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The X-ray diffraction beamline MCX at Elettra: a case study of non-destructive analysis on stained glass

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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. The experimental station houses a large number of instruments facilitating a range of different types of analysis. Recently, a comprehensive study of the alteration products in grisaille paints was performed at the beamline. This type of analysis 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 patina. Here we present the beamline, its instrumentation and its capabilities by showing an example of the study on grisaille paints.

Section: RESEARCH PAPER

Keywords: synchrotron radiation; X-ray diffraction; grisaille; stained glass

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1. INTRODUCTION

The beamline Material Characterization by X-ray diffraction (MCX) is the general purpose powder diffraction beamline at the Elettra synchrotron source in Trieste, Italy, one of currently four diffraction beamlines at Elettra [1]. The beamline is designed to host a wide range of experiments, which 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. Examples can be found in references [2]-[5]. Also in situ diffraction experiments designed for following reaction mechanisms or kinetics can be performed (see e.g. [6], [7]).

One of the strengths of MCX is the well-defined narrow instrumental profile, which allows accurate identification of phases in complex mixtures, which is often the case for objects or fragments that are being studied in the field of cultural heritage. 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 such objects. Here, a non-destructive study performed at the MCX beamline on stained grisaille 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 coloured layer applied on the glass surface. The adherence to the glass is being guaranteed by a low temperature firing of the grisaille without melting the glass support. From a chemical-physical point of view, the obtained material is a system in which the crystalline phases (the pigments) are embedded in an amorphous phase (the 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 the glass window surface.

The Basilica di San Giovanni e Paolo, located in Venice, Italy, has been decorated with windows painted with the grisaille method. The construction of the edifice had been completed around 1430, but the stained glass windows have been placed at the end of the fifteenth century. The long period of exposure to the environment, especially an aggressive environment in the immediate vicinity of seawater, makes these windows excellent case studies for investigating the effect of the environment over a prolonged period of time on these windows. In this study three fragments taken from the large windows of the basilica were analyzed at MCX.

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. In Section 2 we will discuss the setup of the beam line and the possibilities at the experimental station are being outlined. Section 3 gives the experimental details of the study performed on three glass fragments painted by the Grisaille method. In Section 4 the results of this study are being presented and discussed in detail.

2. THE BEAMLINE

2.1. 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

2.2. The optics

The optical setup of the beamline consists 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 are positioned symmetrically around it. The optical setup of the beamline produces an X-ray beam with energy between 6 and 21 keV corresponding to a wavelength between 2.0 and 0.6 Å. The beam spot at the experiment can be varied from point focus (0.3×0.3 mm^2), to line focus (5×1 mm^2). The flux at the sample is ~10^{11} photons per second. The characteristics of the beamline are summarized in Table 1. The effect of the optical elements on the diffraction line profile is discussed in detail in [8].

2.3. The experimental station

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 analyser crystal for improved angular resolution. In a standard diffraction measurement, data is collected in flat plate (reflection mode) or capillary mode (transmission mode). For the latter mode a cryo-stream or a hot air blower may be installed so the samples may be cooled to 100 K or heated to 1273 K.

As an alternative, a multi-channel analyser can be installed. This can be used to eliminate the background signal resulting from the fluorescence of the sample in a diffraction experiment. It also allows measuring X-ray fluorescence from the illuminated spot on the sample. This way chemical element analysis may be performed on the same spot where the diffraction is being measured.

For measurements in reflection mode (often the case for objects rather than powders as for example. in cultural heritage research) a laser interferometer is available for accurate sample positioning. The large space at the sample position in combination with the sample positioning system allows measurements of large objects such as shown in Figure 1.

As an alternative detection setup a MarCCD camera can be installed on the 2θ arm, which can be used both for measurements in transmission mode as well as in reflection mode. As this allows measuring of a large range of the complete diffraction pattern at once, diffraction mapping of objects can be performed in relatively short times. It can also be employed to follow dynamical processes as the exposure time is reduced to 10-60 seconds.

