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Archaeometric studies at the GILDA beamline at the European Synchrotron Radiation Facility^(*)

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Summary. — In the latest years archaeometry scientists have directed a growing interest to synchrotron radiation techniques. The Italian CRG beamline GILDA at the European Synchrotron Radiation Facility provides to the users the access to experimental techniques like X-ray absorption spectroscopy and diffraction that are of great potential usefulness in this field. Here we give a technical overview of the instrumentation available as well as some examples among the archaeometry studies presently in progress on the beamline.

PACS 07.85.Qe – Synchrotron radiation instrumentation.

PACS 61.10.Ht – X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.

PACS 89.90.+n – Other topics in areas of applied and interdisciplinary physics.

1. – Introduction

The use of materials science techniques has long been exploited to address questions posed by archaeologists, particularly those of provenance of ancient materials and technological aspects of production. Identification of the chemical content of ancient objects and of their structures is an important step in these studies and any non-destructive

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technique that can give this type of information is of particular relevance. Synchrotron radiation based X-ray techniques, which have enabled the technological advancement of many fields in materials science, have been recently applied to archaeology and cultural-heritage problems [1-4]. Up-to-date lists of publications on archaeometric studies carried out by Synchrotron Radiation can be found in the databases [5] and [6].

X-ray Absorption Spectroscopy (XAS) [7] has revealed to be a powerful and flexible technique in archaeological studies. It provides for a selected chemical species quantitative information like the local geometrical parameters, number and nature of neighbors, chemical state. It does not need long-range order so it can be applied to the study of amorphous systems or impurities. It can be applied in air, it virtually does not require any restriction on the type and size of the sample, which can be metal, ceramic, glass, cloth, wood, etc. and, finally, it is applicable to most of the elements of interest, even in very low concentrations. All these characteristics are particularly important in archaeological applications, in which samples are precious cultural heritage made of many different materials. The technique is non-destructive *per se*, however occasional phenomena of degradation like reduction of metallic species or local blackening of glasses are reported and the stability of the sample upon intense X-ray exposure should be tested before analysis.

2. – The GILDA beamline

Specifically, at the GILDA beamline [8], XAS technique has been successfully applied to a number of experiments, in the frame of the following main projects:

- Structural study of lustre decorations in glazes of Renaissance pottery.
- Investigations on the ancient production technology and on the origin of color of Roman and Medieval glass artefacts and mosaic tesserae.
- Degradation of pigments of paintings.

The Italian Collaborating Research Group GILDA at European Synchrotron Radiation Facility (ESRF) is a general-purpose beamline using a bending magnet source. It has been operational since 1994, and is mainly dedicated to the investigation of atomic structures. To this purpose, techniques like XAS as well as X-Ray Diffraction (XRD) are used on the beamline. GILDA consists in four experimental hutches: the first contains the optical elements and the others the experimental apparatus. In particular, the X-ray optics consists in a first collimating mirror, a sagittally focusing monochromator [9] and a vertically focusing mirror. The monochromator uses Si(111), (311), (511) and (933) [10] planes to cover an energy range from 4 to 90 keV. The second experimental hutch is dedicated to XAS and is placed in the 1:3 focal configuration to obtain the maximum flux. Typical beam parameters are a size of (hor \times vert) $0.05 \times 0.8 \rightarrow 2 \times 2$ mm², intensity $10^9 \rightarrow 10^{11}$ ph/s and a resolution of $\delta E/E \approx 10^{-4}$ depending on the energy value and on the optics configuration. The wide energy range of the beamline makes GILDA well suited for XAS investigations on mid-heavy elements with the possibility to access the *K* absorption edges from Ca to Au and the *L* edges from Sb on. Experiments are carried out in transmission, fluorescence and total electron yield modes. For the study of highly diluted samples in fluorescence mode an array of 13 high-purity germanium X-ray detectors is currently used, covering a total solid angle of $0.024 \cdot 4\pi$ sr and with an average resolution of 250 eV at the Mn-*K α* line. The maximum flux compatible with a linear response of the detector is about 80 kcps at a shaping time of 0.25 μ s. With this apparatus XAS

measurement with a limit sensitivity for the absorbing atoms of 10^{14} at/cm² or 10 parts per million (p.p.m.) can be carried out. Fluorescence data are collected in digital form so permitting advanced data treatment like dead-time corrections [11] or background removal. Surface sensitive experiments are realized by extracting the absorption coefficient of the sample from the yield of secondary electrons emitted as a function of the energy (Total Electron Yield method, TEY). As electrons have a much shorter mean free path in solids than X-ray photons the typical sampling depth obtained using this method is about $\approx 10^3$ Å. The TEY data collection is carried out by using a He-amplified conversion detector [12] and an example of use of this technique in the analysis of lustres is shown in [13].

