Study and micro-Raman characterization of pigments present on majolicas of historical and artistic interest from Gerace, Italy

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Abstract

In this work, pigments of majolicas made between the sixteenth century and eighteenth century from Gerace have been characterized by micro-Raman spectroscopy. Majolica, known also as pottery, was originally used to identify all objects made from clay materials. In this work, ten samples were analyzed: two vases, six majolica fragments made in Gerace, one vase of uncertain origin (probably Gerace or Caltagirone) and one vase of Venetian origin. The Raman spectroscopic analysis allowed to identify most of the pigments present on the studied cultural heritage pottery above described. Pigments white, yellow, orange, red, blue, and green have been characterized and their attribution allowed to divide the artwork made in Gerace with those made wherever.

Keywords Micro-Raman spectroscopy, Pigments, Majolica, Calabria

Graphical Abstract
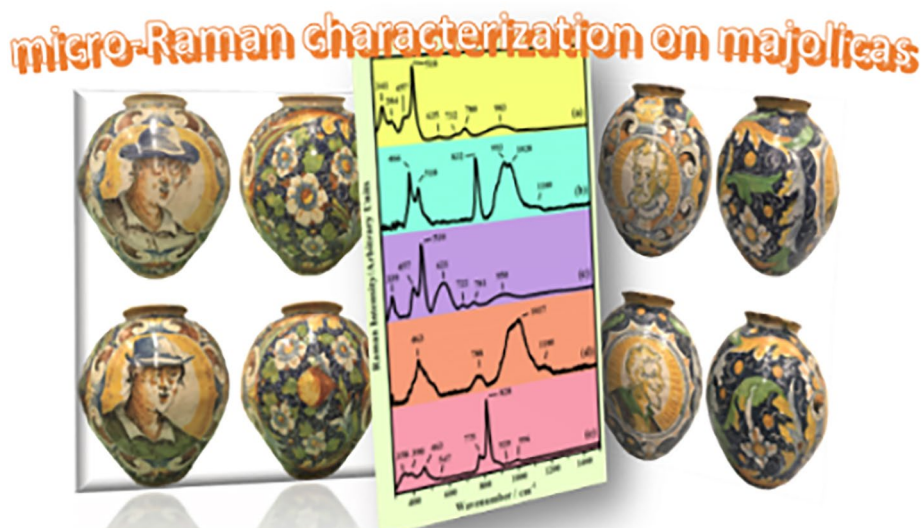
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Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 2 of 15

Introduction

The study of different art-objects is nowadays a best practice of many important research groups over the world [1, 2]. Majolica represent a class of cultural heritage that offer many information on history of the people and their customs and traditions. To perform diagnostic analysis of such art objects will help to identify the best conservation and restoration conditions for themselves. Majolica are, often, knew as pottery [3, 4].

Micro-Raman spectroscopy is a diagnostic techniques extensively used in the field of materials science and nanotechnology [5–8]. Today, micro-Raman spectroscopy is an excellent tool in the characterization of historical finds such as those belonging to the world of Cultural Heritage, both for the total non-invasiveness and non-destructiveness of the measurements [9–16]. In fact, when investigations are carried out, the integrity of the cultural heritage must always be guaranteed, by using different filters with different optical density. A very interesting review on the use of micro-Raman spectroscopy in the field of cultural heritage is reported [17]. The Raman analysis is very specific, high sensitivity, immune from interference, and so on. It gives information concerning the state of conservation of the art object or if it has been subjected to a restoration process or if needs a restoration process and many others information that can improve the knowledge of the cultural heritage.

The heyday of majolica in Italy was the seventeenth century, the century of the *severe style* that was a collective phenomenon [4, 18, 19]. In fact, it is possible to see similarities and affinities in all the productions present in the national territory. Between the sixteenth and seventeenth centuries, there was the transition from the *severe style* to a style that preferred representations of medallions framed by green leaves or various geometries on a blue tint recurring in all the productions [4]. Of all the majolica production centers, particularly flourishing were those of Gerace, Venice and Caltagirone. The undisputed protagonist of the seventeenth century majolica production in Gerace was Jacopo Cefalì, author of one analysed vase. He was born in Lamezia Terme (Italy) and he was both a potter and a painter. In the same century, minor potters' studios and Cefalì's followers were active. The production of 17th-century majolica by Gerace adheres to the Venetian style of the sixteenth century to which Sicily also looked in the eighteenth century. In fact, the floral motifs and the depiction of faces and figures in medallions are Venetian. Chromatically, Gerace's production differs from the Venetian prototypes, unlike the Sicilian production which completely conforms to the Venetian style. The Venetian and Sicilian factories, in fact, are characterized by the use of yellow and blue colours while Cefalì, on the other hand, by the use

of copper green combined with yellow-orange [18, 19]. The main aim of this work is to characterize the different art-objects studied and, if it is possible, to propose some result as tool in order to discriminate the cities where the art-objects have been made.

Experimental

Raman spectroscopy study was performed with a Horiba Jobin–Yvon's Micro—Raman LabRAM instrumentation using a green Nd:YAG laser with emission wavelength of 532 nm and power of 50 mW (at the output of the laser). The instrument is equipped by a notch filter and by a $50 \times$ long working distance objective. The grating used was with 1800 grooves/mm. The spectral resolution was about $1–2$ cm^{-1}. The representative Raman spectra shown in this work fall in the range between 200 and 1300 cm^{-1}. The Raman spectra shown in this work were baseline-corrected. As baseline method has been used the Asymmetric Least Squares Smoothing Baseline (ALS) of the OriginPro 2021b. In Fig. 1 is has been shown just an example of the effect of the baseline correction on the experimental spectra.

As it is possible to see in Fig. 1, the main Raman features are not affected by the baseline correction procedure.

Materials

In this work have been studies 4 vases and six fragments. The first sample is a Majolica Vase made in the second decade of the 1600 s by the Cefalì factory in Gerace denominated MV_1. The second sample is a Majolica Vase made in the mid of the seventeenth century in Gerace denominated MV_2. The third sample is a Majolica Vase of uncertain origin denominated MV_3. The fourth sample is a Majolica Vase datable to the turn of the sixteenth and seventeenth centuries and made in Venice denominated MV_4. The six fragments have been denominated as: FR_1, FR_2, FR_3, FR_4, FR_5 and FR_6.

In Table 1 are summarized the colours of the zones on each samples studied.

Results and discussion

Figure 2 shows different points of view of a Majolica Vase made in the second decade of the 1600 s by the Cefalì factory in Gerace denominated MV_1.

In Fig. 3 are shown the representative Raman spectra acquired on the different pigments present on the sample MV_1 (Fig. 2).

