

Micro-Raman investigation of coloured glazes on majolica sherds from the Monk's Palace waste shaft in Capena (Rome)

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ABSTRACT

Medieval and Renaissance waste shafts (*butti*) offer a unique opportunity to study objects of common use in the past, the majority of findings that emerge from the excavation of these pits are pottery found in fragmentary condition, sherds that provide essential information on the historical periods to which the *butto* belongs.

In the present work Micro-Raman analysis was conducted on a representative group of samples dated back from XIV to XVIII century, coming from the waste shaft pertained to the Monk's Palace sited in Leprignano, the current Capena in the province of Rome. The aim of the study was to characterize the composition of coloured glazes pertaining to majolica sherds, through a technique that has proved to be invaluable for this purpose, according to the amount of published data in recent years.

Differences in terms of structure and constituents of the decorative layers have been observed. Yellow pigments can be ascribed to the family of lead pyroantimonates, in both binary and ternary form, brown and green glazes are constituted by ions dissolved in the glass matrix, while in blue glazes cobalt olivines have been clearly identified for some samples. Polymerization index calculated on vitreous layers shows the presence of a lead-based glaze that is commonly found in majolica referable to the same age and provenance.

The results obtained are in a good agreement with Piccolpasso's treatise, "*The Three Books of Potter's Art*", except for a sherd pertaining to a later Ligurian production.

1. INTRODUCTION

The ancient settlement of Leprignano, the current town of Capena, was one of the first domains in the province of Rome under the jurisdiction of Benedictine Abbey of Saint Paul outside the Walls. It was mentioned for the first time as *Castrum Lepronianum* in the papal bull of Gregorius VII in 1074 and belonged to the so-called *Dioecesis Nullius*, together with the nearby villages of Nazzano and Civitella San Paolo [1].

The original nucleus of the ancient village of Leprignano is constituted by the Monks' Palace: placed on a tuff spur, to be naturally protected from enemies, it can be considered an example of the

process of fortification of the area carried out by the monks during the XI-XII centuries [2].

A Medieval and Renaissance waste shaft (*butto*) pertaining to the palace was excavated in the 80's on its west side, revealing a great variety of materials, ranging from pottery to glass and metals, which date back from the XII to the XX century. The excavation of this ancient rubbish dump allowed to shed light on the everyday life of the village and to reinstate importance to the objects found, that were trashed once, but now have gained a new function of document. These finds are currently conserved in the Clock's Tower, the civic museum of Capena, and have never been studied so far.

In the present work fragments of majolica pertaining to the waste materials of the palace were analyzed by means of micro-Raman in order to characterize the composition of the coloured glazes.

Micro-Raman spectroscopy has been already successfully employed in the study of the majolica's glazes [3-5]. The firing process of these materials gives rise to different structures of the coatings, which depends on their composition and that can be revealed by different Raman features, as described by P. Colomban *et alii* [6].

The results of the analysis have been interpreted on the basis of the information reported in the treatise "The Three Books of the Potter's Art", written by Cipriano Piccolpasso in 1548, which provides the recipes for the production of pigments employed in the ceramic art.

2. MATERIALS AND METHODS

2.1 Samples

A selection of 11 fragments of majolica coming from the *butto* of the Monks' Palace have been analyzed (fig. 1). The list of the samples, showed in table 1, provides a brief description of the sherds. They are dated from the XIV to the XVIII century, including mainly fragments of Archaic and Renaissance majolica coming from Latium area and Rome, but also imported materials related to different production centres.