An independent experimental setup consists in a furnace that allows to measure powders under controlled conditions to

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		**X-rays at the sample**	
Critical energy	3.2 keV (5.5 keV)	Energy range	6-21 keV
Width	0.139 mm (0.197 mm)	Photon flux	10^{11} ph/s
Height	0.028 mm (0.030 mm)	Vertical spot size	0.3-1 mm
Vertical divergence	0.009 mrad (0.009 mrad)	Horizontal spot size	0.3-5 mm
Horizontal divergence	2.0 mrad		

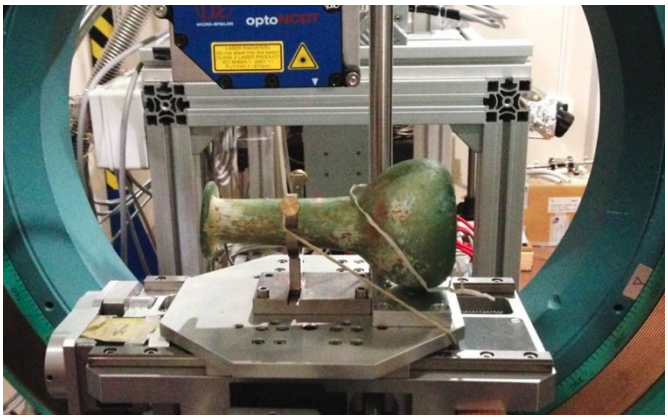

Figure 1. The diffractometer, equipped with the laser interferometer, hosting an object relevant for cultural heritage for x-ray diffraction analysis.

Figure 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).

temperatures up to 1273 K. A special capillary holder has been developed to allow gases to flow through the sample while heating. A translating image plate makes it possible to follow the changes in the diffraction pattern during the heating process. This setup, described in detail in [9], can be used for instance to simulate aging processes in pigments by heating the materials under investigation under a well-defined gas flow in order to speed up the degradation processes that normally occur over a much larger time span.

The beamline is completely controlled by a computer program with a user friendly graphical interface based on the Cyclops suite [10]. The program is written in Python using PyQt for constructing the GUI. New equipment can be easily integrated through its plugin architecture.

3. 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 colours 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 ~2°. The X-ray wavelength was set to 1.319 Å. Diffraction patterns were collected in the 5-60° 2θ range, with a step size of 0.01°. The exposure time was one second per point. The samples were aligned carefully to measure the characteristic areas of the fragments where grisaille paint or patina was located.

The diffraction patterns were subsequently compared with the diffraction patterns of the materials present in the PDF4 database to analyse the crystalline phases present in the illuminated area.

As a control XRF measurements were performed on three points of fragment SSGP1 (glass, grisaille and patina) using an Artax μXRF portable spectrometer from Bruker AXS. The

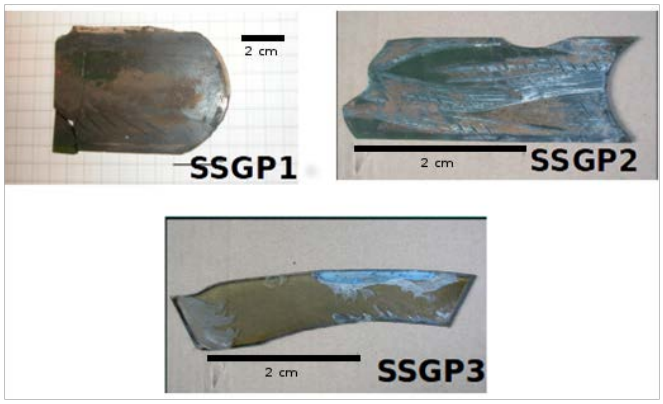

Figure 3. Fragments, SSGP1, SSGP2 and SSGP3 from the Basilica di San Giovanni e Paolo.

spectrometer is equipped with a 50 kV Mo excitation tube, a Peltier-cooled silicon drift detector with an energy resolution of 150 eV at 5.9 keV and 10 × 103 cps. The experimental set-up involves a tube voltage and anode current of 50 keV and 0.7 mA and an acquisition time of 180 s. The incident beam was collimated to a diameter of 1 mm by using a pinhole nozzle. The measurements were performed by fluxing He between sample and detector, in order to increase the detector sensitivity towards the light elements.