The Raman spectrum of yellow pigment (Fig. 3a) shows signals attributable to the triple oxide PbO·ZnO·Sb$_2$O$_3$ at 341 cm^{-1}, 384 cm^{-1}, 457 cm^{-1}, 510 cm^{-1} and 732 cm^{-1} [20, 21]. The other Raman peaks at 635 cm^{-1} and 780 cm^{-1} are assigned to cassiterite (SnO$_2$) and the

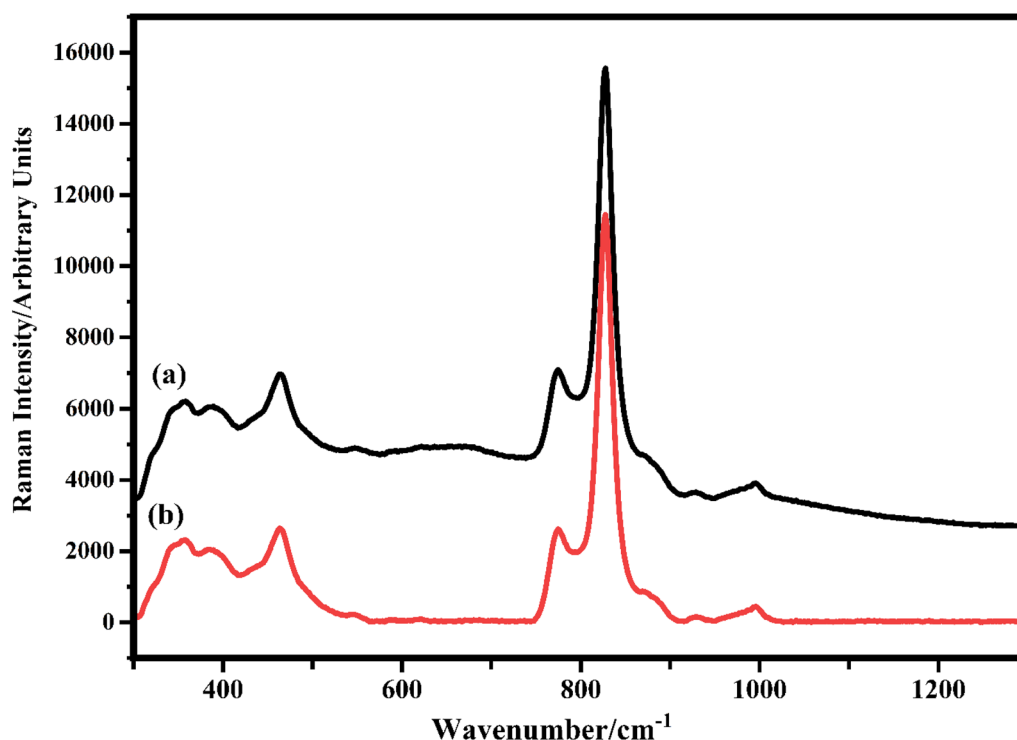Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 3 of 15

Fig. 1 Example of the effect of the baseline correction on the Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the Majolica specimen: **a** experimental Raman spectra (black line) and **b** After baseline correction Raman spectra (red line)

Table 1 Colors of the zones of each specimen studied

Colors	Specimen3s									
	MV_1	MV_2	MV_3	MV_4	FR_1	FR_2	FR_3	FR_4	FR_5	FR_6
Blue	•	•	•	•	•	•	•		•	•
Blue-pale				•				•		
Blue-dark								•		
Brown				•						•
Green	•					•				
Green-pale		•								
Green-dark		•								
Orange	•		•		•					
Red		•								
White	•	•		•	•	•	•	•	•	•
Yellow	•	•	•	•	•					

band at 983 cm^{-1} is ascribed to the lead silicates glass (PbO·SiO$_2$) of the coating used in the production of majolica [22].

The presence of Zn oxide in the triple oxide is supported by the historical document which concerns the use of the additive *tutia allesandrina (ZnO)* to obtain a particular orange-yellow shade [20].

The Raman spectrum of the white pigment, shown in Fig. 3b, shows the following bands: 463 cm^{-1}, 788 cm^{-1}, 1037 cm^{-1} and 1180 cm^{-1}. The peak at 463 cm^{-1} indicates the presence of undissolved quartz (SiO$_4$ bending) while the wide bands at 788 cm^{-1}, 1037 cm^{-1} and 1180 cm^{-1} concern the vitreous coating, consisting of lead silicates glass (PbO·SiO$_2$) [22]. The Raman spectrum

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 4 of 15

Fig. 2 Different point of view of a Majolica Vase made in the second decade of the 1600 s by the Cefalì factory in Gerace. Such sample has been denominated MV_1

Fig. 3 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the Majolica Vase (labelled MV_1) shown in Fig. 2, in the areas coloured by the pigments: yellow **a**, white **b**, blue **c**, green **d** and orange **e**. The Raman spectra shown in this picture were baseline-corrected

of the blue pigment is shown in Fig. 3c. In this spectrum, the peak at 463 cm^{-1} is typical of quartz, the other bands visible at 339 cm^{-1}, 358 cm^{-1}, 390 cm^{-1}, 547 cm^{-1}, 929 cm^{-1} and 996 cm^{-1} are assigned to other polysilicates, such as willemite (Zn$_2$SiO$_4$), and finally, the mode at 775 cm^{-1} is associated to the presence of glassy silicates [22–24]. The last strong band at 828 cm^{-1}, in our knowledge, can be interpreted in two different ways. The first interpretation way assigns the mode at 828 cm^{-1} to the presence of Co-olivine, Co$_2$SiO$_4$ [23] while, the second interpretation way is based on the consideration that the signature of the olivine phase is a doublet and not an isolated peak [25]. For this reason, the peak around 830 cm^{-1} (Fig. 3d) can be ascribed to an arsenate of calcium-potassium lead, apatite type when the shoulder at 780 cm^{-1} is well formed and this is characteristic of the use of smalt as cobalt source [26, 30]. However, both the interpretation ways ascribed to the presence of Cobalt ions the blue pigment observed on the specimen.

The Raman spectrum of green pigment (Fig. 3d) appears as a superposition of that bands obtained from
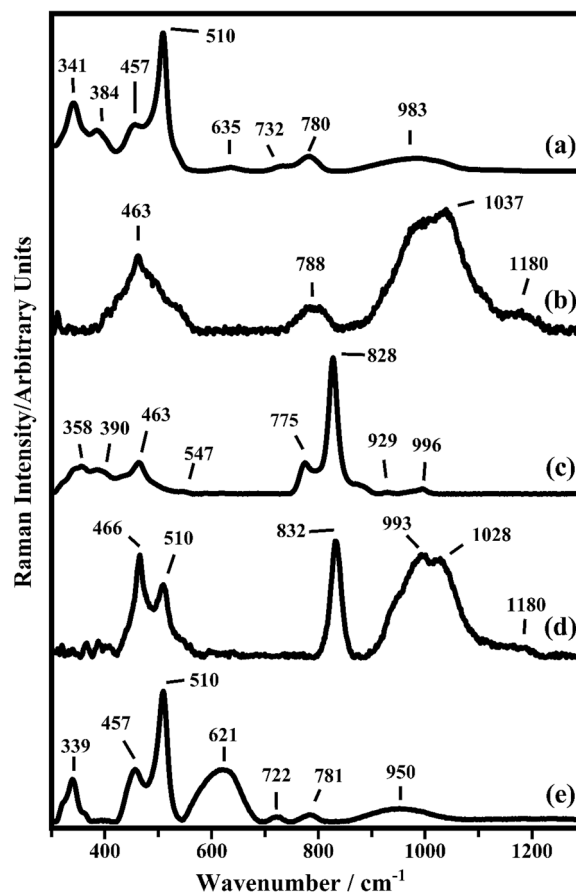
the white pigment, the blue pigment and the yellow pigment. In fact, it is possible to distinguish the peak at 832 cm^{-1} [23, 24], that of quartz at 466 cm^{-1}, that of lead antimoniate [Pb$_3$(SbO$_4$)$_3$] at 510 cm^{-1} and those at 993 cm^{-1}, 1028 cm^{-1} and 1180 cm^{-1} which are attributed to lead silicates glass (PbO·SiO$_2$) [22]. Carratoni et al. [23], states that "*Cobalt is the most common colouring agent used for blue decorations, but generally it dissolves in the glassy phase, giving significant coloration even in low concentrations, but remaining not detectable by Raman analysis. The presence of Co-olivine can be ascribed to a super saturation phenomena, leading to the precipitation of crystalline species...*" confirming that the spectrum 3.d. is a superposition of different contributions. However, as state above, another interpretation of the spectrum of Fig. 3d can be done and the peak at about 832 cm^{-1} (Fig. 3d) can be ascribed to an arsenate of calcium-potassium lead, apatite type

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 5 of 15

when the shoulder at 780 cm^{-1} is well formed, which is characteristic of the use of smalt as cobalt source [26–30].