The third hutch, in 1:1 focal geometry, is dedicated to X-ray scattering and diffraction. In particular, powder diffraction experiments can be performed in a few minutes at GILDA by using a large-area image plate detector [14].

3. – Examples of XAS studies

3.1. Lustre decorations on ceramics. – Lustre is one of the most important decorative techniques of Medieval and Renaissance pottery consisting of a metallic deposition over a tin-opacified lead glaze. Recent works demonstrated that lustre is characterized by a heterogeneous metal-glass nanocomposite film, some hundreds nanometers thick. Silver and copper quasi-spherical nanoparticles are dispersed within the outer layers of the glaze, conferring to the whole system specific optical properties [15]. From the point of view of material science, lustre is a glass-metal nanocomposite, analogous to those presently studied for possible application in optoelectronics [16]. Lustre preparation is described by Cipriano Piccolpasso in the second book of *I tre libri dell'arte del vasaio* dated 1557 [17]. A copper/silver deposition was obtained by putting a mixture of copper and silver salts and oxides, together with vinegar, ochre, and clay, on the surface of a previously glazed pottery. Then, the whole system was heated to about 600°C in a reductive atmosphere, produced by the introduction of smoking substances in the kiln. In these conditions metal ions which remained trapped within the first layer of the glaze were partially reduced to metal. Nanometric metallic particles in a dielectric matrix are known to exhibit an optical response dominated by an absorption band called Surface Plasmon Resonance (SPR) [18]. If it is located in the visible range, it causes the dielectric to assume typical colors, reddish in the presence of Cu clusters and yellowish for Ag clusters. A series of XAS studies on lustres of Italian [19, 13] and Iranian [20] origin have been carried out at GILDA with the aim of studying the local order around Cu and Ag. We have found that the metals were present in reduced and oxidized form: Cu⁰ and Cu⁺ in the red lustres and Cu⁺, Ag⁰, Ag⁺ in the gold lustres. Iranian specimens present Ag also in the red lustre [20]. Metal ions in oxidized form are bound to O atoms with a bond length of about 1.84 Å for Cu and 2.01 Å for Ag, similarly to what observed in soda-lime glasses doped with Cu [21, 22] and Ag [23] by the ion-exchange process. The typical metallic fraction is about 10 → 30% and an increase of this fraction up to 80% is observed when collecting data in TEY mode. This evidences as the reduction of the metal was induced by agents in the furnace atmosphere and interested a surface portion of the metal doped layer [13]. A similar equilibrium between Cu⁺ and Cu⁰ species is also found in Cu in bulk silicate environment as will be presented in the following subsection.

3.2. Roman and Medieval glasses. – In this subsection we describe investigations on the ancient production technology and on the origin of color of Roman and Medieval glass manufactures and mosaic tesserae. Scientific analysis of archaeological glass may provide

important information on the ancient production technology, on the selection and origin of the raw materials and on the addition of further ingredients responsible for color and opaque effects. The color exhibited by glasses can be determined by the oxidation state and the electronic configuration of the metal ions in them. These are usually elements belonging to the transition row of the periodic table, which absorb characteristic frequencies of the visible region as a result of d-d electronic transitions. In particular, ancient glass often contains iron at levels which can impart a typical incidental green coloration. To minimize this problem in transparent artifacts, from around the middle of the first millennium BC, substances were added which tended to neutralize the colorant effects of the iron. Before the Roman period antimony was the main decolorant, while from the second century BC manganese was more frequently used. Concerning opaque vitreous materials, the color and opaque effects were obtained by means of many different substances, depending on the age and on the desired effects (*i.e.* calcium and lead antimonates, lead stannate, quartz, wollastonite). In particular, regarding red glass, color and opacity are generally ascribed to the presence of copper under different speciation (metallic clusters or cuprite dendritic aggregates). Since the characterization of colorant, decolorant, and opacifying components is important in understanding the manufacturing technique of the ancient glasses, XAS was applied to the study of the oxidation state of iron and manganese in a number of transparent glass samples of archaeological interest, characterized by different colors (from green to pale brown to uncolored), and of copper in a series of opaque red musive tesserae. The samples studied at GILDA beamline are: i) transparent fragments of perfume bottles of the 2nd century AD, found in the Patti Roman Villa (Sicily) [24]; ii) “production indicators” of the medieval glasshouse of Val Gargassa, that is, those remains which testify specific operations carried out during the productive cycle, implying fritting, melting, flashing (mixing), boiling and working [25]; iii) opaque vitreous materials (mosaic tesserae and game counters), dated between the I and the III century AD, from Pompeii and two Sicilian sites (Tusa and Lipari- Italy) [26,27]. These research projects were aimed to characterize:

- the different aspects of the ancient glass manufacturing technique;
- the origin of color in findings with different chromatic tonalities and the possible role of decolorants in the colorless transparent glass;
- the influence of the transition metals oxidation state on the color of the glass in the different steps of the production cycle;
- the origin of the colored opaque effects in vitreous mosaic tesserae.

