EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Combined study of the morphology and composition of historical cobalt green pigment: toward a deeper understanding of the pigment synthesis history and aesthetical value	**Experiment number**: HG188
Beamline:	**Date of experiment**: from: 01/12/2023 to: 05/12/2023	**Date of report**: 16/02/2023
Shifts:	**Local contact(s)**: Pierre-Olivier Autran	*Received at ESRF:*

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Beamtime background summary: The synthesis of cobalt green pigments ($(Zn_{1-x}–Co_x)O$) from the 19th century remains unstudied. However, it resulted in pigments with various Co/Zn ratios, that ultimately influenced their optical properties. A multi-technique investigation coupling XRF-CT and scanning 3DXRD was established during beamtime HG188 to provide high resolution data on the morphology and composition of seven 19th century pigment samples, to better understand their synthesis history and its effect on the final optical properties of the pigment particle. More specifically, the enrichment of cobalt inside of the pigment particles can reach very low dimensions or densities, yet have major effect on its visual appearance. Only the high resolution of XRF-CT and s3DXRD make possible to detail the powder heterogeneous composition at the sub-millimetric scale.

Methodology: The first day of experiment has been dedicated to sample preparation and CT measurements (acquired at 43 keV, resolution 1 µm², and flux of 4.10^8 ph/sec). 7 historical, and 1 modern powder samples were mounted on a kapton grid (200 - 75 µm in diameter) using a UV activated glue (an example is shown in Fig.1a and b). After each scan (20 min/scan) the data were analysed and reconstructed using the beamline inhouse software *tomwer*, based on the python library *Nabu* (Fig.1b and d). CT data were vizualized using *ImageJ*. This first step allowed selecting the area of interest for XRF-CT and s3DXRD. First a transmission image was acquired in the CT scan configuration, then when mounted on the 3DXRD branch, the visible image of the aligned sample allowed to define the sample height of interest and proceed with the scan. 1 day was dedicated to troubleshoot XRF-CT, as the Silicon Drift Detector configuration parameters had to be changed. Then the first exploitable scans were acquired. Two days were dedicated to this technique, and 11 scans were acquired on both historical and standard samples. All XRF-CT data were reconstructed on site (Fig. 2) and XRF data were further analyzed after beamtime using the PyMca software. The XRD data have not yet been analysed. It appears that these data have only mono-crystal profile. Currently, there is no software available at the beamline to analyse these data. Further development with the team are on the way. Thanks to the XRF results, we can focus on some areas of interest to get their pattern of diffraction.

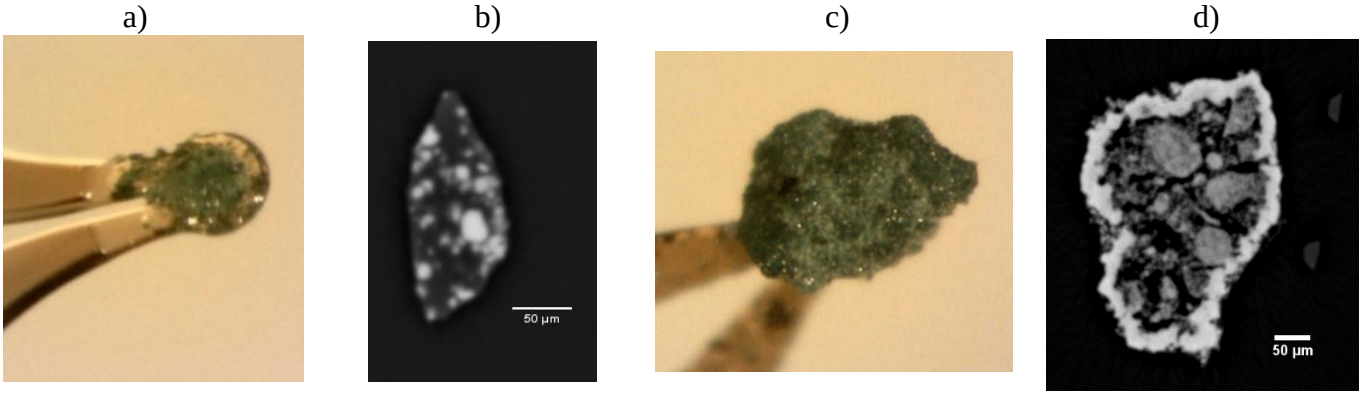

Figure 1: a) Visible image of S1975 on a kapton grid of 75 µm, b) S1975 CT reconstruction (43 keV, resolution 1 μm^2, flux $4*10^8$), c) Visible image of S1976 on a kapton grid of 100 µm, d) S1976 CT reconstruction (same condition as (a))

