

Analysis of inorganic pigments by Nuclear Microprobe: the case of the paintings by the Master HGG

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Abstract. The aim of the presentation is to show results of the collaboration between the Croatian Conservation Institute (CCI) and the Laboratory for Ion Beam Interactions of the Rudjer Boskovic Institute (RBI), based on the applications of the nuclear microprobe facility to the analysis of cultural heritage objects. The collaboration is based on characterization of inorganic pigments, alloys and other materials in paintings, statues and ancient buildings that are currently under conservation process performed by CCI. Elemental composition of samples is determined using ion beam analysis techniques, such as Particle Induced X-Ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS). Current collaborative work with the CCI includes the work in progress on the use of the IRB nuclear microprobe in conservation process studies of a church portal, analysis of a bronze statue recently discovered in the Adriatic Sea, and analysis of pigments from different paintings and polychrome sculptures. The presentation is focused on the current project related to the analysis of inorganic pigments from paintings done by the Master HGG (Hans Georg Geigerfeld), painter who was active in the 17th century at the area between Novo Mesto in Slovenia and Zagreb in Croatia (parts of Austro-Hungarian Empire at that time). The specific work presented here is only a part of large collaboration under which several institutions from Croatia and Slovenia have conducted scientific and technical research with the purpose to find out the painter's use of binding mediums and pigments, learn about his painting techniques and hence understand and compare these findings with existing historical data. Conventional samples of paint-layer cross-sections embedded in polyester resin, as prepared for Optical Microscopy (OM), have been used for the analysis of selected paintings using the focused proton beam from the nuclear microprobe. By the detection of characteristic X-rays of elements present in the samples (PIXE), images of elemental distributions at the microscopic level have been obtained. In combination of the data obtained by OM and PIXE, inorganic pigments used by the painter have been identified on selected paintings. Preliminary results of this on-going activity are presented.

1. Introduction

The main analytical laboratory in Croatia dedicated to the analysis of cultural heritage and art objects operates within the Croatian Conservation Institute (CCI). Scientific analysis of artistic and cultural heritage objects is organized by the CCI to enable their better restoration and/or conservation, while from time to time the CCI organizes systematic analysis of artistic objects, especially paintings, to estimate their authenticity and clarify authorship. Chemical analysis of art objects may be essential step in estimating their authenticity, origin and age; and for selecting appropriate restoration or conservation protocol. As the samples of materials that have to be analyzed (pigments and paint layers, ground layers, alloys, etc.) are unique, analysis has to be either non destructive or quantity of material that can be analyzed should be very small. A number of nuclear analytical techniques are suitable and can be applied in such circumstances. Since the CCI analytical laboratory is equipped only with classical chemical techniques, access to nuclear microanalytical techniques is provided through already long and successful collaboration with the Rudjer Bošković Institute (RBI), where elemental composition is analyzed by using ion beam analysis techniques, such as Particle Induced X-ray Emission (PIXE) and Rutherford Back-scattering (RBS), and for the microscopic samples by using nuclear microprobe.

In this respect we have to mention our long time existing collaboration. One of the first successful collaborations between the RBI the CCI was between 1985-86, when the RBI

participated in a project named “Secret paintings of Josip Račić and Miroslav Kraljević – analysis by physical and chemical methods”. The project goal was to perform scientific analysis of paintings done by two important Croatian painters that were active at the period from the end of the nineteenth to the beginning of the twentieth century, to identify the methods and materials used by artists, to compare them, and to present results to the general public. It included analysis by X-rays, infra-red and UV light. RBI analyzed elemental constituents of pigments on 28 paintings. Analysis of pigments was very important part of the overall analysis. The project ended up with an exhibition (that presented all the scientific work) which was held at the Modern Gallery in Zagreb, between 6th March and 6th April 1986 [1].

