

MCX: a beamline for non-destructive X-ray diffraction experiments used to study stained glass windows

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Abstract – The MCX beamline at the synchrotron Elettra is the general purpose diffraction beamline that is well suited for non-destructive and innovative X-ray diffraction (XRD) experiments in the field of cultural heritage. A comprehensive study of the alteration products in grisaille paints was recently performed at the beamline. Such a study is very important to understand the complex processes involved in the deterioration of this type of glass decoration. An exhaustive characterization of these products and so a full understanding of the mechanism of their formation may lead to the development of new protective materials for conservation and restoration. XRD experiments at the MCX beamline allowed us to recognize the alteration products on the grisailles surface and to propose a mechanism for the formation of alteration patinae. Here we present the beamline and its capabilities by showing an example of the study on grisaille paints.

I. INTRODUCTION

The beamline Material Characterization by X-ray diffraction (MCX), is the general purpose powder diffraction beamline at the Elettra synchrotron in Trieste, one of currently four diffraction beamlines at Elettra [1]. The beamline is designed to host a wide range of experiments, that cover many scientific fields with standard applications such as phase identification and structure determination using the Rietveld method or microstructure determination by line profile analysis (see eg. [2, 3, 4, 5]). One of the strengths of MCX is the well-defined narrow instrumental profile, which allows accurate identification of phases in complex mixtures. The large space that is available at the sample position makes it possible to host a range of custom sample holders to study a wide variety of objects, among which those relevant for the field of cultural heritage. Here, a non-destructive study performed at MCX on stained glass is presented.

Since the end of the XIX century the study of glass corrosion and its weathering products was considered of great interest for cultural heritage science. In the last decades the interest of the scientific community was mainly focused on the characterization of glass corrosion products,

their formation processes, and on the development of new materials and strategies for the protection of the glass surface. An interesting and breaking research field, still nowadays almost unexplored, regards the investigations on stained glass windows alteration, especially on those painted using the grisaille method.

Grisaille can be defined as a painting mixture formed by a finely powdered pigment (mainly transition metal oxides) and glass with a low melting point (lead rich glass) forming a colored layer applied on the glass surface, the adherence to the glass being guaranteed by a low temperature firing of the grisaille without melting the glass support. From a chemico-physical point of view, the obtained material is a system in which the crystalline phases (pigments) are embedded in an amorphous phase (low melting glass) which acts both as a dispersing medium and as an agent fixing the pigments onto the substrate (the stained glass window). The interaction of this surface with the environment (i.e. the effect of pollutant agents) promotes the formation of alteration crusts involving both the grisaille paint layer and glass window surface.

The present paper presents the experimental setup and developments of the MCX beamline and illustrates its capabilities by the characterization of the alteration products of ancient grisaille paint layers using non destructive synchrotron x-ray diffraction.

II. THE BEAMLINE

A. The source

The storage ring of Elettra - Sincrotrone Trieste operates at two different energies: 2.0 GeV with a ring current of 310 mA and 2.4 GeV with a current of 160 mA. MCX is installed on a bending magnet X-ray source. When the ring is operating at an energy of 2 GeV its critical energy is 3.2 keV, at $E = 2.4$ GeV the critical energy is 5.5 keV. The source provides a broad energy spectrum with usable photons of energies as high as 25 keV.

B. The optics

The optics of the beamline consist of two mirrors and a monochromator. The first cylindrical mirror is Pt coated and collimates the beam on the monochromator. The second optical element is a fixed exit monochromator equipped with two Si(111) crystals. The second crystal is mounted on a bending mechanism for focusing in the sagittal plane. The second Pt-coated mirror is placed downstream the monochromator and can be used flat or can be bent, with a radius of 6 km for focusing in the longitudinal direction. The overall optical layout works in a strictly 1:1 configuration, with the monochromator at 18 m from the source and the focus (sample position), and the mirrors positioned symmetrically around it. The optics of the beamline produce an X-ray beam with energy between 6 and 21 keV. The beam spot at the experiment can be varied from point focus ($0.3 \times 0.3 \text{ mm}^2$), to line focus ($5 \times 1 \text{ mm}^2$). The flux at the sample is $\sim 10^{11}$ photons per second. The characteristics of the beamline are summarized in table 1. The effect of the the optical elements on the diffraction line profile is discussed in detail in [6].