Sample	Dating	Description
C1	XVI century	Fragment of plate, corresponding to the external rim
C2	XVI century	Fragment of plate with the decoration "a monticelli" typical of Rome area
C3	XVIII century	Fragment of majolica probably attributed to a Ligurian production with the typical decoration with "birds and parsley"
C4	XVII - XVIII century	Fragment of majolica basin with a decoration typical of Rome area
C5	XVI-XVII century	Fragment of <i>albarella</i> with <i>berettino</i> glaze
C6	XVI-XVII century	Fragment of plate attributed to the Montelupo production with the typical decoration "a giraffi"
C7	XVI century	Fragment of plate attributed to Montelupo
C8	XIV-XV century	Fragment of Roman archaic majolica with zoomorphic decoration
C9	XV century	Fragment of Archaic majolica with a decoration in green-relief (<i>Ramina in rilievo</i>), typical of Central Italy
C10	XVI-XVII century	Fragment of plate attributed to a Roman imitation of the Montelupo production
C11	XV century	Fragment of early Renaissance majolica

Table 1. Description of the samples.

2.2. Experimental methods

Small fragments of the samples have been embedded in epoxy resin and examined with the aid of a polarizing microscope in thin and cross section, in order to have a more precise visualization of the different coloured layers.

Micro-Raman analysis has been carried out on cross-sections with the aid of a Senterra Raman microscope (Bruker), having a spectral resolution of 3-5 cm^{-1} , equipped with 2 laser sources (785 and 532 nm) and objectives 20 \times and 50 \times . Laser power was set on 10-25 mW, with an integration time ranging between 2 and 10 seconds.

The resulting spectra, not normalized and here shown without baseline subtraction, were elaborated with the aid of Opus software and Fityk 0.9.8 [7] for the fitting operations.

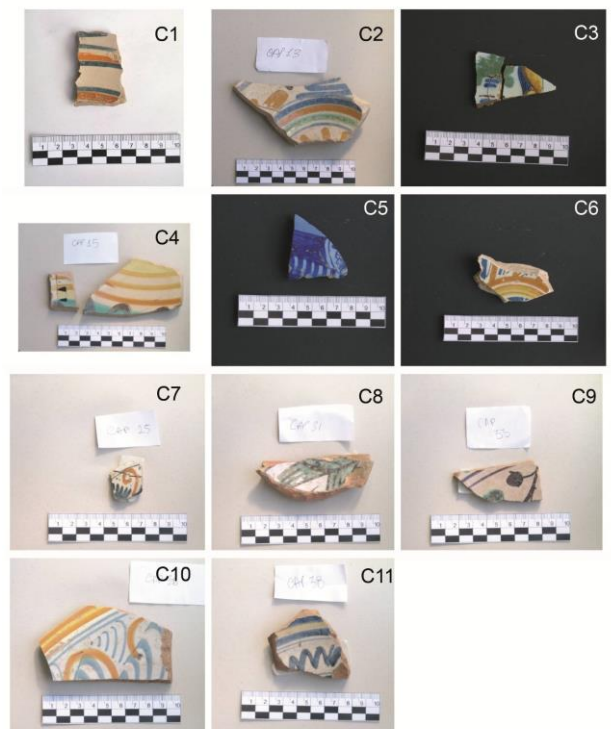


Figure 1: the pottery sherds under analysis.

3. RESULTS AND DISCUSSION

3.1 Microscopic observations

The investigation on cross and thin sections allows to highlight differences in terms of aspect and structure of the glazes.

Our considerations are here limited only to decorative layers. Concerning the pigments, it is possible to distinguish two different situations: in the first case,

i.e. on yellow and orange hues, the coloured layer is sharp and well noticeable on the surface of the glaze thickness, while on green, blue and brown areas, the glaze layer appears as a vitreous matrix homogeneously coloured, as shown in figure 2.

