STUDY OF DECORATED POTTERY FRAGMENTS BY MEANS OF MICRO-RAMAN AND OTHER TECHNIQUES

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1. Introduction

The aim of this work was to apply several spectroscopic methods of analysis to study the decorated pottery fragments found in the excavations of the Medici Villa of Cafaggiolo, near Florence, and of the roman-medieval site of Ferento, near Viterbo (Gaudenzi Asinelli [1], AA.VV. [2]). The results of the analysis performed on the samples coming from these sites have been compared with thin sections mineralogical examination of the same samples.
The main objective of the analysis, performed in the pottery fragments of two site of central Italy, has been to obtain information about the productive processes, the firing temperatures and the materials used in medieval and Renaissance period. Further purposes were to enrich the knowledge and the databases of pottery materials and techniques, to study the evolutions of the productive processes through the history and eventually to try to identify the elements that characterize the two examined Italian productions.
Micro-Raman technique doesn't need a pre-treatment of the samples under test; moreover micro-Raman is a non-destructive molecular method of analysis recently widely applied in the field of cultural heritage (Cuomo di Caprio [3], Smith [4]. In this work the results of micro-Raman analyses of Cafaggiolo pottery are related (Montini [5]). Moreover some mineralogical studies on the Cafaggiolo and Ferento potteries are proposed. The Cafaggiolo potteries were also examined by means of quantitative X-Ray Fluorescence analysis and X-Ray diffraction (Gaudenzi Asinelli [1]).

2. Materials and methods

The micro-Raman analyses were performed by means of a Labram Model, Dilor JobinYvon spectrometer with a spatial resolution of few square microns equipped with a CCD detector. The exiting wavelength was the 632.8 nm red line of a He-Ne laser. The diffused light is recorded in a backscattering geometry by a microscope of variable objective. An online computer allows the immediate restitution of the spectral shape and the possibility of performing spectral treatments to test the reliability of the obtained Raman signals. The stratigraphic analyses were performed on a portion of the samples mounted as polished cross-sections embedded in polyester resin. They were examined with a Zeiss Axioskop polarizing microscope at 25-400x magnification in incident visible and UV lights. Photomicrographs were taken with the digital Zeiss AxioCam MR. The thin sections were examined with the same polarizing microscope in transmitted light.

3. Results

We analyzed nine samples (clay body, engob and glaze composition) from Cafaggiolo and several fragments from Ferento (*concotto*, fire and glazed pottery). The study of the clay body was performed in order to find out the chemical composition but also to evaluate the firing temperature of the ceramics. Some clay compounds, as magnetite (Fe_3O_4), anatase (titanium oxide, TiO_2) and calcite ($CaCO_3$), work as indicators. In an oxidant ambient, magnetite transforms in maghemite (γ-Fe_2O_3) at the temperature of 200 °C and in hematite (α-Fe_2O_3) at the temperature of 400 °C (De Faria [6]). The inverse reactions are also possible in a reductive ambient. Anatase transforms in rutile at temperatures between 750 and 950 °C. Calcite produces calcium oxide (CaO) and carbon dioxide at the temperature of about 900 °C. The reaction is reversible in presence of water and in a CO_2 reach reductive ambient. First we note that the orange-red colour of all the clay body parts (surface and core) suggests that the firing atmosphere was oxidant. This prevents the transformation of hematite in magnetite and the black colour formation. Despite this, magnetite is present in traces in several of the examined samples and often hematite and magnetite spectra appears simultaneously. This fact is quite puzzling because the firing temperature was certainly greater than the magnetite transformation temperature of 400 °C. The oxygen deficiency in the clay body could explain the incomplete magnetite to hematite transformation. This suggestion could be tested by 'ad hoc' laboratory experimental plans we will develop in the near future. In pottery manufactures, calcite is sometimes added to the natural clay body to improve modeling and to increase stability. Since it transforms in CaO and CO_2 at about 900 °C, there is evidence that the firing temperatures were contained within this limit. Indeed, if the temperature had crossed the 900 °C, the inverse transformation of CaO in $CaCO_3$ had required a strong reductive firing ambient which we have to exclude. This maximum temperature limit of 900 °C is consistent with the presence of anatase in two of the examined samples. The XRF analyses of Cafaggiolo samples detected the following main elements present in the clay bodies: Si (57%), Al(18%), Ca(10%), Fe(6%), Mg(4%), K(3%), Na(1%), Ti(0.8%) and Mn(0.1%) (Gaudenzi Asinelli [1]). Major fluctuations around these average values were found for Ca with a standard deviation of 35%, and limit values of 18% and 5.4%. The presence of secondary calcite was detected by means of thin section analysis of the samples.

The engob Raman spectra are characterized by a broad band at about 1300 cm^{-1} and two sharp bands at about 1360 and 1390 cm^{-1}. The broad and sharp spectral shapes occur both together and alone (fig.1).