The glasses from Patti Villa [24] are, from the chemical point of view, rather similar to each other, suggesting a similar mineralogical composition of the raw materials used for their production. In particular, they can be defined as “low-magnesia” glasses, in agreement with their Roman origin. Moreover, all glasses contain iron and manganese, with the exception of one sample characterized by a bottle-green color, which is lacking in manganese. The Fe and Mn *K*-edge XANES (X-ray Absorption Near-Edge Structure) spectra and the detailed structure of the pre-edge peak of these samples and of the reference compounds have shown that in the uncolored ancient glasses iron is mainly present as Fe³⁺, while manganese is present in the reduced form Mn²⁺, confirming the hypothesis of a redox interaction between iron and manganese (Fe²⁺ + Mn⁴⁺ → Fe³⁺ + Mn²⁺), as a result of a deliberate addition of pyrolusite as decolorant during the melting procedure. Similar conclusions were reached for the glass-wares from the Medieval Val

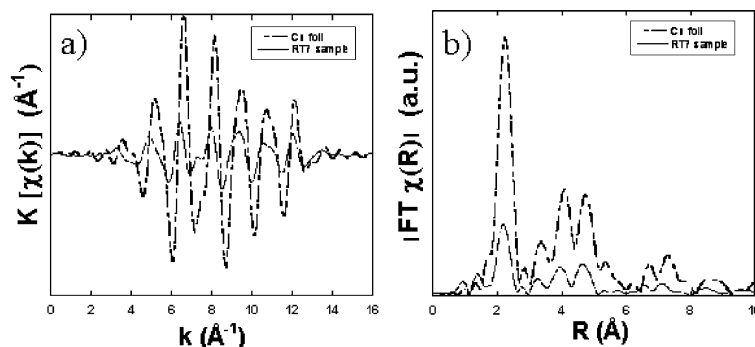


Fig. 1. – Comparison between the moduli of Cu K -edge XAS signals (a) and Fourier transforms (b) of the red tessera from Tusa (sample RT7 [27]) and Cu foil.

Gargassa glasshouse [25]: the color variability is the result of deliberate technical operations applied to obtain different color attributes. The investigated glass-wares have been grouped into two main categories. The main, largely diffused production, from yellow-green to green in color and characterized by a detectable—even if limited—variability in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, could be the result of the “standard” melting procedure, in which a certain variability in the oxidizing and reducing conditions could account for the way in which furnace was conducted (*i.e.* alternating of refuelling and burning) during the glass melting and working. The second, subordinate colorless artefact group, evidences the intentional adding of manganese oxide as bleaching agent. The most interesting result obtained from the XAS studies of the opaque game counters from Pompeii excavations and of mosaic tesserae from Sicily [26,27] is the speciation of copper in the red and green samples. In particular, the chemical analysis and the SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) studies of two opaque red artifacts (a mosaic tessera from Tusa and a game counter from Pompeii) revealed the presence of an anomalously high content of Cu, finely dispersed in the glass ground mass, but did not allow to determine its oxidation state. The absence of cuprite peaks in the X-ray diffraction patterns and of any dendritic agglomerates in the SEM images suggested to rule out the presence of this species. The XAS investigation at the Cu K -edge and the analyses of the high-resolution spectra (fig. 1 for the red tessera from Tusa) indicated the presence of monovalent copper cations incorporated in the glass matrix, accompanied by Cu nano-clusters. These conclusions are congruent with the red color and the opaque aspect of the samples and are in agreement with the results on Renaissance lustres, discussed in the preceding subsection of this paper.

3.3. Blackening of Cu-based pigments. – The blackening of paint layers containing copper-based pigments is an issue of fundamental importance for conservation and restoration of ancient paintings. It has been established that copper-based pigments can play a primary role in oxidation processes of lipid binders [28]; it is believed that these processes involve copper both in the form Cu^+ and Cu^{2+} during redox cycles. Moreover, it has been demonstrated that resin and fatty acids are able to extract Cu^{2+} ions from copper acetate and basic copper carbonate salts producing carboxylic acid complexes [29]. The characterization of the local chemical environment (ligands, bond distances and coordination numbers) and oxidation states of copper embedded both in blackened and in