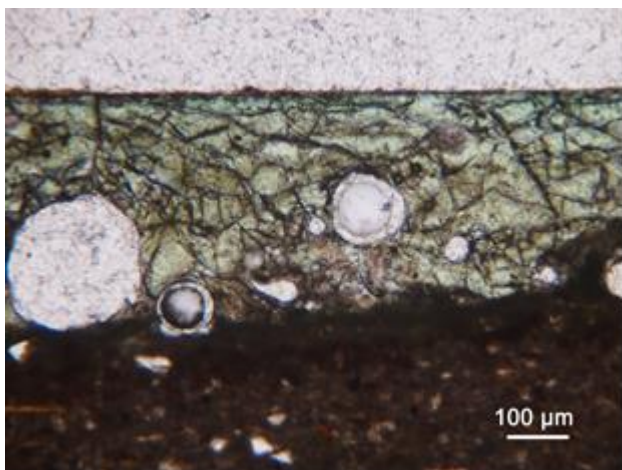
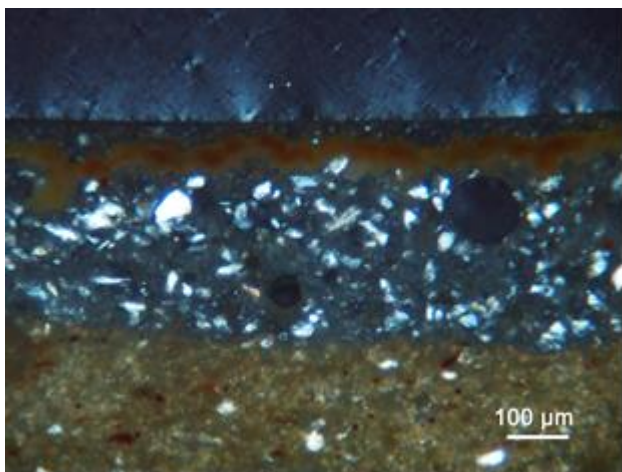


Figure 2: Thin sections of orange decoration on C2 (top) cross polarized light, 100×, and green decoration in C9 (bottom), plane polarized light, 100×, respectively. Sample C2 shows a well definite, coloured layer surmounted by a transparent coperta, angular-shaped quartz grains are dispersed in the glaze matrix, while in sample C9 the glaze is homogeneously coloured.

The glaze layers are well defined and no interaction areas with the body have been observed, allowing to hypothesize a two-step firing process of the objects, where the glaze was applied on the fired biscuit. Furthermore, thin sections in samples C1, C2 and C7 show the presence of a transparent coperta, as reported in table 2 where the thickness of the glazes is also specified.

Finally, sand residues, mainly composed of quartz, have been detected in the glazes. The amount and shape of the grains in samples C1, C2 and C4 could

suggest an intentional addition of sand to the glazing mixture, as also hypothesized by Tite [8] and Antonelli *et alii* [9]. For the other samples, instead, it is possible to suppose that the few residues present in the glazes could be connected to not melted grains pertaining to the marzacotto, which was produced, as described by Piccolpasso, by firing a mixture of sand and wine lees.

Sample	Dating	Thickness (µm)	Coperta	Sand residues
C 1	XVI	170	x	+++
C 2	XVI	350	x	+++
C 3	XVII	550		++
C 4	XVII-XVIII	140		+++
C 5	XVI-XVII	280		±
C 6	XVI-XVII	170		++
C 7	XVI	250	x	+
C 8	XIV-XV	240		±
C 9	XV	400		±
C 10	XVI-XVII	190		++
C 11	XV	380		+

Table 2. Thickness of glazes and particular features. +++ very abundant, ++ abundant, + present, ± rare

3.2. Micro-Raman analysis

Raman spectra of yellow and orange layers show the features of compounds containing antimony: the pigments can be ascribed to the group of lead antimonates, in agreement with the recipes reported by Piccolpasso.

The analysis of the spectra recorded for the yellow decorations allowed us to investigate the structure of lead pyroantimonate compounds and its modifications. As reported in literature, lead antimonate, or Naples yellow, a Pb-Sb oxide, is characterized by a cubic pyrochlore structure that can be modified by the introduction of a third cation, typically Sn or Zn [10].

The comparison with the natural analogous of Naples yellow, whose name is bindheimite, leads to the identification of the presence of an unmodified pyrochlore structure in the yellow layer pertaining to sample C11 (fig. 3). This spectrum shows the presence

of three characteristic bands at 511, 303 and 125 cm^{-1} , the latter related to the Pb-O lattice mode.