4. 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 that, therefore, it is necessary to use synchrotron radiation

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

Fragment	Glass	Grisaille	Patina
SSGP1	Green	Dark	Brown
SSGP2	Green	Brown	White
SSGP3	Bright Yellow	Blue	White

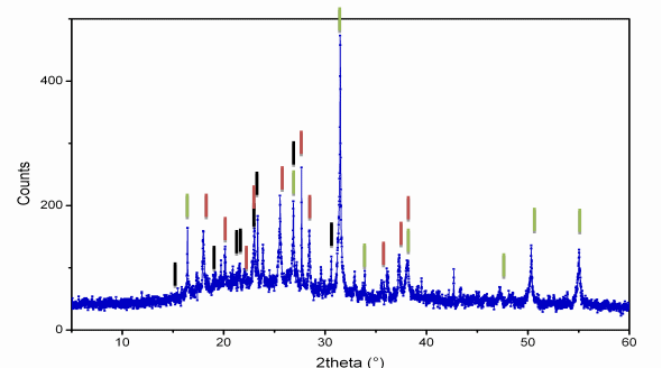

Figure 4. Diffraction pattern of a part of the grisaille of fragment SSGP1. The positions of the diffraction peaks of the spinel $CoAl_2O_4$ (green), laurionite PbCl(OH) (black) and Anglesite $PbSO_4$ (red) are indicated.

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 (PbCl(OH))(JC-PDF card 04-012-3672) and Anglesite ($PbSO_4$) (JC-PDF card 04-008-8386). The remaining peaks were too few and too small to assign to other materials. Laboratory XRF analysis on three points of the same sample (glass, grisaille and patina) confirmed a significantly higher concentration of both lead and cobalt on the grisaille layer.

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 with regards to the quality of the measurements. A low signal to noise ratio was found in all cases, when crystalline material was found at all. In fragment SSGP2 an original pigment was found ($Pb_2Sb_2O_7$) on the grisaille and alteration products of original pigments, such as FeO(OH) and $FeSO_4(OH)(H_2O)_2$. The brown colour of the grisaille of this fragment can be explained by the mixture of yellow lead(II) antimonate darkened by the firing process or in a mixture with brown iron containing salts. In fact two iron containing salts were found on the patina of this fragment. The fact that no iron containing compounds were found on the grisaille may be explained by the nature of the measurements, where some spots are chosen on an inhomogeneous material such as a grisaille layer, where no crystalline iron salts were present. The presence of FeO(OH) and $FeSO_4(OH)(H_2O)_2$ does suggest that iron containing pigments were used in the grisaille of this fragment.

In fragment SSGP1 the dark grisaille shows the presence of $CoAl_2O_4$ together with lead sulfate and lead hydroxychloride, Pb(OH)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 [11], evidences a substitution/restoration of the original XV century stained glass windows. The blue color of the grisaille of fragment SSGP2 is in agreement with the presence of the same pigment.

Furthermore, the analysis performed on the white patina, reveals also the presence of sulfates, $CaSO_4$, $PbSO_4$. Similar results were obtained for the other fragments, in which sulfates are the predominant compounds found on the alteration patina. This result is not surprising as sulfur is present in large quantities in seawater. Because of 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.

Fragment SSGP2 shows the presence of aluminum containing compounds both on the grisaille and on the patina. The origin of these compounds is not clear, although it has been observed in similar studies on stained windows [12]-[14]. Schalm *et al.* [14] in a study of 19th century grisaille paint layers identified the presence of Ca and Al rich particles inside pores in the grisaille suggesting that their origin maybe from burned organic materials used as a painting agent.

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 micro-cracking 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 [15]. Heavy weathering of the samples was

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

Fragment	Grisaille	Patina
SSGP1	$CoAl_2O_4$ $PbSO_4$ Pb(OH)Cl	Amorphous
SSGP2	$Pb_2Sb_2O_7$ $PbSO_4$ $CaSO_4{\cdot}(H_2O)_2$ $CaAl_2Si_2O_8$	FeO(OH) $FeSO_4(OH){\cdot}(H_2O)_2$ $PbSO_4$ $CaSO_4{\cdot}(H_2O)_2$ $Al_2Si_2O_5(OH)_4$
SSGP3	$CoAl_2O_4$ $PbSO_4$ $CaPO_3(OH){\cdot}(H_2O)_2$	SiO_2 PbS $PbSO_4$ $CaCO_3$ $CaPO_3(OH){\cdot}(H_2O)_2$

reported and as a result of the reaction of Pb with the environment, 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.

5. 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 allow 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.

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