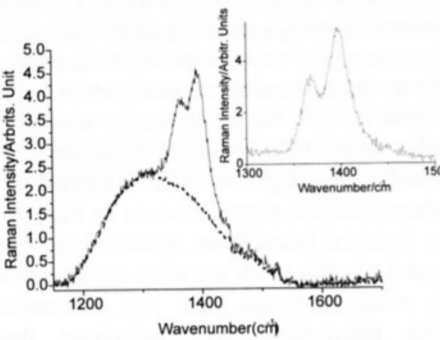

Fig. 1 – Raman spectra of the engob. They show the presence of the amorphous α-alumina (black line) and of crystalline and amorphous (γ-alumina) phases. The crystalline phase was also found alone (inset spectrum).

By comparing with some assignments of literature, we conclude that they are due to alumina (Al2O3) in its crystalline (α-alumina, sharp band) and amorphous (γ-alumina,

broad bands) forms. All the analyzed engobed samples gave the same spectral shapes. So we can conclude that the alumina was systematically used as engob material. This could be an interesting character of the Cafaggiolo production exploitable in studying new sherds from future excavation works. The six glazed samples have the same kind of covering given by lead glaze. The small peak at about 145 cm^{-1} is due to the PbO. The other two broad peaks at about 500 and 1000 cm^{-1} characterize the lead glaze. Glasses exhibit Raman spectra with two main bands at about the same frequencies. They are due to the vibrations of the SiO_4 tetrahedral units which compose the glass network. The oxygen displacements along a line bisecting the Si-O-Si angle yield the bending mode at low frequency (500 cm^{-1}); the Si-O bond stretching yields the high frequency stretching mode (1000 cm^{-1}). These bands change shape and intensity when metallic atoms, inserted in the SiO_4 lattice, break the continuity of the network. In this case, the oxygen atoms, at the vertexes of the SiO_4 tetrahedral units, could be non connected to the glass network.
The colors of the decorations are white, blue, green, orange, red, black and brown. We found the following pigments: the red ochre (Fe_2O_3), massicot (PbO) for the yellow, gypsum ($CaSO_4.2H_2O$) and calcite ($CaCO_3$) for the white (probably the background), carbon for the black, fosterite (Mg_2SiO_4) for the green. The presence of anatase traces confirms that the samples did not reached high temperatures (> 900°C). In the other samples we found Naples yellow ($Pb_2Sb_2O_7$) and red and black iron oxide mixed with Pb/Sn yellow compounds (Pb_2SnO_4 and $PbSnO_3$) to yield the pleasant nuances of the orange. Finally, the vanadium (in the form of vanadite $Pb_2(OH)VO_4$) was detected in some samples. The analyses of blue decorations are in progress; preliminary results showed the presence of lazurite (private communication of prof. Baraldi).

4. Conclusion

The microRaman and stratigraphic analyses of Cafaggiolo pottery fragments yield a great number of details on the ceramics composition from which it is possible to derive self-consistent deductions by looking at all the information simultaneously. Two of the examined sherds belong to the earthenware which is engobed, scratched and covered with a transparent lead glaze (Byzantine ceramics). Three of them belong to the category usually referred to as maiolica because no engob is present and an opaque layer is extended directly on the clay body (Islamic ceramics). To conclude, we can state that the craftsman staff in Cafaggiolo was composed of different expertise able to produce Islamic and Byzantine ceramics. Moreover the presence of sherds showing characters in between these two groups indicates the tendency to the research of new technologies in the ceramic production.
The main results obtained from the mineralogical analyses of Ferento medieval potteries is the use of local materials that reveals the existence of a local production (fig. 2). The examined fire pottery samples showed the presence of sanidine, augite and other minerals found also in local rocks. Further investigations will be carried out to deepen this findings and to the study also the glazes and the pigments used in Ferento ceramics. We intend to apply also the LIBS (Laser Induced Breakdown Spectroscopy) technique to the study of pottery fragments. Unfortunately in this work we were not able to show the results of LIBS analyses because we had some problems with the instruments settings. LIBS is a quantitative elemental and micro-destructive technique that can be considered complementary to the Raman (Anglos [7]). The LIBS analyses will be realized by means of a Quanta System Nd:YAG 100mJ coupled with LLA Instruments CCD and a Spectrometer.

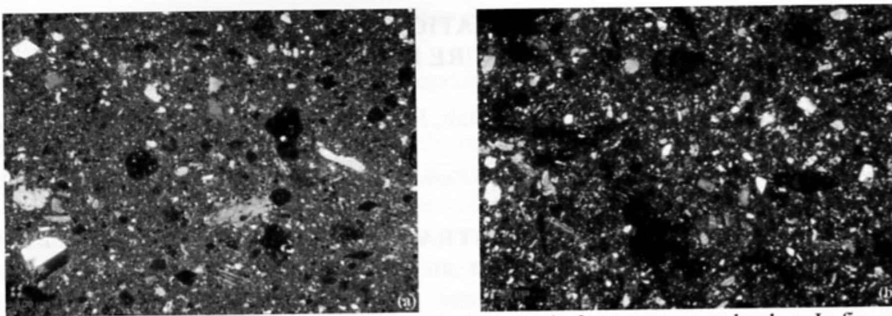

Fig. 2 – Thin sections of Ferento fire (a) and *concotto* (b) ceramic fragments, crossed polars. In fire ceramic sample many sanidine crystals are visible. In *concotto* fragment many augite crystals are visible.

Notes and acknowledgments

We would like to commemorate Prof. Alberto De Santis died three months ago. He left a terrible void in our team.

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