was used in mixture and is not found on the surface enough to be revealed.

The third wall shows again the use of Fe-based red and hematite in the skirt of the back-turned man running away behind Bucephalus (Fig.4, line 4).

3.2 Purple

The composition of the purple areas by XRF is the same as the red ones. Raman spectroscopy individuates instead strong hematite signals in all the purple zones, as for example the dress of Dario's wife in the east wall. It is red/purplish and has the same elemental composition as the red one of Darius's daughter, depicted next to it. Nevertheless the same elemental composition, Raman analysis indicates a strong presence of hematite only for the former. The difference in the chromatic tone is hardly appreciated in the reflectance spectrum but becomes clearer if the first derivative of the same spectrum is considered. Here we note, with respect to the daughter's red dress, a shift of the maximum of about 10nm towards the red and at the same time the narrowing of the minimum to 640nm and the consequent steep climbs up to 700nm (Fig.5). These features recur in the purple areas of each of the three walls and more particularly in the purplish red of the robe of Statira II, wife of Darius, depicted on the east wall, of the half-naked Hephaestion on the north wall, and on the skirt of a running, back-turned figure on the third wall, the *Taming of Bucephalus*.

The purple/gray toned areas consist of hematite and enamel blue, as indicated by the Co presence its associated impurities as Bi and As from XRF. The presence of enamel blue is not straightforward in the reflectance spectrum which retraces mostly the hem atite-based purples.

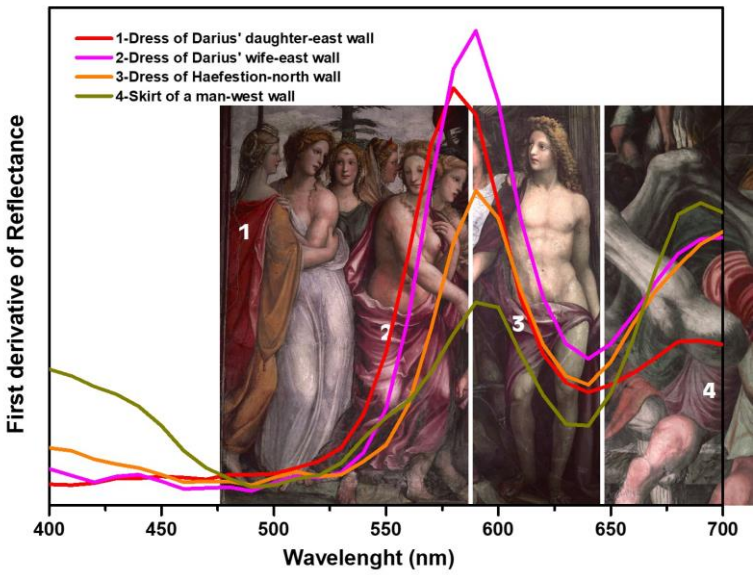

Figure 5. Comparison of first derivative reflectance spectra, from selected red and purple areas.

3.3 Yellow

The yellow areas are quite articulated, being a mixture of two or three different yellow pigments. Their composition emerged to be mostly of two types: one containing Fe and Pb, and the other Fe, Pb and Sb. The simultaneous presence of Sb and Pb indicates the use of Pb antimonate, also known as Naples yellow, and coincides always with lighter yellow hues. On the east wall the use of Naples yellow is found on the lighter parts of the dress of Darius's daughter on the left of the fresco, where XRF indicates Fe, Pb and Sb. The first derivative of its reflectance spectrum is mostly that of yellow ochre (Fig.6, line 1) but a little broader, according to Naples yellow features [10]. In the yellow skirt of Hephaestion, XRF indicates Fe and Pb but no Sb. Since there is no evidence of lead white in this area, the Pb is due to litharge, a Pb-based yellow, as can be seen from the first derivative of reflectance spectrum with the maximum at 530nm [10] (together with yellow ochre which can be noted in its weakened maximum at 450nm (Fig.6, line 2). An abundant use of litharge still accompanied by a background of yellow ochre as suggested by Fe presence, is even clearer in the landscape on the north wall, where XRF indicates only three main elements: Ca, Pb, Fe and the reflectance shows in first derivative mostly the spectrum of litharge a little modified by yellow ochre (Fig.6, line 4). The yellow dress of Roxane's maid on the left is characterized by Fe and Pb, and shows essentially the presence of yellow ochre, so in this case the source of Pb should be other than litharge (Fig. 6, line 3). All the three types of yellows, yellow ochre, litharge and Naples yellow can be found in Roxane's dress, where Naples yellow is used to obtain lighter cold tones. The main elements Fe, Pb and Sb suggest the presence of Naples yellow and yellow ochre but reflectance spectra allowed also for litharge individuation. Its presence can be argued by the first derivative where Roxane's dress shows the main features of yellow ochre namely the relative maximum at 445nm and the broader shape of the main band like Naples yellow, together with a further growth at 509nm (Fig.6, line 5), which suggests the presence of litharge, impossible to establish on the basis of XRF data alone, due to the joint presence of Pb and Sb. Litharge signals are more evident if the second derivatives are checked.

