

Archaeometry and urban archaeology: the case study of *Sant'Agata la Vetere* church (Catania, Sicily)

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Abstract - The church of *Sant'Agata la Vetere* in Catania is located in a complex area of urban stratification and, according to historical sources, it is considered the first cathedral of the city. The occasion of archaeological excavations in the area of *Sant'Agata la Vetere* yielded many finds. Among these, frescoes, fragments of glass and mosaic tiles were dated, on an archaeological basis, to the 3rd and 4th centuries BC. The aim of the present work is to provide a scientific contribution to the archaeological classification of the site through the characterization of the finds from a compositional and colorimetric points of view in order to gain insight about their manufacture. The different kinds of finds called for combined non-destructive methodologies for having complete and expanded information. The techniques employed were XRF for the compositional investigation and visible spectrophotometry for the colorimetric analysis coupled with the Raman spectrometry for pigment identification.

I. INTRODUCTION

The church of *Sant'Agata la Vetere* is located in a complex area of urban stratification. It is situated along an imaginary line that connects three religious buildings: *Sant'Agata alla Fornace*, *Sant'Agata al Carcere*, and the aforementioned *Sant'Agata la Vetere* (Fig. 1). All these churches are closely linked to the religious tradition and the worship of *Sant'Agata*, Catania's patron saint and are placed in a strategic position at the core of Roman and Late Antique *Catania* [1, 2, 3]. During the restoration works of the church of *Sant'Agata la Vetere*, four campaigns of archaeological excavations (2003/2004, 2005 and 2008) were conducted in order to study the complex site around the religious building [4, 5, 6].

The archaeological interest in the site lies in the fact that it seems to have been affected by a progressive

raising of the ground with filling materials coming from the

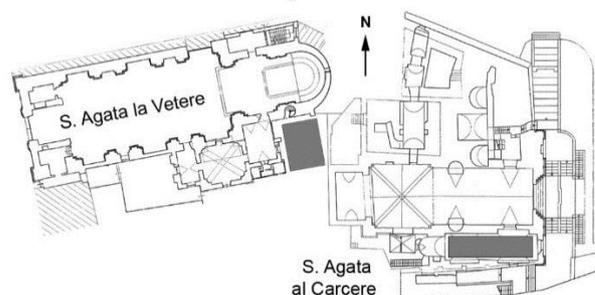


Fig. 1. Plan of *Sant'Agata la Vetere* and *Sant'Agata al Carcere*.

dismantling of a *domus* dating back to the period from the 2nd to 4th centuries AD. This *domus* would have been built between the martyrdom of Saint Agatha (251 AD) and the construction of the church of *Sant'Agata la Vetere*, the first cathedral of Catania (313 AD).

The materials possibly related with the dismantling of a nearby *domus* come from a homogenous series of layers (US, 6, 11, 13, 16, 17, 22, 23 and 24) which has to be interpreted as a sort of dump yard for disrupted architectural elements (Table 1).

Table 1. Stratigraphic units and excavation area in which were found the materials under study.

US	Description
6	Large quantity of broken ceramic sherds, broken and deposited in a way to form a level. This level is composed by fragments of tiles, bricks, glass, the bones of birds and ruminants, and shells.

11	Large quantities of ceramic sherds from different periods.
13	
16	Many sherds of <i>terra sigillata</i> .
17	Soil with fragments of architectural decorations, marble flakes, pieces of broken pavement, pieces of mosaics, and fragments of frescoes.
22	Soil and fragments of various types
23	A compact stratum, like US 17, consisting of mixed soils, small fragments and pieces of polychromatic frescoes.
24	An accumulation of rocks of medium size with various types of finds.

In an urban context of great complexity, such as the case of Catania may be, where the accumulations of anthropic deposits are alternated with layers of eruptive phenomena from Etna, archaeometric techniques are even more fundamental in the interpretation of these data.

The scope of this contribution is to aid archaeologists in resolving issues related to complex stratigraphy in urban contexts through the use of scientific methods.

The use of scientific analyses has been distinguished on the basis of the materials being investigated and has been aimed at acquiring essentially compositional information. Specifically, for glass and frescoes, X-Ray Fluorescence (XRF) was applied to understand the respective manufacture and the palette of pigments used, respectively, while for mosaic *tesserae* the XRF analysis has been integrated with that of the electronic microscope scanning, in order to meet the sensitivity limit of the technique with respect to lighter elements.