Since then, a continuous collaboration between the RBI and CCI exists in providing supplementary analysis of samples that require elemental characterization. Collaboration is based on characterization of inorganic pigments, alloys and other materials in paintings, statues and ancient buildings. This is done by analysis of microscopic samples taken from objects at the RBI nuclear microprobe located at the one of the beam lines of the RBI tandem accelerator. Elemental composition is analyzed by using ion beam analysis techniques, such as PIXE and RBS.

Current collaborative work with the CCI includes the work in progress on the use of the IRB nuclear microprobe in a conservation process studies of the southern portal of the St. Marco church in Zagreb, Croatia [2,3], which originates from late 14th to beginning of 15th century, and is currently under the process of conservation. The other projects include analysis of the Apoximenos statue that was recently discovered in the Adriatic Sea, and analysis of pigments from different paintings and polychrome sculptures.

This presentation will be focused to the on-going project related to the analysis of paintings of the 17th century early baroque painter Hans Georg Geiger (HGG). He lived in Slovenia but was engaged at the time equally by the Croatian and Slovenian nobility. He lived in Novo Mesto in Slovenia between 1641 and 1680; while most of preserved documents witness that he had spent a great deal of time in Croatia, working in Zagreb and other towns for Jesuits and Franciscans. In 17th century both Slovenia and north Croatia belonged to the Austrian Monarchy and artists were allowed to circulate throughout its territory. Due to various historical reasons the 17th century artistic heritage in Croatia has been reduced to the minimum so that 32 preserved works by this early Baroque painter represent an important contribution to the history of art in Slovenia and Croatia. About half of his paintings are in Slovenia and the other half in Croatia. The work of the Master HGG presented a challenge since most of his preserved works had not been signed. Recently systematic analysis of Master HGG paintings attracted attention of both Slovenian and Croatian conservators, which resulted in bilateral cultural cooperation. Therefore, the specific work presented here is only a part of larger collaboration under which several institutions from Croatia and Slovenia conducted scientific and technical research with the purpose to find out the painter's use of binding mediums and pigments, learn about his painting techniques and hence understand and compare these findings with existing historical data. In addition, the goal of the project has been to ascertain the authorship of certain paintings for which there was no definite data. The Slovenian colleagues started their work on the Master HGG paintings in Slovenia earlier and they already completed their scientific analysis. The work done in Croatia started later and is still in progress. Therefore, here we will present only results obtained so far.

2. Measurements

Altogether 15 Master HGG paintings located at various places in Croatia (mostly churches) have been analyzed by X-ray imaging, Optical Microscopy (OM) and PIXE in combination with the nuclear microprobe.

X-ray imaging can reveal brushstrokes, over-painting, pentimenti (author's changes to the painting) and in some cases also pigments used. The right side of the Figure 1 shows a detail of the painting of St Michael from Gračani, while the left side shows an X-ray image of the same detail. The difference between the church towers indicates over-painting and a possibility that some kind of restoration was done in the past.



Figure 1. Left: Detail of the painting of St Michael from Gračani. Right: The X-ray image of the same detail. The difference between the church towers indicates that some kind of restoration of this painting was done in the past.

OM is used to investigate paint layers in order to ascertain painting techniques, materials and over-painting. The method requires collection of small samples from the painting that should be embedded in polyester resin and further prepared by grinding and smoothing to a suitable form to investigate paint layers' cross sections under the microscope by using visible or ultraviolet light. Figure 2 shows three samples taken from the painting of St Michael from Gračani prepared for OM. About 100 such samples have been prepared from the paintings.

The same conventional samples of paint layers cross sections embedded in polyester resin as prepared for OM have been used for the analysis using the focused proton beam from the nuclear microprobe. Altogether 28 such samples have been investigated so far at the nuclear

microprobe. By the detection of characteristic X-rays of elements present in the samples by PIXE technique, 2D images of elemental distributions at the microscopic level have been obtained and local elemental concentrations determined from the corresponding PIXE spectra. Pigments used by the painter have been identified on the basis of OM investigations and 2D PIXE images and corresponding spectra.