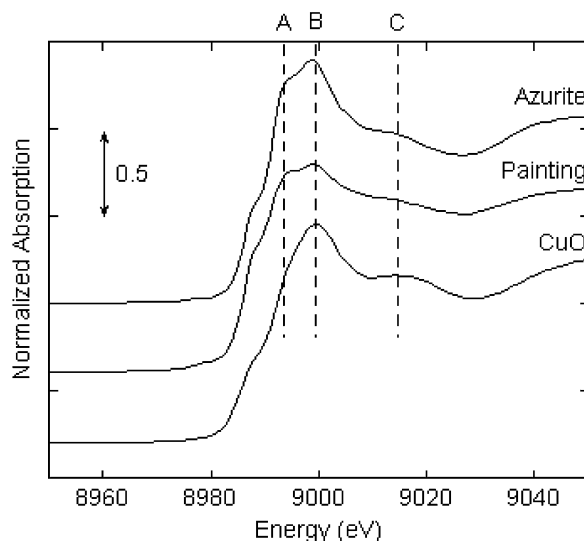


Fig. 2. – Comparison of the XANES spectra of crystalline azurite, tenorite and a blackened portion of the painting containing azurite.

unaltered painting layers can provide key information for clarifying the alteration mechanism. To this purpose, XAS measurements at the Cu-*K* edge have been carried out on small painting fragments (collected during a restoration session) belonging to an original fifteenth-century easel by *Niccolo Liberatore* that showed a blackening alteration for three of the most important green and blue copper-based pigments: copper resinate (copper resin acid salts) and azurite and malachite (copper basic carbonate salts). Measurements were compared with spectra from unaltered pigments. Preliminary characterization by micro-FTIR (Fourier Transform Infra Red spectroscopy), micro-XRD, SEM-EDS (Energy Dispersive Spectroscopy) and GC-MS (Gas Chromatography-Mass Spectrometry) techniques allowed us to gather information on the composition, the stratigraphy and the morphology of altered and unaltered painting layers. Particularly, it has been established that the binder is constituted by a combination of proteinaceous and lipid components. Moreover, it has been found that in the case of copper resinate, all the layer (organic pigment + binder) appears completely blackened.

Figure 2 shows the XANES spectra of crystalline azurite, the blackened part of the painting and crystalline CuO (tenorite). XANES spectra usually contain complex features that can be used as fingerprints for the detection of different chemical states. If we consider the features labelled as *A*, *B* and *C* in fig. 2 they are located at the same energy and have similar amplitudes (though small differences are evident for feature *B*) for the painting and azurite. On the contrary feature *A* is greatly depressed in tenorite with respect to the other spectra and shoulder *C* appears at higher energy. This indicates that at least the most part of Cu in the painting is not in the form of tenorite structure. Regarding possible reduction processes involving copper, no edge energy shifts are evident in the XANES spectra indicating the presence of the Cu⁺² oxidation state only. In this case, as confirmed by optical microscopy, the blackening is not caused by an alteration of the azurite grains of the pigment.

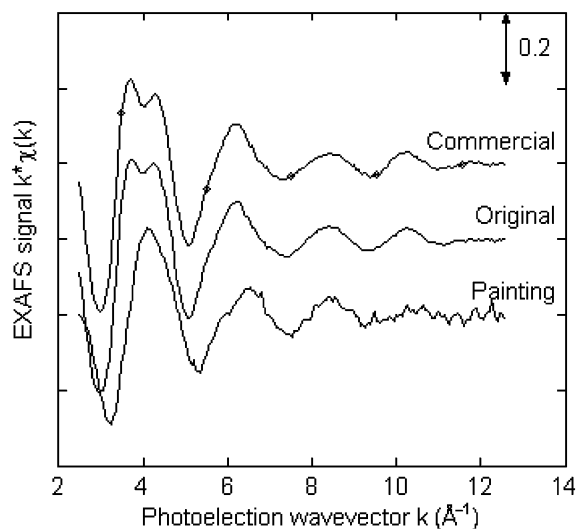


Fig. 3. – Comparison of the XAS spectra of copper resinate (obtained with the original recipe and a commercial product) and the blackened painting.

A different situation is found in the case of copper resinate. The XAS spectra of a blackened portion of the pigment and copper resinate models (*Original*, *i.e.* produced with the same ancient recipes and *Commercial*, a commercial product) are shown in fig. 3.

The oscillations present in the painting show different features when compared to the model compound spectra, in particular the minima appearing at 3 and 5 \AA^{-1} in the models are shifted at higher k values in the painting and the double peak appearing at 4 \AA^{-1} in the models disappears in the altered pigment. From a preliminary analysis we note an increment of the Cu-Cu distance from 2.61 \AA in the unaltered pigment to 2.71 \AA in the blackened painting. Further analyses, devoted to establish a link between the microstructure around Cu and the optical properties, are in progress.

4. – Conclusion

In this paper we have presented an overview of the GILDA beamline operative at the ESRF with particular attention to the instrumentation potentially useful in the study of archaeometry. Examples of studies carried out on this instrument have been given in the fields of ceramics, glasses and pigments denoting the fruitful activity that is at present in progress on the subject.

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