Table 1. Characteristics of the beamline MCX with the storage ring of Elettra working at 2.0 GeV. The corresponding values for 2.4 GeV are given in brackets.

| | |
|-----------------------|-------------------------|
| The source | |
| Critical energy | 3.2 keV (5.5keV) |
| Width | 0.139 mm (0.197 mm) |
| Height | 0.028 mm (0.30 mm) |
| Vertical divergence | 0.009 mrad (0.009 mrad) |
| Horizontal divergence | 2.0 mrad |
| X-rays at the sample | |
| Energy range | 6-21 keV |
| Photon flux | 10^{11} ph/s |
| beamsize at sample | 0.3 mm x 0.3 mm |

C. The experimental setup

The experimental setup is based on a 4-circle Huber diffractometer, equipped with a high-count rate fast scintillator detector. The 2θ arm can be equipped with a pair of slits or an analyzer crystal for improved angular resolution. In a standard diffraction measurement, data is collected in flat plate (reflection mode) or capillary mode (transmission mode). In the latter case the samples may be cooled to 100K or heated to 1273 K.

As an alternative, a multi-channel analyzer can be installed. This can be used to eliminate the background signal resulting from the fluorescence of the sample in a diffraction experiment, or can be used to perform chemical analysis.



Fig. 1. The diffractometer, equipped with the laser interferometer, hosting an object relevant for cultural heritage for x-ray diffraction analysis.

A laser interferometer is available for accurate sample positioning. The large space at the sample position, together with the the sample positioning system allow measurements of large objects such as shown in Figure 1

The setup shown in Figure 1 allows the measurements of objects in reflection mode. Alternatively, a Mar345 image plate can be used for measurements in transmission mode. As this allows to measure the complete diffraction pattern at once, diffraction mapping of objects can be performed in relatively short times.

An independent experimental setup consists in a furnace that allows to measure powders under controlled conditions to temperatures up to 1273 K. A special capillary holder has been developed to flow gases through the sample while heating. A translating image plate allows to follow the changes in the diffraction pattern during the heating process. This setup, described in detail in [7], can be used for instance to simulate aging processes in pigments. The beamline is completely controlled by a program with a user friendly graphical interface based on the Cyclops suite [8]. New equipment can be easily integrated through its plugin architecture .

III. EXPERIMENTAL

Three glass fragments from The Basilica di San Giovanni e Paolo in Venice were selected to study the alteration processes. The original location in the large windows is shown in Figure 2. Figure 3 shows the fragments, SSGP1, SSGP2 and SSGP3. In table 2 the colors characteristic of the fragments are listed for the glass, the grisaille and the patina.

The glass fragments were measured in grazing incidence geometry. The incidence angle was kept fixed during the measurement at $\sim 2^\circ$. The X-ray wavelength was set to 1.319 \AA . Diffraction patterns were collected in the $5\text{-}60^\circ$ 2θ range, with a step size of 0.01° . The exposure time was

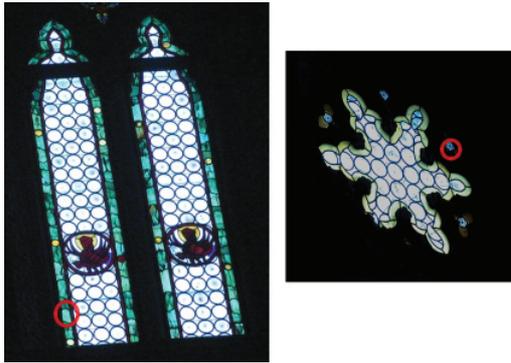


Fig. 2. Windows of the Basilica di San Giovanni e Paolo from which the fragments were selected. The red circle shows the location from which the fragments originate (SSGP1 and SSGP2 left, SSGP3 right)