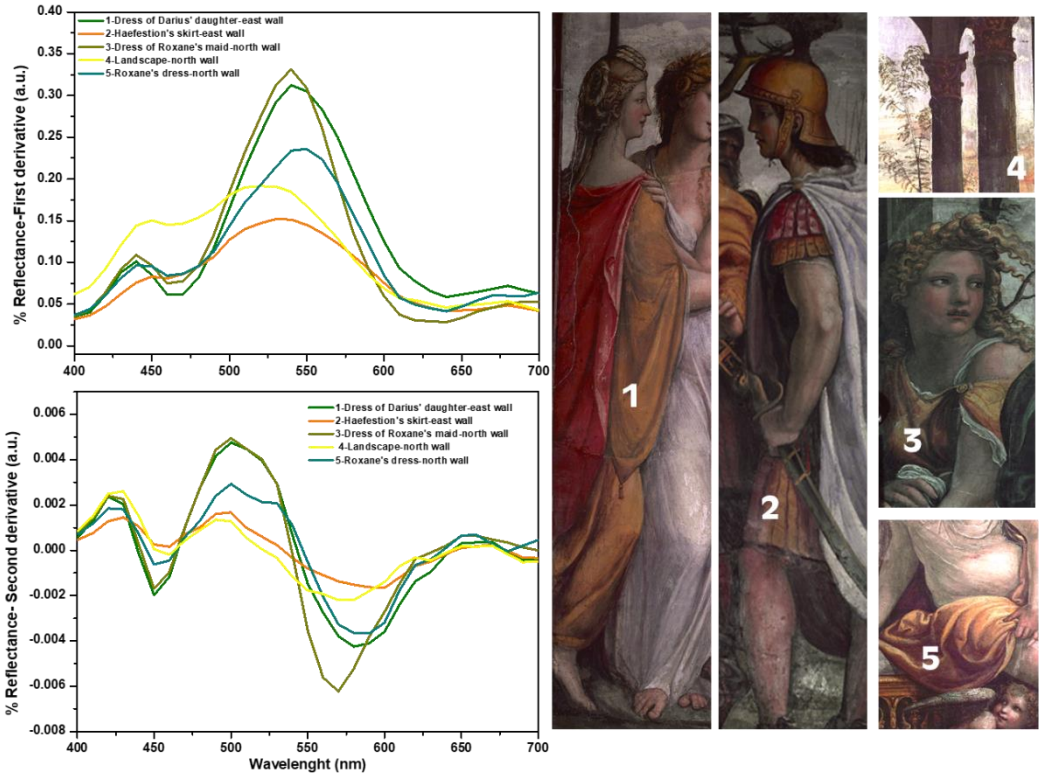

Figure 6. Comparison of first and second derivative reflectance spectra, from selected yellow areas.

In fact if we consider the second derivatives, the mixture of yellow ochre and Naples yellow (Fig.6, line 1), does not account for the trend between 465 and 550nm of the Roxane's dress (Fig.6 line 5) which can be explained by the presence of litharge already seen in the landscape (Fig.6, line 4) with the two relative max at 494 and 529nm which also appear in this spectrum, facilitating the identification of litharge in a situation difficult to decipher due to the overlapping of common elements. Naples yellow is also easily individuated by its Raman features [11] (Fig.7).