The preliminary results are presented here with each of the techniques mentioned above. Further investigations are underway, especially in regards to the qualitative and quantitative composition of the glass and mosaic tiles.

II. MATERIALS AND METHODS

A. Materials

Thirteen glass fragments were selected among the more diagnostic and recognizable glass finds according to the system of reference provided by Isings [7]: SLV46/1-4 from US 6C, SLV47/1-4 from USF 14, SLV48/1-2 from US 22, SLV49/1-3 from US 24 (Figs. 2-3).

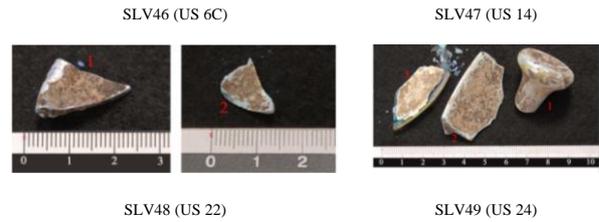


Fig. 2. Selection of glass fragmentary vessels from US 6C, US 14, US 22, US 24

Twelve samples of frescoes were studied from US 17 and 23: SLV53_1, SLV53_2, SLV53_3, SLV53_4, SLV53_5,

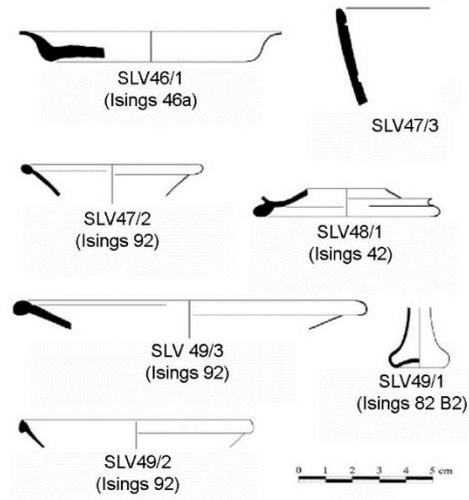


Fig. 3. Identification of main glass shape typologies according to Isings system (Drawings by D. Cali)

SLV53_6, SLV53_7, SLV53_8, SLV53_9, SLLV53_10, and SLV53_11 from US 17 and SLV52 from US 23 (Fig. 4).

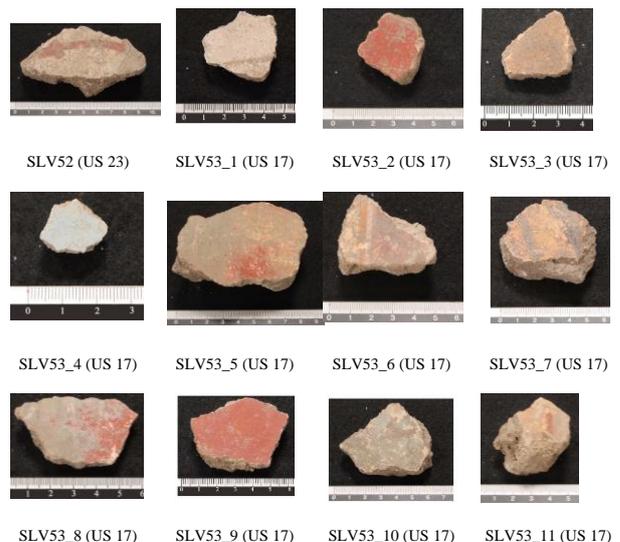


Fig. 4. Selection of frescoes from US 17 and US 23.

The mosaic *tesserae* were selected from US 11 (SLV50, four yellow *tesserae*) and US 16 (SLV51 including 2 blue, 14 orange, 19 white and 12 black *tesserae*) (Fig. 5).



Fig. 5. Selection of mosaic *tesserae* from US 11 and US 16.

B. Methods

Non-destructive and non-invasive methods were employed for the characterization of the finds. XRF analysis, Raman spectrometry, and analyses using Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) were conducted. The four methods provide the various information and the cross of different technical data allows to obtain information both from a physical, chemical elemental, molecular points of view.

The X-Ray Fluorescence analysis was performed using the Lithos 3000. The X-ray source is equipped with a conventional Molybdenum tube, operating at a maximum acceleration voltage of 30 kV and a maximum current of 0.5 mA. The detection system includes an energy dispersive detector that is 600 μm thick, with 7 mm^2 of active area and a resolution of 160 eV at 5,9 keV. The pointing system relies upon a laser interferometer, which measures the distance between instrument and sample. This system allows the positioning of the firing point within a 15 μm margin.