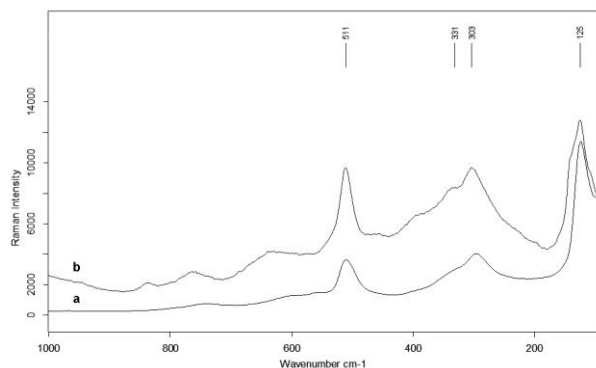


Figure 3: Spectra collected on C11 (b) compared with bindheimite (a). Reference spectrum from RRUFF project, n. R050546. Measurement conditions: 785 nm, 25 mW, integration time 3 s, 50 coadditions.

The yellow pigments used in ceramic objects and, in particular, the modification of the lead pyroantimonate structure reflected by changes in its Raman spectrum, have been investigated and discussed in previous literature [10-14]. In particular, Rosi *et alii* [10] in a first paper describe a strong change in intensity of the band at 510 cm^{-1} corresponding to the symmetric stretching of the Sb-O octahedra, and a shift towards higher wavenumbers of the Pb-O lattice mode signal, the shift corresponding to a structure modified by Sn as a third cation showing a doublet at 125 and 142 cm^{-1} . Moreover at low wavenumbers they report changes in the intensity of the band at around 330 cm^{-1} assigned to vibrational modes of Pb-O and Sb-O bonds, the major increase of this signal attributed to the introduction of Zn as a third cation. The same authors [14] noted in 2011 that the shifting of the bands pertaining to Pb-O lattice stretching (120-145 cm^{-1}) cannot be considered a reliable parameter to obtain information on the pyrochlore structure, their position depending also on the firing temperature and on the Pb:Sb ratio.

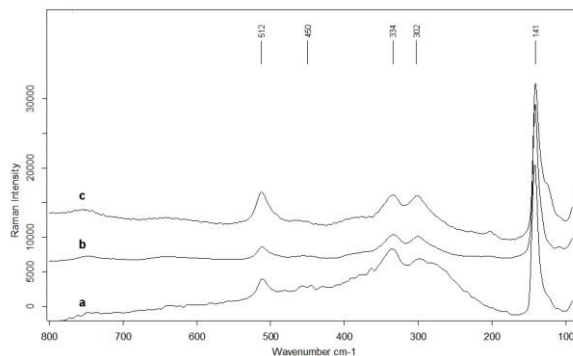


Figure 4: Raman spectra of yellow layers of C1 (a), C2 (b) and C7 (c), showing the band around 510 cm^{-1} decreased in intensity. Measurement conditions: (a) = 532 nm, 20 mW, integration time 3 s, 30 coadditions, (b) = 785 nm, 25 mW, integration time 2 s, 5 coadditions, (c) = 532 nm, 20 mW, integration time 3 s, 30 coadditions.

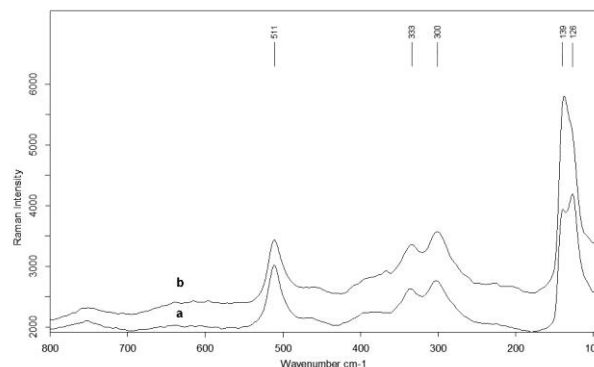


Figure 5: Raman spectrum of the yellow layer in C4 (a) and C10 (b): partially modified structures. Measurement conditions: (a) = 785 nm, 10 mW, integration time 3 s, 30 coadditions, (b) = 785 nm, 25 mW, integration time 6 s, 5 coadditions.