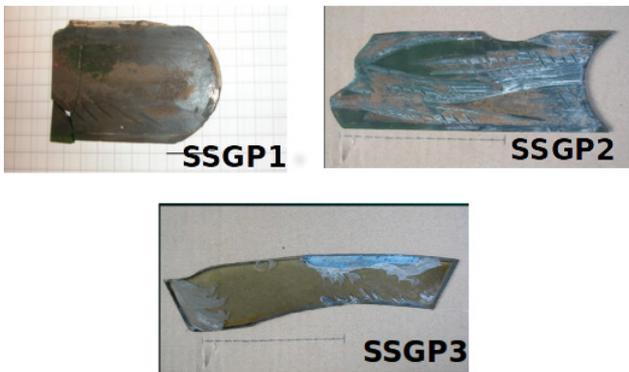


Fig. 3. Fragments, SSGP1, SSGP2 and SSGP3 from the Basilica di San Giovanni e Paolo

one second per point.

The diffraction patterns were subsequently compared with the diffraction patterns of the materials present in the PDF4 database.

IV. RESULTS AND DISCUSSION

A typical diffraction pattern is shown in figure 4. Clearly, the signal to noise ratio is low with a large number of diffraction peaks. The maximum count rate obtained for this measurement was ~ 400 counts per second. This is a clear indication that the amount of crystalline material is very small and, therefore it is necessary to use synchrotron radiation to study these fragments in order to get some information out of the data.

The peaks in the diffraction pattern of the grisaille part of fragment SSGP1 were confronted with the patterns in the PDF4 database. Most of the peaks could be attributed to CoAl_2O_4 (JC-PDF card 01-082-2422), Laurionite ($\text{PbCl}(\text{OH})$) (JC-PDF card 04-012-3672) and Anglesite (PbSO_4) (JC-PDF card 04-008-8386). The remaining peaks

Table 2. Characteristic colors of the glass, grisaille and patina regions of the glass fragments

| Fragment | Glass | Grisaille | Patina |
|----------|--------------|-----------|--------|
| SSGP 1 | green | dark | brown |
| SSGP 2 | green | brown | white |
| SSGP 3 | brigh yellow | blue | white |

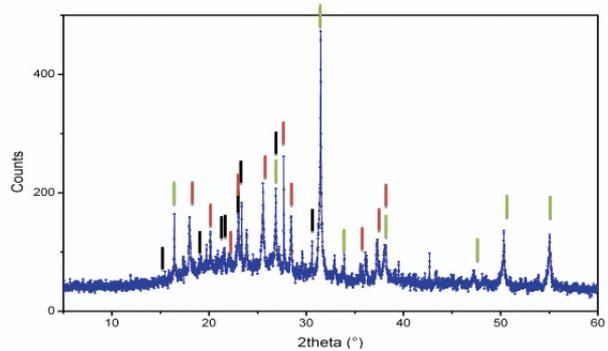


Fig. 4. Diffraction pattern of a part of the grisaille of fragment SSGP1. The positions of the diffraction peaks of the spinel CoAl_2O_4 , (green), laurionite $\text{PbCl}(\text{OH})$ (black) and Anglesite PbSO_4 (red) are indicated.

were too few to assign to other materials.

Phase identification was performed for all measured patterns. In many cases patterns showed no peaks at all and the sample was moved until a signal was detected. For the patina part of SSGP1 no diffraction signal was found. As X-ray diffraction only detects crystalline materials it can be concluded that the material of the patina of SSGP1 is amorphous. The crystalline compounds that were detected on the grisaille and the patina parts of the fragments are listed in Table 3.