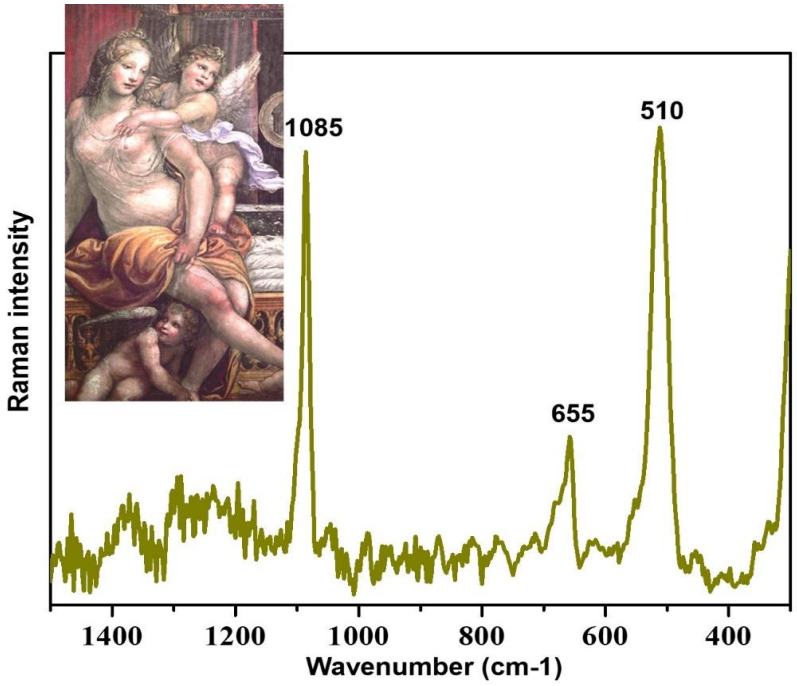

Figure 7. Raman spectrum of Roxane's yellow dress the presence of lead antimonate (Naples yellow).

The presence of Naples yellow revealed by XRF and Raman is found also in the third wall, mixed once again with yellow ochre and litharge in the lighter parts of the yellow-orange garments. The reflectance spectra derivatives of these areas shows the prevailing trend of litharge thus allowing its otherwise difficult identification, due to the simultaneous presence of Pb and Sb.

Au was also identified to highlight the elements in on the canopy columns, as well as in the frame of the mirror behind Roxane and on the finishes of Alexander's dress. In the third wall we find the same mixtures of yellow pigments already present in the east and north walls.

3.4 Orange

In orange areas, the most evident and common feature of the three walls is the disap pearence of Sb from the XRF analysis. In Alexander's mantle on the north wall, the use of red ochre added to the yellow one was identified. In addition, the presence of Pb by XRF and the second derivative of reflectance, suggest the presence of litharge in this area as well, which is not so strange due to its yellow/orange hue.

Also in the third wall the orange areas are characterized by mixtures of yellow and red ochre, with the presence of Pb at XRF. The use of litharge is not always visible by reflectance. It can be seen in the dress of young Alexander comparing the second

derivative, but not in the dress of Alexander's father, Philip II of Macedon, where, however, XRF identified the presence of Pb.

3.5 Blue

The blue areas in each of the three walls studied, are characterized by the presence of Co which corresponds - in most cases - to the reflectance spectrum of enamel blue. Along with Co, associated impurities are always found from its production process.

On the east wall enamel blue is used to create the shades in the white robe of one of Darius's daughters and in the white cloak of Hephaestion. It is also found in a mix ture with hematite to obtain the gray/purple hue of Sisigambi's dress as already high lighted above. On the third wall the use of only enamel blue returns as indicated by the presence of Co, Bi, As in the dark blue areas of Alexander's father's robe, Philip II of Macedon, and in the white cloth of the young Alexander taming the horse Buceph alus. The first derivative of the reflectance spectra measured in the same points con firm the use of enamel blue (Figure 8).