In our case, in samples C1, C2, C6, C7 it has been possible to point out the presence of some signals that can be connected to a modified structure, although other techniques are requested to definitively identify the third cation involved. In the spectra acquired from the yellow and orange areas of those samples, the band around 510 cm^{-1} strongly decreases in intensity and becomes comparable, or slightly smaller, to the band around 300 cm^{-1} (see figure 4 for spectra pertaining to yellow areas on samples C1, C2 and C7). Furthermore, the band around 330-335 cm^{-1} becomes well defined in comparison to the unmodified structure and it is noticed the appearance of a weak band around 450 cm^{-1} . Spectra collected from samples C4 and C10 reflect a partially modified pyrochlore structure, showing mainly features of a bindheimite-like structure where the band at around 510 cm^{-1} only partially decreases

in intensity and the Pb-O vibrational mode at 330 cm^{-1} is not as intense as in a ternary compound (fig. 5). Dark particles mixed with the orange pigment, which turned out to be hematite (fig. 6), were observed only in the orange layer from sample C2, suggesting the addition to the antimonate of this compound to obtain the desired colour. The addition of iron oxide to the yellow antimonate is reported also by Piccolpasso, who describes the use of *Ferraccia* (rust) together with lead and antimony to produce the colour called *Zallo*.

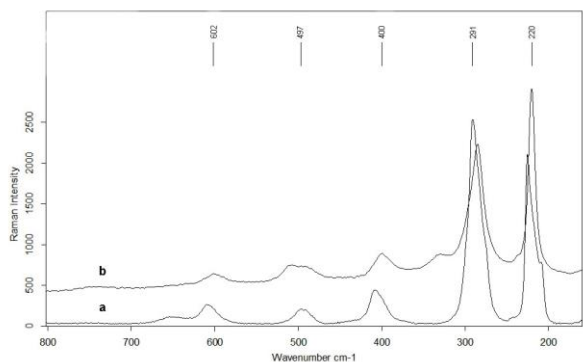


Figure 6: Raman spectra of hematite particles in sample C2 orange area (b) in comparison with hematite standard from RRUFF project n. R050300 (a). Measurement conditions: 785 nm , 25 mW , integration time 2 s , 5 coadditions.

Finally, Raman signals of the yellow and orange pigments in sample C6 show almost the same features. Anyway it is noticeable a slight increase of the band at 267 cm^{-1} in the spectra collected on the yellow area (spectrum (a) shown in figure 7) and a more defined band at 300 cm^{-1} (corresponding to Pb-O mode) for the orange one (spectrum (b) in figure 7). It is possible to hypothesize a very similar recipe for the two tonalities, which could possibly show a slight difference depending on the firing temperature or the Pb:Sb molar ratio [14], as inferable by the little shift of the Pb-O lattice mode from 138 cm^{-1} in the yellow decoration to 142 cm^{-1} in the orange one.

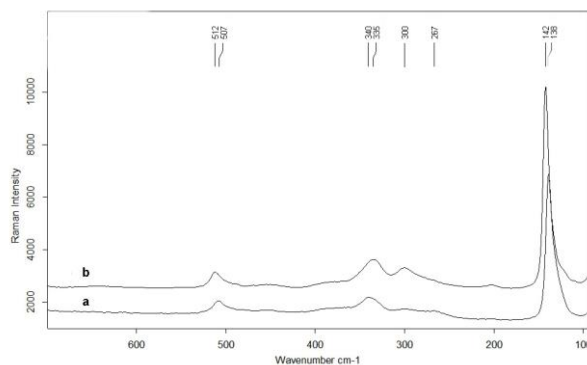


Figure 7: Raman spectra of yellow area (a) and orange area (b) for sample C6. Measurement conditions: (a) = 785 nm , 25 mW , integration time 4 s , 5 coadditions, (b) = 785 nm , 25 mW , integration time 2 s , 5 coadditions.