The XRD patterns collected show similar results for all fragments. In some cases the original pigments are found such as $\text{Pb}_2\text{Sb}_2\text{O}_7$ or alteration products of the original pigments, such as $\text{FeO}(\text{OH})$ or $\text{FeSO}_4(\text{OH})(\text{H}_2\text{O})_2$. In one fragment the dark grisaille shows the presence of CoAl_2O_4 together with lead sulfate and lead hydroxychloride, $\text{Pb}(\text{OH})\text{Cl}$. The color of cobalt aluminate, a deep blue pigment, which turned to dark, may be due to candle soot deposition or to the overfiring of the glass during the fixing process. The presence of CoAl_2O_4 , which is a pigment first synthesized in the XVIII century [9], evidences a substitution/restoration of the original XV century stained glass windows.

Furthermore, the analysis performed on the white patina, reveals also the presence of sulfates, CaSO_4 , PbSO_4 , and of iron oxyhydroxides, FeOOH . Similar results were obtained for the other fragments, in which sulfates are the

Table 3. Identified compounds on the grisaille and patina regions of the fragments

| Fragment | Grisaille | Patina |
|----------|--|--|
| SSGP 1 | CoAl ₂ O ₄ PbSO ₄ Pb(OH)Cl | amorphous |
| SSGP 2 | Pb ₂ Sb ₂ O ₇ PbSO ₄ CaSO ₄ (H ₂ O) ₂ CaAl ₂ Si ₂ O ₈ | FeO(OH) FeSO ₄ (OH)(H ₂ O) ₂ PbSO ₄ CaSO ₄ (H ₂ O) ₂ Al ₂ Si ₂ O ₅ (OH) ₄ |
| SSGP 3 | CoAl ₂ O ₄ PbSO ₄ CaPO ₃ (OH)·2H ₂ O | SiO ₂ PBS PbSO ₄ CaCO ₃ CaPO ₃ (OH)·2H ₂ O |

predominant compounds found on the alteration patinae. This result is not surprising as sulfur is present in large quantities in seawater. Because of the the location of the Basilica di San Giovanni e Paolo in Venice there has obviously been contact with seawater in the form of aerosols or other.

The presence of phosphates such as found on the patina of SSGP3 is less obvious and has probably a biological origin. This may be due to the fume from burning wax candles.

On the basis of these evidences, a deterioration mechanism can be proposed. An aggressive environment with large thermal variation, typical of the Venice lagoon, can promote microcracking on the grisailles surface. These micro-breaks, together with the natural roughness of the grisailles layer, may favor the condensation processes on the surface. In this way, the formation of a deterioration-induced porous system can act as a series of micro-reactors for leaching phenomena with the subsequent salt precipitation.

Similar results have been reported recently on Spanish 17th century grisailles [10]. Heavy weathering of the samples was reported and as a result of the reaction of Pb with the enviroment, many lead salts, including phosphates and sulfates, have precipitated. A glassy layer with low glass content is observed in the reaction glass/grisaille layer. The investigation presented here does not provide any depth information regarding the identified compounds. In order to get insight in possible layered structures in a further investigation into these samples depth information will be obtained by varying the incidence angle of the diffraction experiment.

V. CONCLUSIONS

The experimental set-up of the MCX beamline at Elettra is described in this paper along with the possibility for non destructive synchrotron X-ray diffraction experiments, especially in the field of cultural heritage research. The characteristics of the beamline and the large space available at the experimental setup allows the study of large objects without the need to remove parts for analysis. The beamline also allows for other type of experiments with the aid of additional equipment such as a furnace, which can be used for example for simulating alteration processes.

The capabilities have been illustrated by the characterization of alteration products on grisaille glass originating from large windows of the Basilica di San Giovanni e Paolo. With the aid of diffraction a large number of degradation products and original pigments could be identified, which allowed the proposition of a deterioration mechanism.

The results presented here show that the bending magnet beamline for X-ray diffraction, MCX, offers excellent opportunities for analysis in the field of cultural heritage. MCX takes part in the project ECHO: Elettra Cultural Heritage Office.

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