The Raman spectrum of Fig. 3e, relative to the orange pigment, shows the following peaks: 339 cm^{-1}, 457 cm^{-1}, 510 cm^{-1}, 621 cm^{-1}, 722 cm^{-1}, 781 cm^{-1} and 950 cm^{-1}. The peaks at 339 cm^{-1}, 457 cm^{-1}, 510 cm^{-1} and 722 cm^{-1} were assigned to the triple oxide $PbO \cdot ZnO \cdot Sb_2O_3$ [20, 21]. The two bands, at 621 cm^{-1} and 781 cm^{-1} are assigned to the presence of cassiterite while the band at 950 cm^{-1} is ascribed to the presence of lead silicates glass ($PbO \cdot SiO_2$) [22].

Figure 4 shows the Majolica vase made in the mid of the seventeenth century in Gerace and denominated MV_2. The representative Raman spectra collected on the different pigments present on the vase MV_2 (see Fig. 4 for the colors) are shown in Fig. 5.

The spectrum drawn in Fig. 5a is representative of the white pigment of the MV_2 vase. The Raman spectrum shows only two significant bands at 548 cm^{-1} and 1098 cm^{-1} that are ascribed, as stated above, to the lead silicates glass ($PbO \cdot SiO_2$) [22]. The Raman spectrum of the red pigment is shown in Fig. 5b with peaks at:

Fig. 4 Different point of view of a Majolica Vase made in the mid of the seventeenth century in Gerace. Such artwork has been denominated MV_2

548 cm^{-1} and 1106 cm^{-1}. Both peaks can be assigned to lead silicates glass ($PbO \cdot SiO_2$) [22].

Nevertheless, a typical red pigment is represented by a mixed of lead oxides, $PbO_2 \cdot 2PbO$ whose expected main Raman bands are situated in the region around 330 cm^{-1} and 540 cm^{-1} [31–33]. However, here, it is not possible to discriminate between the Raman signals of such red pigment and those due to the lead silicates glass ($PbO \cdot SiO_2$). The Raman spectrum of yellow pigment, Fig. 5c, like that of the previous vase, shows peaks that fall at 347 cm^{-1}, 386 cm^{-1} and 512 cm^{-1}, which can be ascribed to the presence of the triple oxide $PbO \cdot ZnO \cdot Sb_2O_3$ [20] [21]. The two remaining bands, at 787 cm^{-1} and 1113 cm^{-1}, are due to lead silicates glass ($PbO \cdot SiO_2$) [22]. The Raman spectrum shown in Fig. 5d was collected on the blue pigment. Three Raman bands are detected: at 548 cm^{-1}, 826 cm^{-1} and 1098 cm^{-1}. The peak at 826 cm^{-1} is due to Cobalt-olivine Co_2SiO_4 [13] or to arsenate of calcium-potassium lead (see comments to Fig 3c, d), while the other two Raman bands at 548 cm^{-1} and 1098 cm^{-1} are due to lead silicates glass ($PbO \cdot SiO_2$) [22]. The Raman spectra of the green pigment of MV_2 vase were collected on area with different shades: pale green and dark green, drawn in Fig. 5e and f, respectively.

The Raman spectrum collected on the pale green shows two main bands at 505 cm^{-1} and at 1101 cm^{-1}. The first band, 505 cm^{-1}, is ascribed to the triple oxide $PbO \cdot ZnO \cdot Sb_2O_3$ [21] while the latter, at 1101 cm^{-1}, to lead silicates glass ($PbO \cdot SiO_2$) [22]. The bands of the spectra collected on the dark green area, Fig. 5f, are broad and fall at 563 cm^{-1}, 939 cm^{-1} and 1107 cm^{-1}. The first mode, 563 cm^{-1}, can be ascribed to the presence of chromium oxide (Cr_2O_3), a typical compound used to create green pigments [32, 33], while the other two modes at 939 cm^{-1} and 1107 cm^{-1} are ascribed to the glass coating lead silicates glass ($PbO \cdot SiO_2$) [22]. Another possible interpretation indicates that the bands around 450–550 cm^{-1} and 950–1100 cm^{-1} are ascribed to the ending and stretching modes of the glass SiO_4 tetrahedra [34] which, in fact, makes explicit, in terms of the modes of the SiO_4 unit, what was stated above.

In the same spectrum of Fig. 5f, it is possible to see the modes at 637 cm^{-1} and 780 cm^{-1} which indicate the presence of traces of cassiterite (SnO_2) [21, 30].

Figure 6 shows the Majolica vase denominated MV_3, the origin of which is not sure because it can be made or in Gerace or in Caltagirone. The representative Raman spectra collected on the different pigments present on the vase MV_3 (see Fig. 6 for the colors) are shown in Fig. 7.

On this vase three different pigments were analysed: yellow, orange and blue. The Raman spectrum of the yellow pigment, Fig. 7a, shows peaks at 337 cm^{-1}, 379 cm^{-1}, 449 cm^{-1}, 503 cm^{-1}, and 716 cm^{-1}, attributed to the