The measurement parameters are: 150 mA, 25 keV. The acquisition times have been changed in relation to the type of material analyzed: for frescoes it ranged from 300 to 750 seconds, for glasses 300 seconds, for tesserae 700 seconds.

Measurements were made using a combined system for Raman and fluorescence spectroscopy, the microSPEC produced by Jobin Yvon. This system uses a TRIAX 190 spectrometer. The signal is acquired by a Spectrum ONE charge-coupled device (CCD) detector. The laser used in this occasion is a diode laser at 780 nm. Neutral density filters were used to reduce the intensity of the laser radiation on the finds. The optical groups for the excitation and collection of the signal consist of an Olympus BX40 confocal microscope and a long working distance objective.

The Scanning Electron Microscope (SEM) used for sample investigation is a FEI Quanta 400 FEG (Field-

Emission-Gun). It enables imaging in three modalities: high vacuum, low vacuum, and E-SEM (Environment-SEM) mode. It is designed to provide the maximum amount of data (imaging and microanalysis) for any samples and it does not require sample preparation. Microanalysis was performed with an Energy Dispersive (EDS) detector, associated with the SEM.

III. RESULTS AND DISCUSSION

The results are presented based on the type of the analysed material. The finds come from a section of the excavation that was rich in different materials and have been analysed with the object of gathering information on their composition to characterize and individuate their manufacture and, in the case of the frescoes, to identify the pigments used in the polychromatic areas. All the information was then cross referenced in order to resolve the underlying archaeological problems within this work. These problems, as was discussed in the introduction, essentially concerns the discrimination of materials belonging to complex stratigraphy in an urban context in order to be able to ascribe to them, in terms of provenance, to a *domus* dating to the period between the 2nd and 3rd centuries AD that, according to historians, can be found in the excavation area under examination.

A. Glass

All of the glass undergoing study was characterized by an evident layer of alteration of its surface. The deterioration of glass is essentially due to chemical-physical processes that principally involve water. Water is responsible for two mechanisms that are involved: dealkalization (commonly referred to as leaching) and network dissolution or corrosion.

Fragments of glass have been unearthed in different stratigraphic units, from the oldest (US 24, third century AD) to the more recent one (US 6, sixth century AD). The composition of the analysed samples, from a chemical-elemental point of view, is similar across all the stratigraphic units. As an example the sample SLV49_3 is shown in Figure 6.

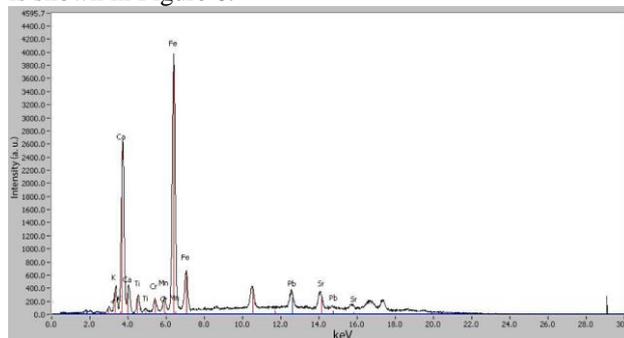


Fig. 6. XRF spectrum of the find SLV49_3

The glassy matrix is essentially constituted by Ca, Fe, Sr, K, and Ti. The presence of silicon and sodium is not detected with XRF analysis, which are surely present, one being the primary constituent and the other as a

lattice modifier, due to the intrinsic limits of the technique.

On the basis of the collected data, it is possible to hypothesize that the composition of the analysed glass is ascribable to the Roman period that is known. The chemical composition of the glass, in the Roman and Late Roman periods, remained quite homogenous [8, 9].

In absence of quantitative assessments, the elements shown in figure 6 at least provide some general information on the production process.

Silica was the main chemical constituent of alkali or alkali lime Roman glass and was derived from sand. The alkali (Na_2O e K_2O) needed to lower the melting point of the silica was obtained either from naturally occurring minerals or from ashes formed by burning plants. Lime (CaO) is added during the process as a stabiliser and it is also a typical component of the composition of roman glass [10].

The lack of magnesia [11] and potash impurities in Roman glass indicates that the source of Na was mineral and not plant ash [12].