Figure 2. Typical samples as prepared for OM are suitable for nuclear microprobe investigation. Samples 8207C, 8208D and 8211G are presented here from left to right. They were taken from the painting of St Michael from Gračani.

PIXE measurements were performed by using 10 mm² X-ray SDD detector at the RBI microprobe facility shown on the Figure 3. The scattering chamber is located in the central part of the figure. Two Oxford Microbeam focusing quadrupoles are visible on top. Sample manipulator is on the left and the load-lock chamber for sample insertion into the scattering chamber is visible at the right side. Elements of the beam line for insertion of ion beams from the EN Tandem Van De Graaff accelerator into the microprobe facility are visible on the top left part of the figure. More details about the RBI microprobe facility may be found in [4]. For the measurements, 3 MeV proton beam of about 100 pA current was focused to about 5x5 μm^2 spot size. Elemental distribution maps for major elements were created from the PIXE spectra with the help of the SPECTOR data acquisition and analysis software [5]. The collection time for each 2D elemental map was about 10 to 20 minutes. Point PIXE analysis was done on selected areas of interest and spectra recorded for off line analysis.

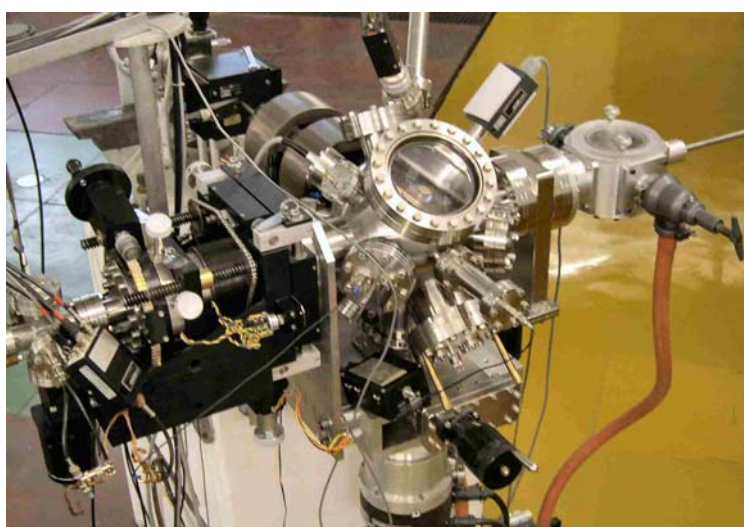


Figure 3. Nuclear microprobe setup at the Rudjer Bošković Institute in Zagreb.

3. Data analysis

Figures 4 and 5 show examples of elemental distribution maps for major elements extracted from the measured PIXE spectra by using the SPECTOR data acquisition and analysis program. They show 2D elemental maps corresponding to the samples 8208D and 8211G that were taken from the painting of St Michael from Gračani (see Figure 2).

Figure 4 shows 2D maps related to the sample 8208D corresponding to K(K), Ca(K), Fe(K), Ni(K), Cu(K) and Pb, where Pb is represented with two maps, corresponding to Pb(L) and Pb(M) X rays. In addition, it shows the corresponding PIXE spectrum that was used to prepare 2D maps. Figure 5 shows 2D maps related to the sample 8211G corresponding to Si(K), K(K), Ca(K), Fe(K), Pb(L), Hg(L) and S(K)+Pb(M)+Hg(M) X rays. In addition, it shows the corresponding PIXE spectrum that was used to prepare 2D maps.

Point PIXE analysis was done on selected areas of interest. As example, in case of the sample 8208D (see Figure 2), four PIXE spectra were collected: one at the surface of the sample, one in the green area (rich in Cu, see Figure 4, Cu 2D map), one in the white area below the green one (rich in Pb, see Figure 4, Pb(L) and Pb(M) 2D maps), and one below the white area (rich in Ca, see Figure 4, Ca 2D map).