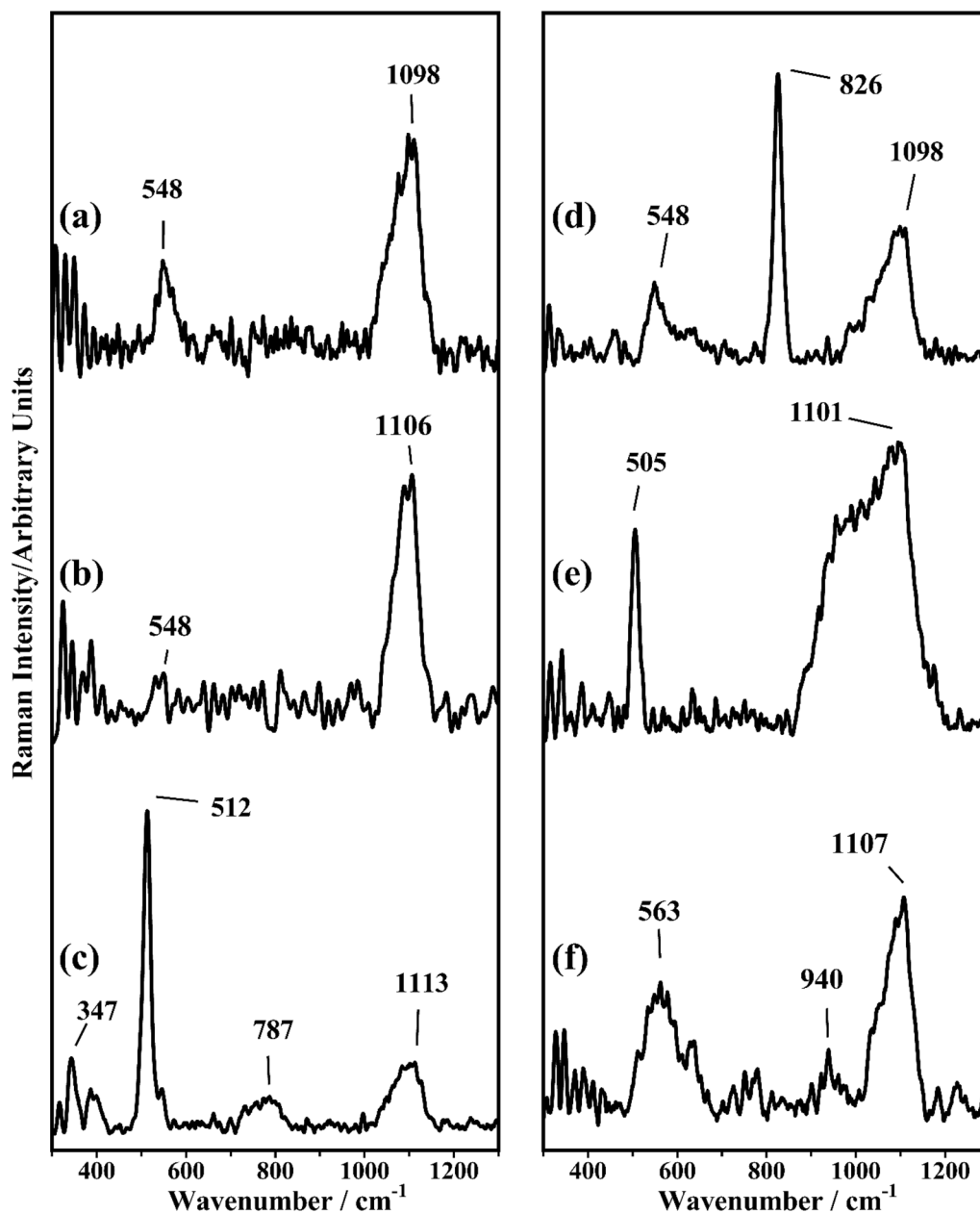Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 6 of 15

Fig. 5 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the Majolica Vase (labelled MV_2) shown in Fig. 4, in the areas coloured by the pigments: white **a**, red **b**, yellow **c**, blue **d**, pale green **e** and dark green **f**. The Raman spectra shown in this picture were baseline-corrected

triple oxide PbO·ZnO·Sb$_2$O$_3$ [21]. The weak mode at 640 cm^{-1} together with the mode at 777 cm^{-1}, indicates the presence of cassiterite (SnO$_2$) [22, 30] and the broad band at 1093 cm^{-1} is due to the coating, lead silicates glass (PbO·SiO$_2$) [22].

The Raman spectrum collected in correspondence with the orange pigment drawn in Fig. 7.b shows

the following bands: 339 cm^{-1}, 449 cm^{-1}, 509 cm^{-1}, 640 cm^{-1}, 731 cm^{-1} and 1108 cm^{-1}.

As expected, the signals at 339 cm^{-1}, 449 cm^{-1}, 509 cm^{-1} and 731 cm^{-1} are similar to those present in the yellow pigment described above and, therefore, those peaks can be attributed to the presence of ternary oxide PbO·ZnO·Sb$_2$O$_3$ [21].

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 7 of 15

Fig. 6 Different point of view of a Majolica Vase of uncertain origin. Such artwork has been denominated MV_3
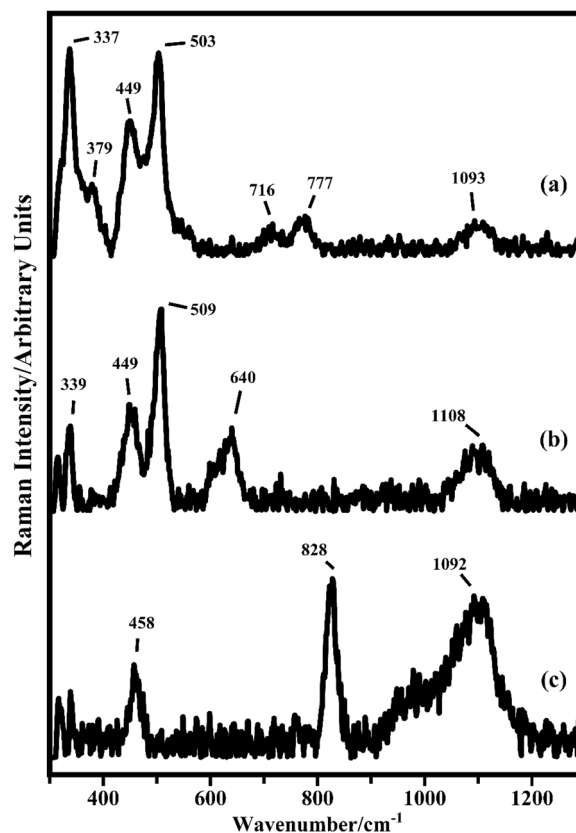

Fig. 7 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the Majolica Vase (labelled MV_3) shown in Fig. 6, in the areas coloured by the pigments: yellow **a**, orange **b** and blue **c**. The Raman spectra shown in this picture were baseline-corrected

The presence of the peak at 640 cm^{-1} is ascribed to magnetite, Fe_3O_4 ($FeO + Fe_2O_3$) [31], responsible of the difference in the colour hue which is obtained by mix magnetite and yellow pigments. Anyway, to the Fe_2O_3 has been ascribed the responsibility of the red colour to add to the yellow colour to obtain the orange pigment [15]. The Raman band at 1108 cm^{-1} is due to the coating, lead silicates glass ($PbO \cdot SiO_2$) [22]. The representative Raman spectrum of Fig. 7c collected on blue areas, shows a band that falls at 828 cm^{-1}, which is typical of cobalt olivine Co_2SiO_4 [23], or to arsenate of calcium-potassium lead (see comments to Fig. 3c, d), another band at 458 cm^{-1}, ascribed to the presence of quartz (SiO_2) and one last band at 1092 cm^{-1} which, as stated above, is assigned to the presence of lead silicate lead silicates glass ($PbO \cdot SiO_2$) [22].

Figure 8 shows the last Majolica vase, denominated MV_4, datable to the turn of the sixteenth and seventeenth centuries and made in Venice.

In Fig. 9 are shown the representative Raman spectra collected on the different pigments present on the vase MV_4 (Fig. 8).