Results

Phase contrast CT: Two types of particule morphology were distinguished among the pigment powders analysed: i) five sample powders present a very fine yet heterogeneous structure, in which we can determine a particule size ranging from 4 µm to 50 µm, and ii) two samples have an aspect of large agglomerate, with a core composed of individual particles surrounded by an homogeneous shell with a slightly higher phase coefficient.

These mapping have been extremely useful to define region of interests for XRF-CT and 3sDXRD.

XRF-CT: Two main results, correlated with previous CT scans, were observed:

- two different groups inside the fine powder samples were distinguished:
  *four historical samples with an homogeneous repartitions of Zn correlated to various ratios of Co (Fig. 2a). This repartition corroborate the µXRF results previously acquired. These four historical pigments are also those with the closest tints (dark green).
  * one sample with an homogeneous repartition of Zn and a single particle with a sort of cavity of a very high concentration of Co and a low concentration of Zn (Fig. 2b, c). This sample presents a blue-green tint.
- the large agglomerates provide unexploitable data. Indeed, due to the large size and density of these samples, X-rays are re-absorbed by the sample core. These results highlight the importance of the sample selection.

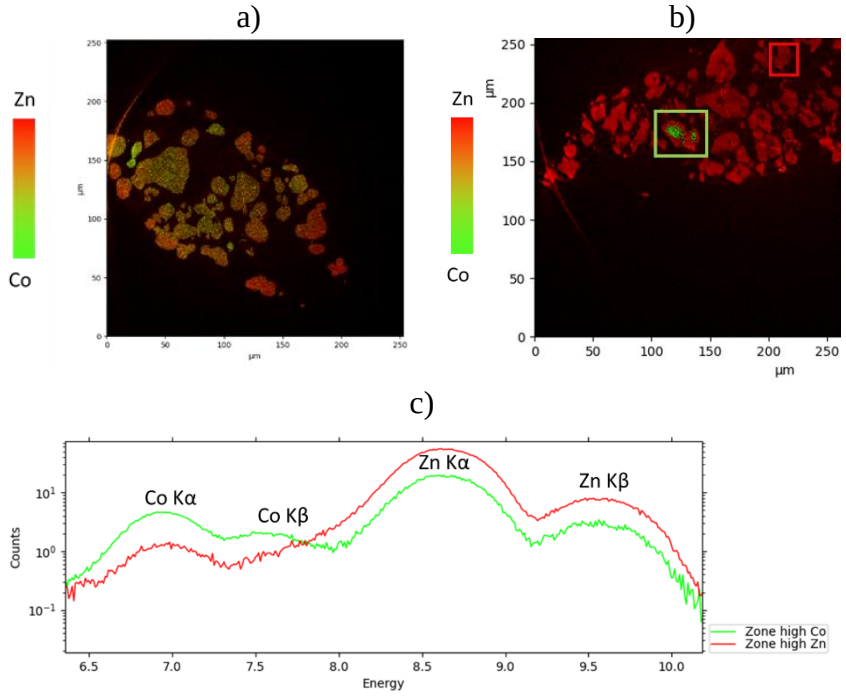

Figure 2: XRF reconstruction (43,56 keV, pixel size : 0,63 µm, image size: 2048x2048 px) of (a) S1975 and (b) S76, c) XRF spectrum of S76, in area of high Co amount (green curve corresponding to the green square in (b)) and low Co amount (red curve corresponding to the red square in (b))

Conclusions:

The whole set of samples (7 historical pigments) have been analyzed with XRF-CT and s3DXRD. The spatial resolution and sensitivity of the approach allowed the study of the Co/Zn distribution at the particle scale. The XRF results highlight two categories of pigments based on the Co and Zn repartition inside the sample that correlate with their tint. XRD results must bring us more information about the cristallography structure (i.e addition or substitution of cobalt on zinc) within the next months.