In case of the sample 8211G (see Figure 2), two PIXE spectra were collected: one corresponding to the light red area close to the surface (rich in Hg, see Figure 5, Hg 2D map), and the other one corresponding to the dark red area (with the presence of Pb and without Hg, see Figure 5, Pb and Hg 2D maps).

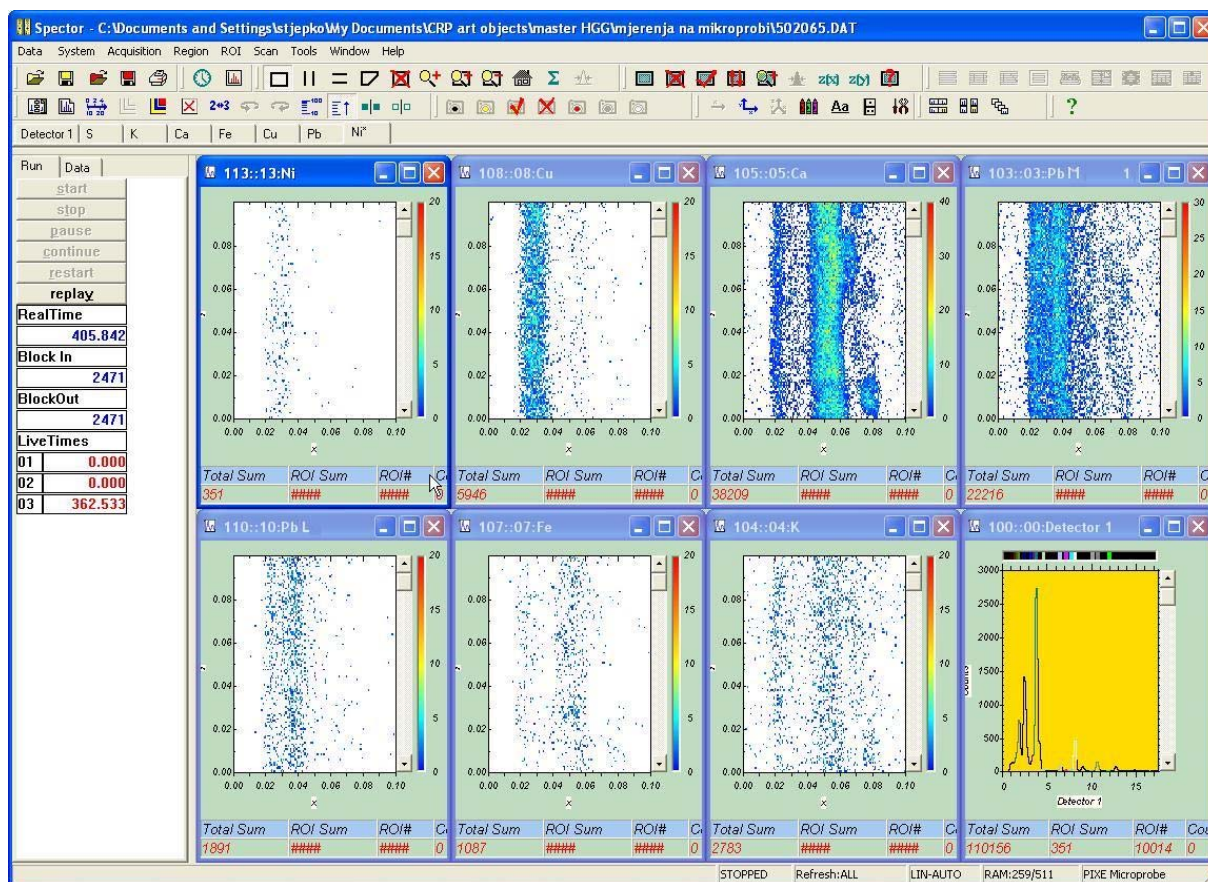


Figure 4. 2D elemental distributions for the sample 8208.

Elemental concentrations were calculated off-line from such measured PIXE spectra by using the GUPIX PIXE analysis program [6]. The pigments used by the painter have been identified by using the data obtained by OM in combination with 2D elemental maps and elemental concentrations calculated from the collected PIXE spectra.