In Fig. 9a, the Raman spectrum collected on the white pigment shows the following Raman features: 635 cm^{-1}, 777 cm^{-1} and 1109 cm^{-1}. The peaks at 635 cm^{-1} and 777 cm^{-1} were ascribed to cassiterite (SnO_2) and the peak at 1109 cm^{-1} to lead silicates

glass ($PbO \cdot SiO_2$) [22, 30]. The spectrum collected on the yellow pigment, Fig. 9.b, shows peaks at 346 cm^{-1}, 397 cm^{-1} and 513 cm^{-1}, that are assigned to pigment Pb– Sn – Sb triple oxide micro-crystals dispersed in a silica matrix [20, 21, 23]. The Raman spectrum acquired on blue pigment, Fig. 9c, shows the following Raman bands: 552 cm^{-1}, 830 cm^{-1} and 1091 cm^{-1}. These Raman bands are assigned as follows: the peak at 830 cm^{-1} is due to Cobalt -olivine Co_2SiO_4 [22] or to arsenate of calcium-potassium lead (see comments to Fig 3c and d),while the other two peaks at 552 cm^{-1} and 1091 cm^{-1} are due to lead silicates glass ($PbO \cdot SiO_2$) [20]. In Fig. 9.d it is shown the Raman spectrum acquired on the pale blue pigment. The Raman bands fall at 824 cm^{-1}, assigned to the Co_2SiO_4, at 547 cm^{-1} assigned to lead silicates glass ($PbO \cdot SiO_2$) [20, 22] and at 1086 cm^{-1}, due to the presence of calcium carbonate $CaCO_3$ [32, 33], a typical white pigment, probably used to dilute the intense blue colour of cobalt silicates. The Raman spectrum collected on the brown pigment, Fig. 9e, shows features such as 326 cm^{-1}, 389 cm^{-1},

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 8 of 15

Fig. 8 Different point of view of a Majolica Vase datable to the turn of the sixteenth and seventeenth centuries and made in Venice. Such artwork has been denominated MV_4
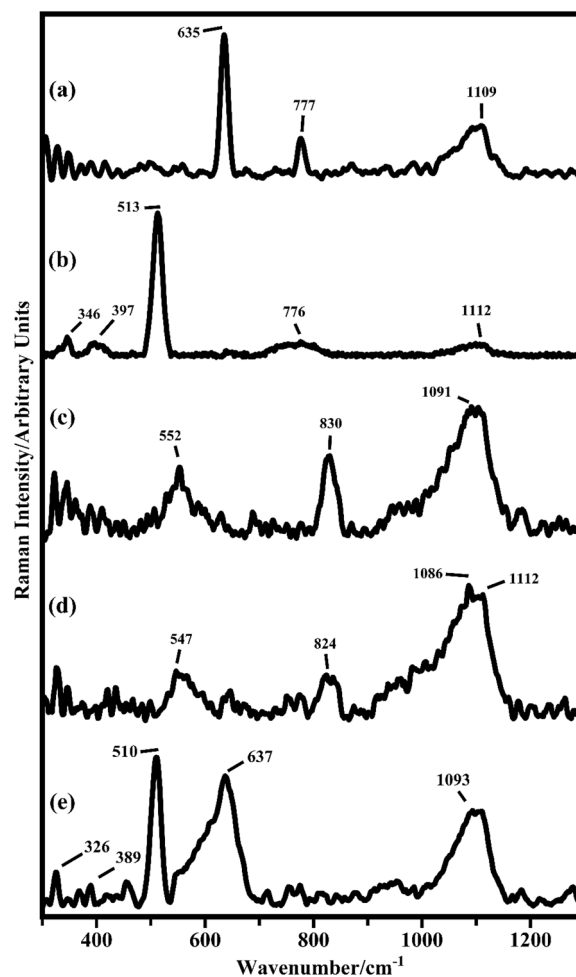

Fig. 9 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the Majolica Vase (labelled MV_4) shown in Fig. 8, in the areas coloured by the pigments: white **a**, yellow **b**, blue **c**, pale blue **d** and brown **e**. The Raman spectra shown in this picture were baseline-corrected

458 cm^{-1} and 510 cm^{-1} assigned to the yellow lead antimoniate [Pb$_3$(SbO$_4$)$_2$] and the band at 637 cm^{-1} which is due to the presence of magnetite [Fe$_3$O$_4$ ie: FeO$\cdot$ + Fe$_2$O$_3$] [31].

In Fig. 10 are shown six fragments found in 2012 in Gerace during an excavation.

The pigments present on the FR_1 fragment (see Fig. 10a) were subjected to Raman investigations which made possible to characterize the white, blue, yellow and orange pigments and the relative representative spectra are shown in Fig. 11.

The Raman spectrum collected on the white enamel of the FR_1 specimen is shown in Fig. 11a. In this spectrum a very intense Raman peak fall at 464 cm^{-1}, indicating the presence of quartz (SiO$_2$) [20]. The Raman Spectrum acquired on the blue pigment is shown in Fig. 11b. In this spectrum it is possible to observe the bands of cobalt olivine, Co$_2$SiO$_4$, of the fayalite type at 819 cm^{-1} and 840 cm^{-1} [23, 35, 36] the wide bands at 484 cm^{-1} and 984 cm^{-1} ascribed to the presence quartz and the band at 1088 cm^{-1} assigned to lead silicates glass (PbO$\cdot$SiO$_2$) [22].

The Raman spectrum collected on the yellow pigment is shown in Fig. 11c.

Such spectrum shows similar Raman features the band at 505 cm^{-1} typical of lead antimoniate (Naples Yellow [Pb$_3$(SbO$_4$)$_2$], the bands at 386 cm^{-1} and 459 cm^{-1} which also indicate the presence of the ternary oxide PbO$\cdot$ZnO$\cdot$Sb$_2$O$_3$ [20, 21, 23] and the bands at 785 cm^{-1} and 965 cm^{-1} due of those seen in the spectrum of the yellow pigment (Fig. 11c).

The last representative Raman spectrum collected on the specimen FR_1, concerns the orange pigment and it is shown in Fig. 11d. In particular, it is possible to notice the strong band at 506 cm^{-} of the lead antimoniate [Pb$_3$(SbO$_4$)$_2$] while the others small bands at 384 cm^{-1} and 456 cm^{-1} (shoulder) are ascribed, as stated above, to the presence of the ternary oxide: PbO$\cdot$ZnO$\cdot$Sb$_2$O$_3$ [23, 35, 36]. The small peak at 728 cm^{-1} confirms the presence in the pigment of zinc oxide.

Raman characterization of the pigments present on the specimen FR_2, shown in Fig. 10b, has been performed and the relative representative Raman spectra

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 9 of 15

Fig. 10 Six fragments found in 2012 in Gerace during an excavation. The fragments have been denominated: FR_1 **a**, FR_2 **b**, FR_3 **c**, FR_4 **d**, FR_5 **e** and FR_6 **f**

Fig. 11 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_1, shown in Fig. 10, on the following pigments: white **a**, blue **b**, yellow **c** and orange **d**. The Raman spectra shown in this picture were baseline-corrected

are drawn in Fig. 12. In particular, the studied pigments, of the specimen FR_2, have been white, blue and green.

The Raman spectrum relative to the white pigment is shown in Fig. 12a. It presents two peaks at 464 cm^{-1} and at 998 cm^{-1} that are typical of quartz (SiO$_2$), the former, and ascribed to lead silicates glass (PbO·SiO$_2$), the latter [22]. The Raman spectrum of the blue pigment is shown in Fig. 12b. It shows the Raman band that falls at 822 cm^{-1}, which is assigned to the cobalt olivine Co$_2$SiO$_4$ [23], or to arsenate of calcium-potassium lead (see comments to figg 3.c and 3.d), the peak at 507 cm^{-1} that, as above, is ascribed to the lead antimoniate [Pb$_3$(SbO$_4$)$_2$] [20] and the bands at 475 cm^{-1}, 1013 cm^{-1} and 1098 cm^{-1} that are due to lead silicates glass (PbO·SiO$_2$) [22].

The representative Raman spectrum of the green pigment of the specimen FR_2 is shown in Fig. 12.c. In this spectrum, it can be seen two broad bands that fall at 787 cm^{-1} and at 998 cm^{-1} that can be ascribed to the presence of cassiterite and lead silicates glass (PbO·SiO$_2$) [22]. The green colour may be due to some pigment called green earths, that unfortunately, show peaks that, perhaps, have been covered by the others signals and, therefore, have not been detected.