Raman spectra from brown areas of the glazes in samples C4 and C8 gave no relevant signals, allowing to hypothesize that those areas were obtained with a pigment, likely a manganese oxide, dissolved in the glassy phase, as other authors report for similar decorations [15].

The observation of the blue and green parts in cross-section shows a coloured glassy matrix without any possibility to isolate pigment particles.

Anyway, in the blue areas of the samples C2, C5 and C6, it was possible to detect the presence of a *Co-olivine* (CoSiO_4), characterized by a strong band at 824 cm^{-1} (fig. 8). 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 [16, 17], but according to Vieira, who analyzed ceramic sherds of Portuguese production dated back to early XVI and XVII centuries [18, 19], this phenomenon occurs when the temperature of the kiln is high enough to allow the formation of the cobalt silicate. In support of this theory, it has been stated by Pishch and Rotman [20] through a systematic study on silicate pigments that orthorhombic structure of cobalt olivine starts to form in the range $1000 - 1100\text{ }^\circ\text{C}$.

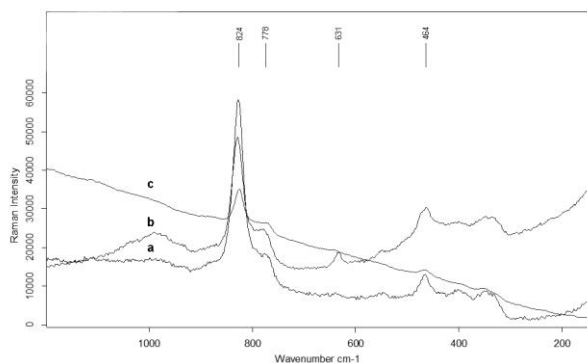


Figure 8: Samples C6 (a), C5 (b) and C2 (c) showing Co-Olivine features (band at 824 cm^{-1}) in the blue areas analyzed. Signals at around 631 and 778 cm^{-1} belong to cassiterite, while signals at 464 cm^{-1} are attributable to quartz.

Measurement conditions:

- (a) = 532 nm, 10 mW, integration time 2 s, 20 coadditions,
- (b) = 532 nm, 20 mW, integration time 2 s, 30 coadditions,
- (c) = 785 nm, 25 mW, integration time 2 s, 5 coadditions.

For the blue areas of the remaining samples (C1, C3, C7, C10 and C11), signals ascribed to the glassy matrix have been registered: in particular, the broad bands around 500 and 1000 cm^{-1} are evident in the Raman spectra.

The bands associated to cassiterite, quartz and feldspars are generally present in blue areas, as shown in figure 8: cassiterite acts like an opacifying agent, while quartz and feldspars constitute undissolved phases of the raw materials in the matrix, added intentionally or not, as hypothesized observing the glazes in thin section.

The presence of cassiterite has been detected also in green layers, where a strong signal related to it is particularly noticeable in Raman spectra pertaining to Archaic majolica, in C8 and C9 (see figure 9).

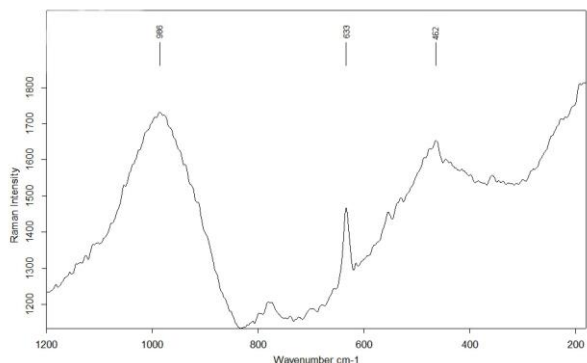


Figure 9: Raman spectra of green layer on an Archaic majolica sherd, sample C9. The signal at 633 cm^{-1} pertains to cassiterite, while the broad bands at 462 and 986 cm^{-1} are related to the glassy phase. Measurement conditions: 532 nm, 10 mW, integration time 3 s, 30 coadditions.