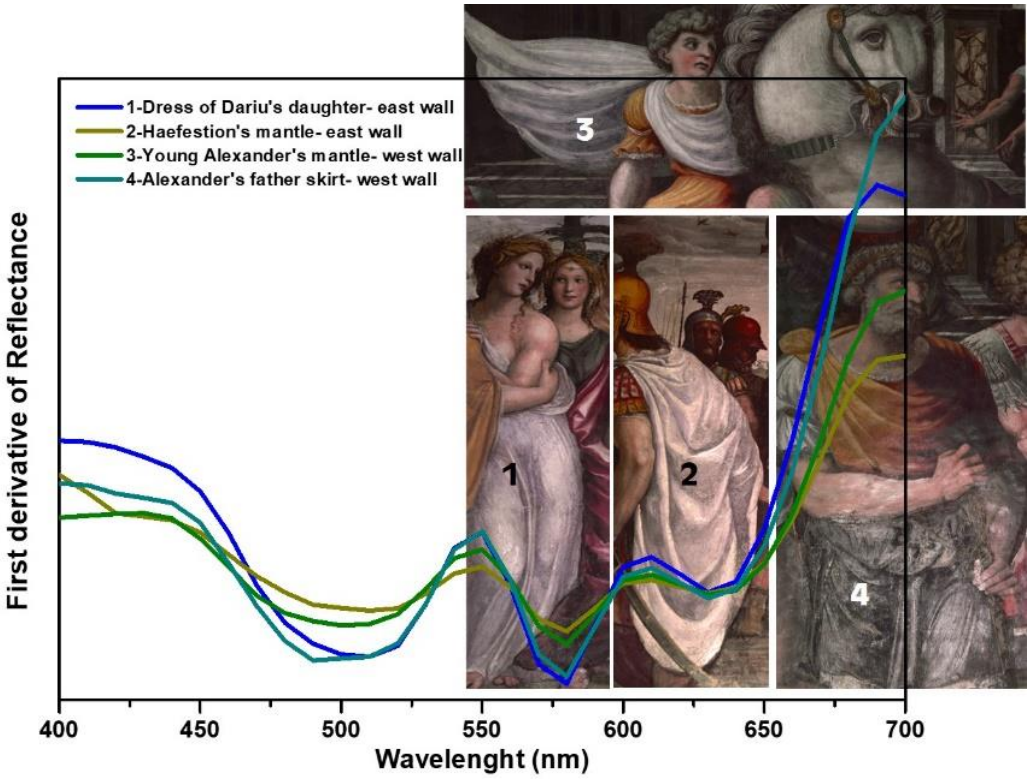

Figure 8. Comparison of first derivative reflectance spectra, from selected blue areas.

On the north wall, two different blue pigments were individuated: enamel blue and lapis lazuli, this latter univocally identified by MIR (Fig. 9) thanks to its characteristic infrared band at 2340 cm^{-1} [12]. Both these pigments have been used to obtain different shades of blue including:

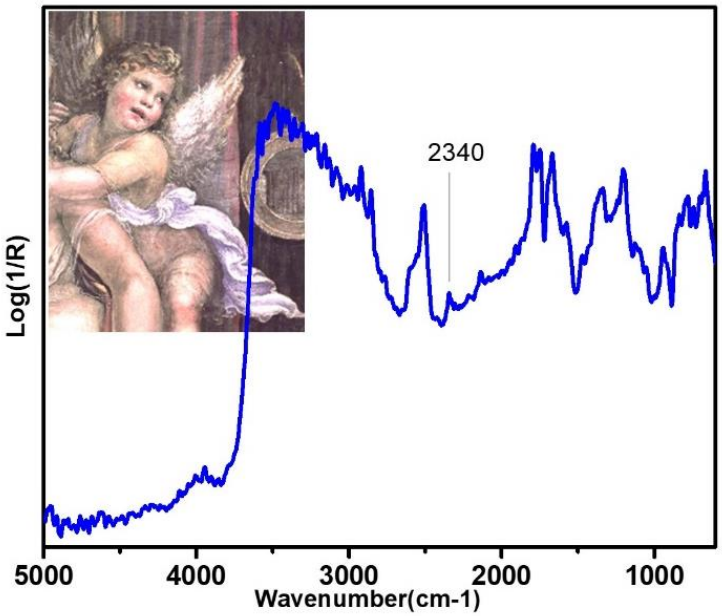

Figure 9. Infrared spectrum recorded on putto's dress, north wall.

1) The use of lapis lazuli, only on the north wall, for the blue highlights on white draperies such as on the white dress of the putto that helps Roxane to get ready (Fig.9).

2) The use of enamel blue. It is found used alone for the blue highlights of the white dress of Hymenaeus: from XRF the characterizing elements Co, Bi and As emerge, and the reflectance spectrum corresponds to that of enamel blue. It is also found in those areas currently perceived as gray, such as in the helmet in the foreground, on the north wall. XRF indicates the presence of Co, Bi, As, throughout the whole helmet, while the reflectance shows only some remains of the enamel blue spectrum (Fig.10, line 7).