The representative spectra of the white and blue pigments present on the FR_3 sample (see Fig. 10c) are shown in Fig. 13a, b respectively.
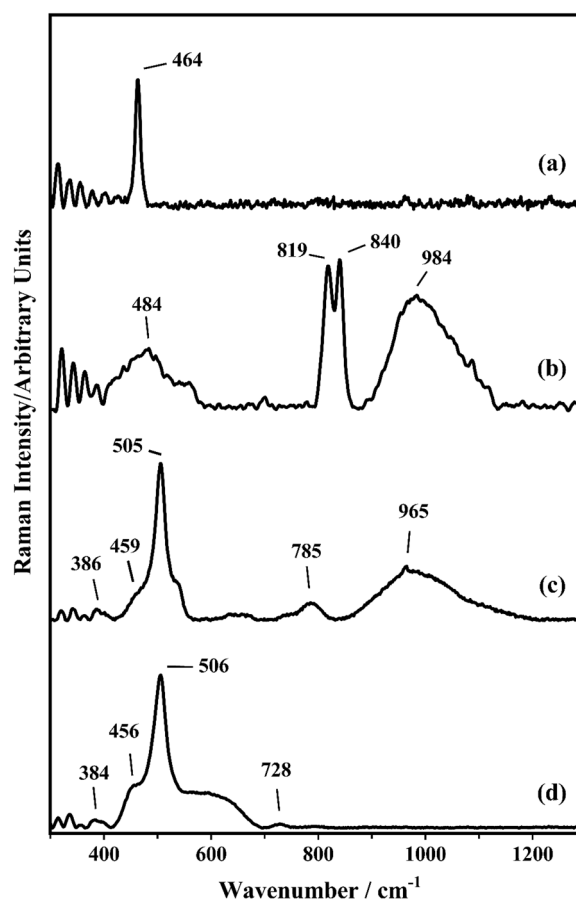
The Raman spectrum of Fig. 13a shows the following Raman bands: 631 cm^{-1}, 774 cm^{-1} and 978 cm^{-1}. The first two bands at 633 cm^{-1} and 774 cm^{-1} are ascribed to the cassiterite (SnO$_2$) while the other peak, at 978 cm^{-1}, is ascribed to lead silicates glass (PbO·SiO$_2$) [22, 30].

The spectrum of Fig. 13.b shows bands very similar to those shown above in the spectrum of Fig. 9.a: 631 cm^{-1}, 779 cm^{-1} and 965 cm^{-1}.

The first two bands, at 631 cm^{-1} and 779 cm^{-1} are assigned to the presence of cassiterite while the band at 965 cm^{-1}, as said above, is ascribed to the presence of lead silicates glass (PbO·SiO$_2$) [22, 30]. The additional band at 480 cm^{-1}, no present in the spectrum of Fig. 9.a, is ascribed to the presence of the cobalt (II) blue silicate pigment, CoO·nSiO$_2$ [33].

In Fig. 10.d the specimen FR_4 can be seen and the relative Raman analysis, relative to the pigments white, dark blue and pale blue, has been shown in Fig. 14.
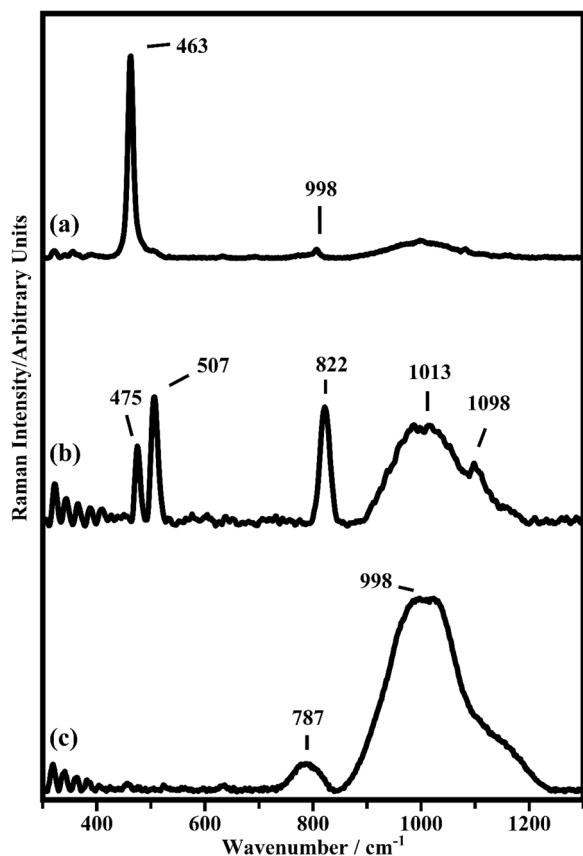
Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 10 of 15

Fig. 12 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_2, shown in Fig. 10b, on the following pigments: white **a**, blue **b**, and green **c**. The Raman spectra shown in this picture were baseline-corrected
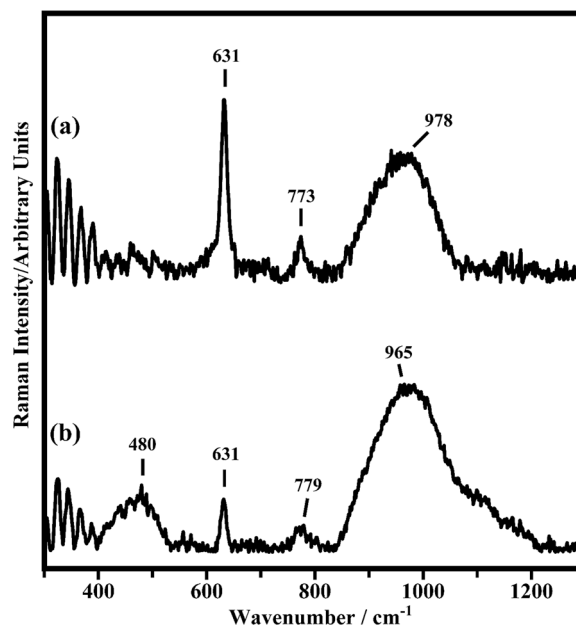

Fig. 13 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_3, shown in Fig. 10c, on the following pigments: white **a** and blue **b**. The Raman spectra shown in this picture were baseline-corrected

The spectrum acquired in correspondence with the white enamel (Fig. 14a) shows the presence of quartz (SiO$_2$), attested by the characteristic peak at 465 cm^{-1}. The Raman spectrum of Fig. 14b collected on the dark blue area shows two peaks that fall at 466 cm^{-1} and 691 cm^{-1} that are assigned to the presence of cobalt tetroxide Co$_3$O$_4$ (2CoO·CoO$_2$) [37]. The cobalt tetroxide is a powder that decomposes into cobalt monoxide when subjected to high temperature annealing (around 800 °C). In the Raman spectrum of Fig. 14b, the other band, at 963 cm^{-1}, is ascribed to lead silicates glass (PbO·SiO$_2$) [22]. As it can be seen in Fig. 14c, the Raman features of the spectrum collected on the pale blue area are similar to those seen in the spectrum of Fig. 14b. Also in this case, to the cobalt tetroxide Co$_3$O$_4$ (2CoO·CoO$_2$) are due the bands that fall at 467 cm^{-1} and 689 cm^{-1} [37], whereas the others two bands at 960 cm^{-1} and

1109 cm^{-1} indicate the presence of lead glass, which is SiO$_2$ + PbO.