The presence of iron is justified by the fact that the oxides of this element are present as an impurity in the sand. Such oxides impart a coloration that varies from yellowish (Fe^{3+} yellow-green) to a clear blue (Fe^{2+} blue) based on the state of oxidation of the iron. In general, the colour is influenced by the type and ionic state of the metal ion, as well as the furnace conditions used [13]. Unfortunately, due to the very poor state of conservation of the surfaces of the finds, the original colours of the glass analysed are only hypothesized on the basis of the elements identified with XRF.

In general, mixing of ionic colouring agents and opacifying colourants led to a more differentiated palette of colours [14]. Ionic colouring agents are Mn^{3+} for violet, Cu^{2+} for light blue, Co^{2+} for deep blue and Fe^{3+} for brown translucent colours. Calcium antimonates, lead antimonate and cuprite are the colourants responsible for white, yellow and red colours, respectively, and additionally serve as opacifiers.

All of these elements, excepting cobalt have been found in the chemical elemental composition of the finds of Sant'Agata la Vetere. In particular, in the stratigraphic unit 6 were found four fragments of apiombic glass that present two principal types of behaviour. The first behaviour is represented by SLV46_1 and the other by SLV46_2, SLV46_3, and SLV46_4. In the first case the analysis of X-ray fluorescence demonstrated, other than those of Ca, Fe, Mn, and Sr, the presence of the elements Ni, Cu, and Zn. In the stratigraphic unit 14, the glass can be distinguished by the presence of chromium, in particular the samples SLV47_3 and SLV47_4. The samples from stratigraphic unit 22 are leaded and show traces of Zn. All the samples from the stratigraphic unit 24 were leaded with the presence of Cr.

Some of the glass analysed showed the presence of lead and some not. Lead is known as a yellow colourant in crystalline pigments such as Neaple's Yellow, but can act as glass former when higher concentrations are

incorporated directly in the glass matrix. The presence of lead can be justified in two ways, under the form of antimonate for giving a yellow colour or use as an opacifier. In the attempt to individuate a general trend, it is possible to say that the older samples of Sant'Agata la Vetere show evidence of lead while the more recent samples (from US 6) are unleaded.

Manganese was present in all the glass analysed. However, as the state of oxidation was not well known, we were unable to obtain information about its origin, if it is a residue from the refining process or from its use as a decolourizer, added intentionally. Furthermore, on the basis of the investigations carried out, we do not know whether the titanium is present as a colouring agent or as an impurity of the raw material used for the manufacture of the samples. However, as far as strontium is concerned, instead, present in almost all of the analysed samples, its presence is explained taking into account the fact that it is incorporated, within the glass, through the raw materials carrying calcium: clam shells, limestones or the ashes of plants. Generally, the high presence of Sr indicates the addition of calcium through clam shells, low presence [15, 16]. In the case of the samples of Sant'Agata la Vetere, Strontium would seem to come from the use of calcareous sands.

B. Frescoes

The finds of frescoes were subjected to Raman and XRF measurements for characterization of their composition. The data were in the end cross referenced to identify pigments used in the realization of the frescoes.

The carbonate nature of the support of the painted area of the fragments was confirmed by the XRF analyses. All of the XRF spectra of the finds show the predominant presence of calcium.

As far as the chromatic range of the fragments of frescoes found, it is very restricted. The pigments are all ascribable to a very wide period of use.

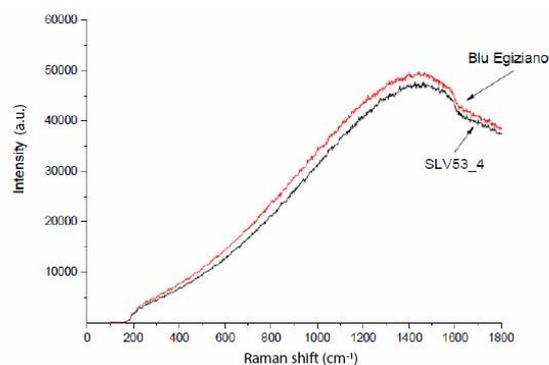


Fig. 7. Raman spectra of frescoes find SLV53_4 compared to Egyptian Blue pigment.

Table 2 summarizes the results obtained for all of the fresco finds. For each group of finds, subdivided by their perceived colour, is reported the pigment used by cross listing the measurements with those of the Raman.