The green layers are generally characterized by broad bands around 500 and 1000 cm^{-1} related to the glassy matrix. The colouring agent usually employed for this kind of tonality was based on copper compounds and Piccolpasso refers to this pigment as *Ramina*: as reported by Colomban [21], copper ions dissolve in the glassy phase and are not detectable by Raman spectroscopy.

The only exception in green decoration has been observed in sample C3, where in cross-section a sharp layer is visible over the white enamel: it is composed by greenish yellow grains in a bluish matrix, as shown in figure 10 (box). The Raman analysis of this green layer shows the presence of a lead antimonate probably mixed with a compound containing cobalt, as suggested by the small band around 830 cm^{-1} .

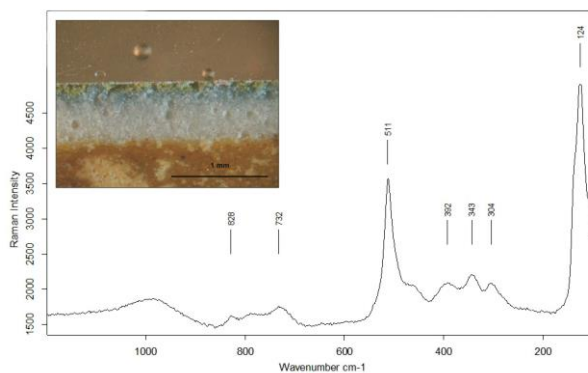


Figure 10: Raman results for the green area of sample C3. Inside the box, cross section of the green layer analyzed, visible light, 40 \times . Measurement conditions: 532 nm, 20 mW, integration time 2 s, 30 coadditions.

As mentioned, the majority of the spectra recorded for green and blue decorations shows the presence of two broad bands around 500 and 1000 cm^{-1} , which are related to the glassy matrix and correspond to the Si-O bending and stretching mode respectively [21]. Colomban et alii [22, 23] proposed the use of a parameter, the polymerization index (I_p), to study the glassy phases: it is calculated as the ratio between the area under the band at 500 cm^{-1} and the area of the band at 1000 cm^{-1} . In the present study, we applied this calculation to our samples and the resulting values are listed in table 3 together with the Si-O stretching maximum wavenumber (ν_{max}). This last value is linked with the glassy phase connectivity and it is influenced by the presence of fluxing agents [24, 25].

Sample	Colour	Ip	v max Si-O stretching
C 1	blue	0.50	961
C 2	green	0.40	969
C 3	blue	0.60	993
C 4	green	0.37	989
C 5	blue	0.72	1008
C 7	blue	0.24	981
C 8	green	0.44	985
C 9	green	0.20	986
C 10	blue	0.61	989
C 11	blue	0.25	972

Table 3: Ip values and v max Si-O stretching wavenumbers for green and blue areas of samples showing the characteristic bands of glass.

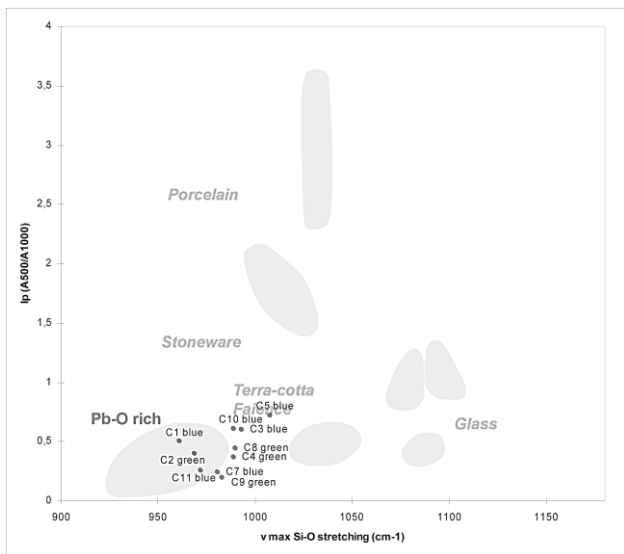


Figure 11: v max Si-O stretching vs Ip values for green and blue layers. The samples lay close to the area typical of lead-based glazes, as shown through the grey areas on the graph, taken from Colomban et alii [22].