The representative Raman spectra collected on the specimen FR_5 of Fig. 10e are shown in Fig. 15. The Raman spectrum of Fig. 15a shows the typical mode at 458 cm^{-1} due to the quartz (SiO$_2$).

The spectrum displayed in Fig. 15b collected on the area green/blue shows two bands similar to those seen previously in the case of the spectrum of Fig. 12c. In this case, the bands at 779 cm^{-1} and 984 cm^{-1} are assigned to the lead silicates lead silicates glass (PbO·SiO$_2$) [22, 33]. The green colour, as state above, can be due to some pigments called green earths, that unfortunately, have not been detected [22, 33].

Last specimen, shown in Fig. 10f and denominated FR_6, has been characterized and the relative Raman spectra are shown in Fig. 16, where are displayed the representative Raman spectra collected on the areas white, blue and green. As seen in almost all the samples studied, the white area shows a Raman spectrum, Fig. 16a, with the typical mode at 463 cm^{-1} which is ascribed to the presence of quartz (SiO$_2$) [22]. The Raman spectrum collected on the blue pigment area is shown in Fig. 16b and it shows the modes at 823 cm^{-1}, 962 cm^{-1} and 990 cm^{-1}. The peak at 823 cm^{-1} is due

Fig. 14 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_4, shown in Fig. 10d, on the following pigments: white **a**, dark blue **b** and pale blue **c**. The Raman spectra shown in this picture were baseline-corrected
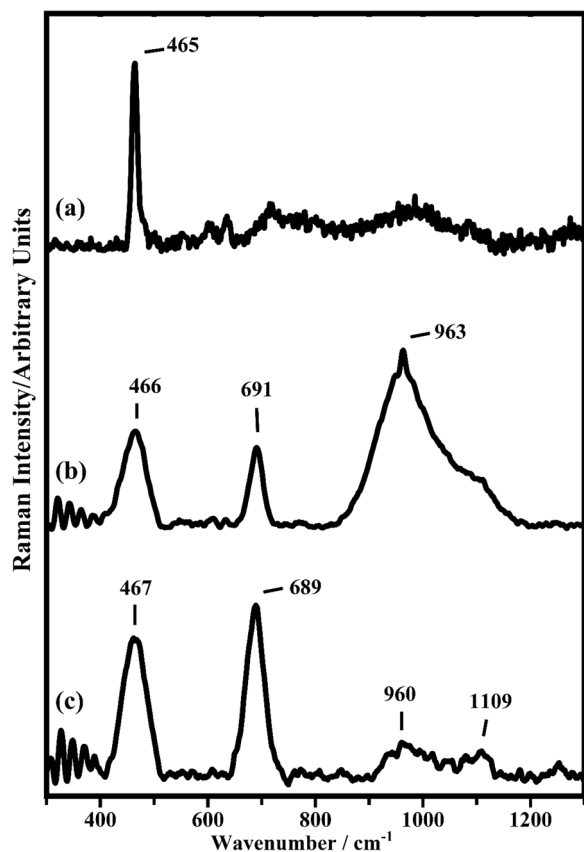

Fig. 15 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_5, shown in Fig. 10e, on the following pigments: white **a** and blue/green **b**. The Raman spectra shown in this picture were baseline-corrected

Conclusions

Micro Raman spectroscopy has been used to characterize the pigment present on four vases and six fragments of majolica: two vases were from Gerace (MV_1 and MV_2) one was of uncertain origin between Gerace and Caltagirone (MV_3), made between the fifteenth century and the eighteenth century, and one from Venice (MV_4); the six specimens were found in Gerace (Fig. 10).

All the results of such studies are summarized in Tables 2 and 3.

As usual in the productions of the time, similarities were found in the pigments used on the samples analysed.

As can be seen from Tables 2 and 3, the white pigment is due, for all the samples, mainly to lead silicate lead silicates glass (PbO·SiO$_2$) and to quartz, SiO$_2$, which are materials that are also found in the other pigments, probably due to the coating of the specimens.

The blue pigment widely used in the majolica specimen studied is cobalt olivine Co$_2$SiO$_4$ or to arsenate of calcium-potassium lead (see comments to Fig. 3c, d), Moreover, it is quite interesting the identification of two additional blue pigments found in the FR_3 and FR_4 fragments: cobalt silicate (II), CoO·nSiO$_2$ in the FR_3

to cobalt olivine, Co$_2$SiO$_4$, [23] or, to arsenate of calcium-potassium lead (see comments to figg 3.c and 3.d), and the other two modes, that fall at 962 cm^{-1} and 990 cm^{-1} are ascribed to lead silicates glass (PbO·SiO$_2$) [22].

Figure 16c shows the Raman spectrum collected on the specimen FR_6 (see Fig. 10f) on the green pigment area. The Raman modes present in this spectrum fall at 633 cm^{-1}, 786 cm^{-1} and 984 cm^{-1}. The mode at 633 cm^{-1} is due to the presence of cassiterite SnO$_2$ [30].

In this case, the bands fall at 786 cm^{-1} and 984 cm^{-1} are assigned to the lead silicates lead silicates glass (PbO·SiO$_2$) [22, 33]. The green colour the Cu^{2+} ions present in the silicates but not detected, that unfortunately, have not been detected because are covered by the signal that fall at 786 cm^{-1} and 984 cm^{-1}.
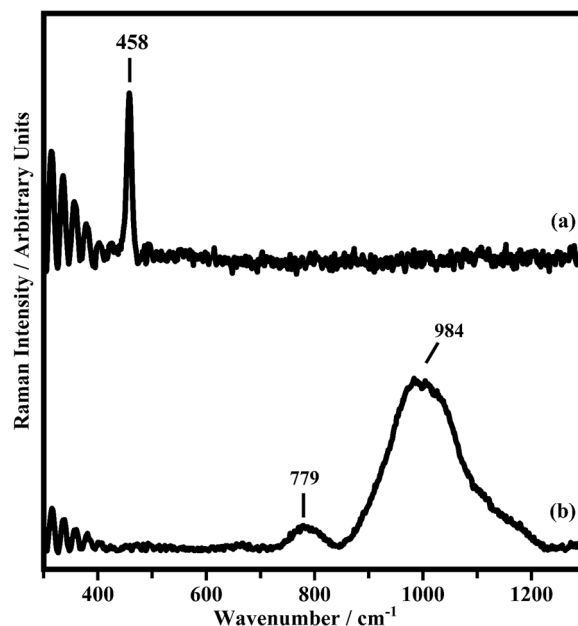
Barba Castagnaro *et al. Heritage Science*   (2023) 11:24
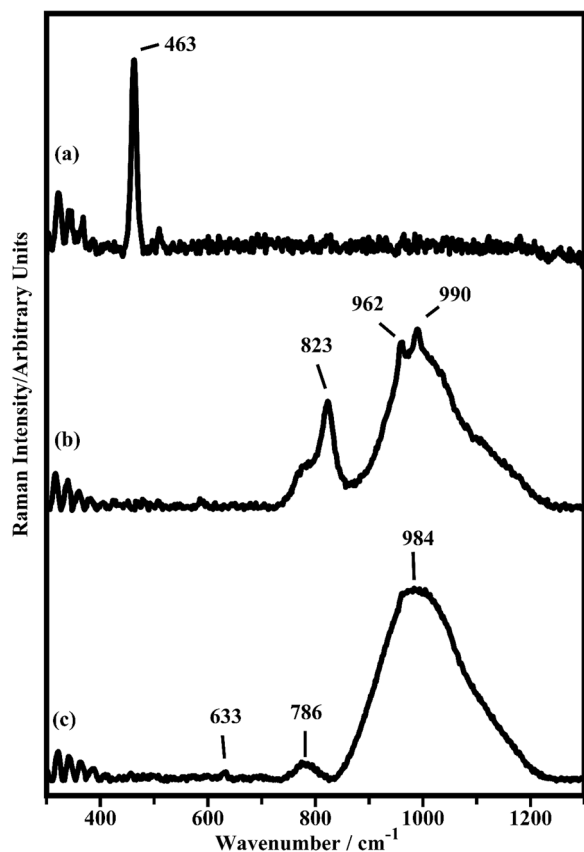
Page 12 of 15

Fig. 16 Representative Raman spectra, in the range between 300 and 1300 cm^{-1}, collected on the specimen denominated FR_6, shown in Fig. 10f, on the following pigments: white **a**, blue **b** and green **b**. The Raman spectra shown in this picture were baseline-corrected

fragment and cobalt tetroxide Co_3O_4 ($2CoO \cdot CoO_2$) in the FR_4 fragment.