3) The use of enamel blue and lapis lazuli in single superimposed layers, being lapis lazuli on the surface, distinguishable only with the joint use of XRF and reflectance spectroscopy because this latter individuates only pigments on the surface. This is the case of the upper part of Alexander's dress where the characteristic elements of the blue enamel emerge from the XRF, but its reflectance is almost entirely attributable to that of lapis lazuli, whose elements cannot be revealed by XRF (Fig.10, line 6).

4) The use of both pigments mixed together is evident from the reflectance spectra of the points analysed, in which the characteristics of both pigments are found. This is the case of the lower part of Alexander's dress and that of the putto on the right, intent on playing with Alexander's shield (Fig.10, line 8).

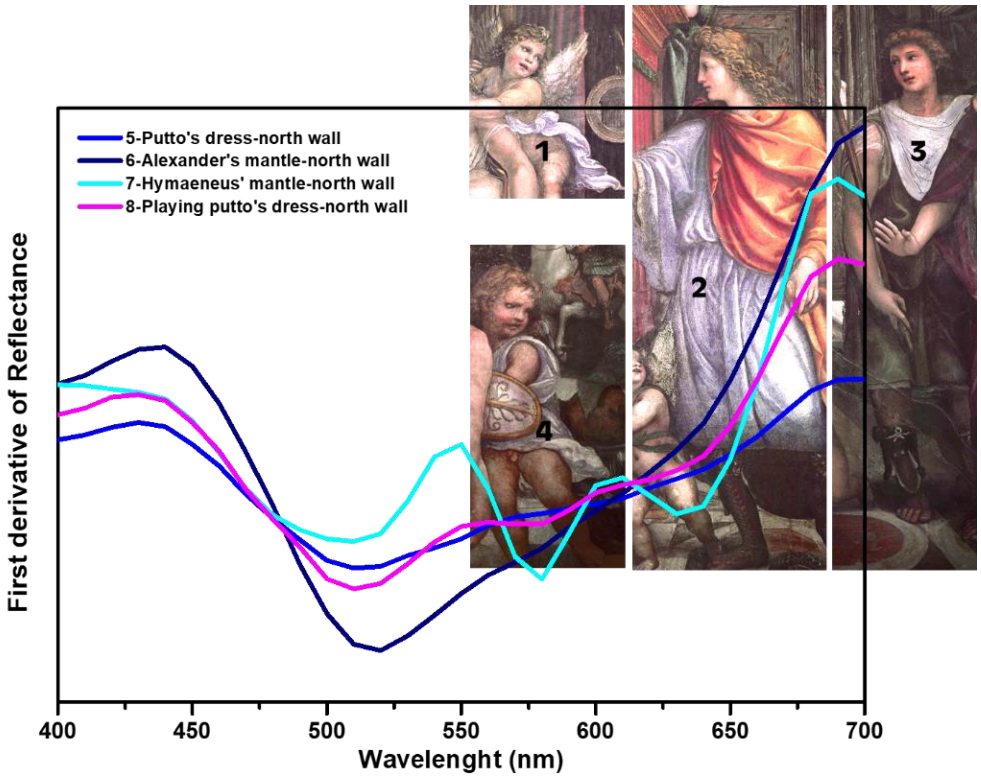

Figure 10. Comparison of first derivative spectra of visible reflectance from selected blue areas.

Further lapis lazuli finishes would also seem by now lost or seriously compromised as can be seen from the heavy repainting of some mantles, to restore the outlines that are no longer perceptible, including Alexander's dress which presents elements attributable to restoration interventions such as Ti and Zn.