Table 2. Finds grouped based on perceived colour and the identified pigments.

Finds	Perceived Colour	Pigment
SLV52, SLV53_2, SLV53_5, SLV53_6, SLV53_8, SLV53_9, SLV53_11	Red	Red Ochre
SLV53_2, SLV53_3, SLV53_5, SLV53_6, SLV53_7, SLV53_8, SLV53_9, SLV53_11		Cinnabar
SLV53_5, SLV53_7	Yellow	Ochre
SLV53_3, SLV53_6, SLV53_11	Orange	Ochre
SLV53_4, SLV53_8, SLV53_10	Blue	Egyptian Blue

The use of pigments, in particular red and blue pigments, permits us to make some observations regarding the Roman *domus* from which these finds most likely came from. It must have belonged to an aristocratic owner. It is possible to gather this information, above all, from the use of Egyptian blue as a pigment for in-paint of the colour blue. Egyptian blue, in fact, was particularly expensive in antiquity. Figure 7 shows, for example, the Raman spectra of the measured blue in-paint for the frescoes find SLV53_4 identified through the comparison with a spectrum of literature of Egyptian blue.

Moreover, comparisons in compositional terms were made between the frescoes found on the site of Sant'Agata la Vetere and those from other *domus* sites at the Monastero dei Benedettini and via Crociferi in Catania. These comparisons demonstrated that the pigments used in these samples were all the same for the main colours [17, 18].

C. Mosaic tesserae

The mosaic *tesserae* came from two stratigraphic units: four from US 11 and 47 from US 16. The X-ray fluorescence analysis identified the principal material as limestone. These are, in fact, most likely stone *tesserae* used most likely for pavements [19].

Only two blue *tesserae* were found, in US 16, which, instead, were made of a glass paste and were used in wall decorations [19]. For these, the X-ray fluorescence measurements yielded a lead-based composition, further investigated with the scanning electron microscope. We show, for example, the SEM/EDS acquisition performed on the find SLV51_2 in Figure 8. That acquisition permitted the localization of the presence of Si, Al, Na, Ca, Fe, K, Mn, and Pb. It is possible to see in Figure 6, apart from the area measured, maps in false colours the relative concentration of various elements. On the basis of this preliminary data, it seems that the composition is similar to those of the Roman period [20].

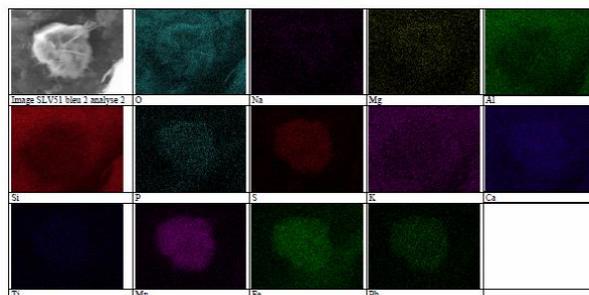


Fig. 8. SEM/EDS captures on the vitreous tessera SLV51_2.

The two glass paste *tesserae*, found in US 16, very likely come from the Roman *domus* and confirm that it must have belonged to an owner of the wealthy class.

IV. CONCLUSIONS

The materials found during the archaeological excavation of the area in front of the church of Sant'Agata la Vetere in Catania were studied through non-invasive and non-destructive techniques for the characterization and identification of pigments. The finds, belonging to different stratigraphic units, belong to three categories: glass, frescoes, and mosaic *tesserae*.

The problems covered in the present study were essentially the provenance of the materials. According to archaeologists, they could come from a Roman *domus*, the existence of which should fall before the the martyrdom of Sant'Agata (251 AD) and the construction of the church of Sant'Agata la Vetere, the first cathedral of Catania (313 AD).

The stratigraphy of urban contexts like that of Catania, continually inhabited and characterized by the presence of materials and events linked with volcanic eruptions, is particularly complex and puts in place the need to cross reference archaeological data with those deriving from the application of archaeometric studies.

On the basis of these initial results, it would seem that the mosaic *tesserae*, especially those made of glass paste, and the pieces of fresco come from a Roman *domus* hypothesized by archaeologists. As far as the glasses are concerned, it is difficult to say where they might come from and if they are ascribable to the Roman period.

Hopefully a resume in the archaeological investigation in this part of the historical district of Catania will shed

new light on such complex problems and help archaeologist in the delicate work or contextualizing the findings in the main historical picture.

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