As shown in table 3, the polymerization index varies between 0.20 and 0.72: such values are correlated to the maximum stretching wavenumber of Si-O in figure 11, where they are positioned in an area typical for lead-based glazes, as reported in literature. The

presence of a lead-based glaze is consistent with the description given by Piccolpasso in his treatise.

Furthermore, Colomban *et alii* [22] describes a relationship between the index of polymerization and the temperature of firing of the glaze: in particular, they estimate a temperature <700°C for $Ip < 0.3-0.5$ and around 800°C for $0.5 < Ip < 0.8$.

In our case the presence of the colouring agents, such as cobalt, can cause a decrease of the polymerization [26], so referring to the values noticed in the present work, they could be connected to a slightly higher temperature respect to that supposed in literature. Furthermore, it is worth noting that polymerization degree could be affected also by weathering phenomena of the glazes, considering the particular conditions which could have taken place in the burial environment of the sherds (a waste shaft).

4. CONCLUSIONS

The micro-Raman analysis of the glazes allowed us to acquire information about the raw materials and the technology used in the decoration of majolica sherds found in the *butto* of the Monk's palace.

According to Ip values, it has been possible to ascribe all our samples to the lead-based glazes area, as shown in figure 11, even taking into account that the introduction of colouring agents leads to a decrease in these values.

Sample C5 shows the highest value of polymerization index, while the spectra collected on its blue layer show the Raman signature of Co-olivine, in agreement with the hypothesis of a high temperature of the kiln and a quantity of oxides enough to allow the formation of the cobalt silicate. We can certainly affirm that the majority of the ceramic sherds here analyzed have been made following Piccolpasso's recipes, with the exception of sample C3. The blue layer of this sherd shows no evident Raman signals, being it a glassy matrix in which Co- ions are dissolved, and its Ip value indicates the presence of a lead based glaze also for this sample. On the other hand, the green layer shows a particular composition and it was obtained by mixing together a lead antimonate based pigment with a cobalt blue, this latter in a sufficient amount to lead a precipitation of the cobalt silicate, as previously seen. The presence of Co-olivine allows to hypothesize a firing temperature sufficiently high.

C3 has been ascribed to the XVIII century Ligurian production thanks to its typical decoration with "*birds and parsley*", so it belongs clearly to a different

temporal and geographical context respect to the rest of the samples here analyzed.

As a result in our study, we can note as the differences in composition of the coloured glazes could reflect in some way the belonging of the samples to different historical periods.

Yellow layers in the form of ternary lead antimonates are present in sherds dated from XVI century, while archaic ceramic fragments show decorations only in green and brown colours, colouring agents dispersed in a glassy matrix, and a non modified lead-antimonate yellow appears in a sherd dated back to the first period of the Renaissance (second half of XV century). Concerning the blue layers, cobalt olivines are found in samples pertaining to a later production, when a higher temperature was commonly reached by the kilns. As shown in cross section, all yellow and orange decorations appear in thin layers over the glaze, while the colouring agents used to obtain the remaining hues diffuse in the vitreous matrix.

Finally, through the microscopic analysis it has been stated that there is no evident interaction between glazes and bodies for all the sherds here studied, thus leading to the consideration that a two-step firing process was a technological choice widely diffused even through time, while the intentional addition of sand to the glazes, perhaps with the aim of enhance the viscosity, seems to be an expedient in use from XVI century, as no traces of quartz irregularly shaped are noted in the archaic majolica examined.

Our work represents the first scientific study carried on the ceramic materials coming from the waste shaft of the Monk's palace of Capena. Even limiting our attention to a restricted group of finds, it has been possible to point out the differences between the various sherds, as a result of different technology choices and materials employed. Those differences reflect the large chronological range of the artefacts and the wide area of provenance of the majolicas, that comprises not only local centres (Latium and Rome) but also Florentine and Ligurian ones, this data being of a primary importance for the better comprehension of the majolica's network of trade and the purchasing capacity of the Monk's Palace inhabitants.

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