The yellow pigment, widespread among the samples studied, was mainly ascribed to Naples yellow or lead antimoniate [$Pb_3(SbO_4)_2$]. Quite often this chemical specie was mixed with zinc oxide and when this addition was relevant, the resulting chemical specie associated to the yellow pigment is indicated as ternary oxide $PbO \cdot ZnO \cdot Sb_2O_3$, also present in orange and brown pigments.

In the brown colour of the MV_3 vase, the pigment identified has been the magnetite [Fe_3O_4 i.e.: $FeO \cdot + Fe_2O_3$]. The green pigments found have different chemical composition. In particular, the MV_1 vase presents the Raman modes typical of Naples yellow and cobalt olivine which suggest that this green pigment was created from the mixture of yellow and blue colours. Indeed, in the other specimens, FR_2, FR_5 and FR_6, the green colour, as state above, can be due to some pigments called green earths, that unfortunately, have not been detected because are covered by the signal of lead silicates. In the MV_2 vase traces of chromium oxide (Cr_2O_3) have been found. Lead silicates glass ($PbO \cdot SiO_2$) has been ascribed to green earths and in the MV_2 vase traces of chromium oxide (Cr_2O_3) have been found.

The red pigment, present only in the MV_2 vase, has been associated to the presence of a mixture of lead oxides $PbO_2 \cdot 2PbO$.

In conclusion, such investigation has allowed the identification of many pigments present on the majolica samples studied which can be very useful for restoration and conservation procedures of such art-objects. Moreover, by looking at the Table 3, it is possible to see that the magnetite it is not present in the art-objects made surely in Gerace while it is present in the others two samples (MV_3 and MV_4) and it could be used as a marker in order to discriminate the cities where the art-objects have been made.

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 13 of 15

Table 2 Pigment associated to the chemical species and to the specimen, vase or fragment, studied

Colour pigment	Chemical species	VASE/MV_				FRAGMENTS/FR_					
		1	2	3	4	1	2	3	4	5	6
White	Quartz (SiO_2)	x				x	x		x	x	x
	lead silicates glass ($PbO·SiO_2$)	x	x		x		x	x			
	Cassiterite (SnO_2)				x			x			
Blue	Willemite (Zn_2SiO_4)	x									
	Quartz (SiO_2)	x		x							
	Cassiterite SnO_2							x			
	Cobalt -olivine a Co_2SiO_4	x	x	x	x	x	x				x
	lead silicates glass ($PbO·SiO_2$)		x	x	x	x	x	x	x		x
	Lead antimoniate $Pb_3(SbO_4)_2$						x				
	Cobalt silicate (II), $CoO·nSiO_2$							x			
	Cobalt tetroxide Co_3O_4 ($2CoO·CoO_2$)								x		
Pale Blue	lead silicates glass ($PbO·SiO_2$)				x						
	Cobalt -olivine Co_2SiO_4				x						
	Calcium carbonate $CaCO_3$				x						
Yellow	Triple oxide $PbO·ZnO·Sb_2O_3$	x		x	x	x					
	Cassiterite SnO_2	x		x							
	lead silicates glass ($PbO·SiO_2$)	x	x	x	x	x					
	Naples Yellow-Lead antimoniate + traces of zinc oxide $Pb_3(SbO_4)_2·ZnO$		x		x						
	Lead antimoniate $Pb_3(SbO_4)_2$					x					
Green	Triple oxide $PbO·ZnO·Sb_2O_3$	x	x								
	Cobalt -olivine Co_2SiO_4	x									
	lead silicates glass ($PbO·SiO_2$)	x	x				x				x
Dark Green	Chromium oxide Cr_2O_3		x								
	Cassiterite SnO_2		x								x
	lead silicates glass ($PbO·SiO_2$)		x								
Orange	Triple oxide $PbO·ZnO·Sb_2O_3$	x		x		x					
	Cassiterite SnO_2	x									
	Magnetite, [Fe_3O_4 namely: $FeO + Fe_2O_3$]			x							
	lead silicates glass ($PbO·SiO_2$)	x		x							
	Lead antimoniate $Pb_3(SbO_4)_2$					x					
Red	Lead oxide mix $PbO_2·2PbO$ (traces)		x								
	lead silicates glass ($PbO·SiO_2$)		x								
Brown	lead silicates glass ($PbO·SiO_2$)				x						
	Naples Yellow-Lead antimoniate + traces of zinc oxide $Pb_3(SbO_4)_2·ZnO$				x						
	Magnetite, [Fe_3O_4 namely: $FeO· + Fe_2O_3$]				x						

Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 14 of 15

Table 3 Chemical species associated to the pigment and to the specimen, vase or fragment, studied

Chemical species	Colour pigment	VASE/MV_				FRAGMENTS/FR_					
		1	2	3	4	1	2	3	4	5	6
Quartz (SiO_2)	White; Blue	x		x		x	x		x	x	x
lead silicates glass ($PbO \cdot SiO_2$)	All pigments	x	x	x	x	x	x	x	x	x	x
Cassiterite (SnO_2)	White; Blue; Dark Green; Orange	x	x		x			x			x
Willemite (Zn_2SiO_4)	Blue	x									
Cobalt -olivine a Co_2SiO_4	Blue; Pale Blue; Green	x	x	x	x	x	x				x
Lead antimoniate $Pb_3(SbO_4)_2$	Blue; Yellow; Orange					x	x				
Cobalt silicate (II), $CoO \cdot nSiO_2$	Blue							x			
Cobalt tetroxide Co_3O_4 ($2CoO \cdot CoO_2$)	Blue								x		
Calcium carbonate $CaCO_3$	Pale Blue				x						
Triple oxide $PbO \cdot ZnO \cdot Sb_2O_3$	Yellow; Green; Orange	x	x	x	x	x					
Naples Yellow-Lead antimoniate + traces of zinc oxide $Pb_3(SbO_4)_2 \cdot ZnO$	Yellow; Brown		x		x						
Chromium oxide Cr_2O_3	Dark Green		x								
Magnetite, [Fe_3O_4 namely: $FeO \cdot + Fe_2O_3$]	Orange; Brown			x	x						
Lead oxide mix $PbO_2 \cdot 2PbO$ (traces)	Red		x								

Availability of data and materials
The data presented in this study are available on request from the corresponding author.

Declarations

Competing interests
The authors declare no competing interest.

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Barba Castagnaro *et al. Heritage Science*   (2023) 11:24

Page 15 of 15

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