4 Discussion

The presence of hematite, verified by Raman spectroscopy, seems always to coincide with a purplish hue. In fact, if we exclude the cases in which it is added to a Fe-based pigment to obtain a darker red tone, all the other areas rich in hematite are purple. No organic compound has been identified in conjunction with these purple areas, which show the same composition and the same impurities as the red ones without hematite and, compared to these, show a definitely different shade. This chromatic diversity with the same elemental composition and in the absence of organic dyes, suggests the use of hematite as a purple pigment in its own right, perhaps in the form of *caput mortuum* [13]. The use of this purple pigment based on

hematite occurs in all the three walls. The yellow areas show a very articulated construction. They are all characterized by the presence of yellow ochre to which other yellow pigments are added. From the joint analysis of XRF and reflectance it was possible to highlight the presence of Pb yellow as litharge, which would otherwise be impossible to identify by the elemental analysis alone. The presence of the Pb-antimonate, Naples yellow, recurs in the yellow areas that characterize the main characters. Naples yellow is one of the most synthetically produced pigment known and lost and rediscovered a number of times through the history [14,15]. It comes from glassmakers' tradition and its use as a pigment at the beginning of XVI century, it is very early and unexpected.

It is worth to note that Naples yellow has been individuated in Villa Farnesina, also in the Loggia of Cupid and Psyche, both in the figurative part of the scenes and in the fruits of the vegetable festoons [16]. In the Alexander and Roxane's Wedding Room it is used in the walls painted by Sodoma to lighten the yellow tones giving a lighter and cold shade. Also in the third wall were used the same three yellow pigments but with an interesting difference. In the walls by Sodoma, the Na ples yellow is always detectable by reflectance, and this means that it is on the surface, as a final touch of the lighter shades.

In the third wall, on the other hand, Naples yellow is present in the yellow areas because it is individuated by XRF, but the reflectance does not always detect it, prevailing instead, litharge or yellow ochre.

So, even if we found for each of the three walls the total coincidence of the pigments used and in particular the same yellow pigments, however, it is equally important to note a diversity of the "final touch" concerning the yellows by the painter of the third wall who, although he uses the same materials as Sodoma, Naples yellow mixed with yellow ochre and litharge, nevertheless he does not seem to prefer one in particular for finishing. The further evidence that Sb disappears in the orange areas both in the two and in the third wall as well, indirectly confirms the precise choice by both Sodoma and the unknown painter, to use Naples yellow only for light yellow areas. The enamel blue that is widely used in each of the three walls studied, has the characteristic of having, associated with the Co, some impurities of As and Bi. In particular, the latter allow the pigment to be placed within a specific processing method that obtained the blue of enamel from the bismuth slag, locating its extraction both geographically, as a German manufacture from the Erzgebirge, and chronologically as well, attesting to it within the XVI century [17]. This means that the decoration on the third wall is realistically ascribable to the 16th century. It must be remembered that the third wall was the one that housed the double bed of Agostino Chigi and Francesca Ordeaschi, who both died in 1520, *terminus post quem* from which to start the decoration of the third wall. There are documentary testimonies attesting the presence of Sodoma in Rome to settle and open a workshop in 1521 [18]. However, the same sources exclude any kind of Sodoma's pictorial production in the capital from that date, apart from few drawings [18]. This fact does not exclude he had passed on his knowledge to the students in the workshop. These information together with the scientific evidences on the painting material let support the

hypothesis that the third wall is practically coeval to the other two and painted by one who has someone who had attended the Sodoma's workshop and had learned his painting techniques and his painting materials as well.

4 **Conclusions**

The results obtained show a substantial uniformity in the typology of the pigments used on the east, north and west walls of the Alexander and Roxane's Wedding Room in Villa Farnesina, Rome. Also the execution technique relative to the mixtures of pigments used, turns out to be the same; such as in the rendering of yellows and their different shades from colder tones to golden ones, and in blue reflections on a white background. Although it is not known how much time passed between the execution of the two frescoes, it should be noted that the palette of the east and north walls is the same as the third, the west one. In particular, all those pigments that in the two walls frescoed by Sodoma were a reason of interest because they were still uncommon or because they were available in a limited period of time, such as the Naples yellow, the caput mortuum and the enamel blue, are found, used in the same way, also in the third wall. Combining the spectroscopic evidences resulting from the study of pigments, with historical sources, we hypothesize that the decoration of the third wall, which represents Bucephalus's taming, was carried out shortly after 1520 but within the sixteenth century, as evidenced by the use of enamel blue with Bi impurities. Moreover the decoration of the third wall should be accomplished by an artist who surely knew very well Sodoma's painting technique, as evidenced by the same materials used and the same execution technique for painting particular areas. This work demonstrates how investigations on pictorial materials can reveal very useful details like documentary sources, in order to obtain –totally non-invasively- crucial information about some still uncertain artistic productions.

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