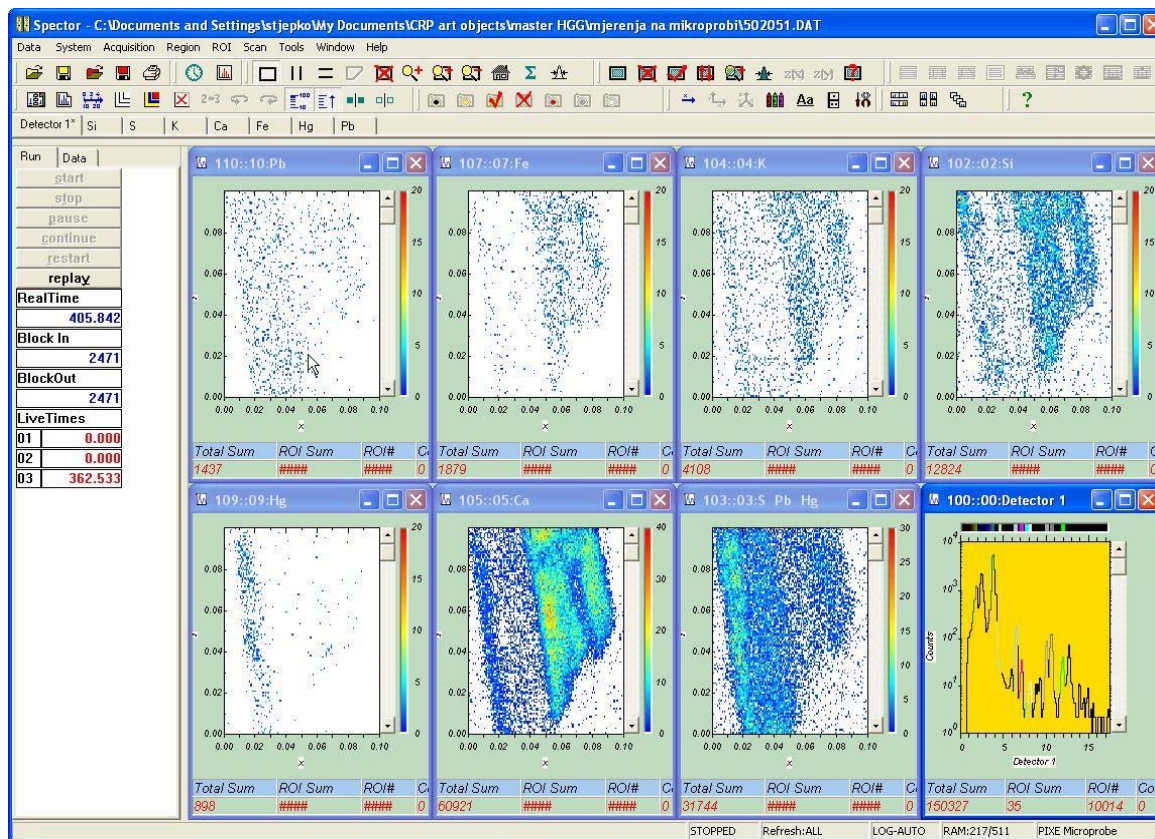


Figure 5. 2D elemental distributions for the sample 8211.

4. Results

As a result of the analysis done, a number of pigments used by the painter have been identified. We can summarise the findings as follows:

- It has been determined that lead white is the only white pigment in almost all of the paintings. This is in agreement with findings of our Slovenian colleagues who investigated the Master HGG Slovene opus.
- Fe yellow ochre is the yellow pigment identified on five paintings.
- Four different red pigments were found: Fe red ochre, HgS (zinniber, vermilion), minium and alizarin. The most common of them is Fe red ochre, that was found on six paintings. In one of the paintings the artist used three different red pigments.
- The most commonly used blue pigment identified is smalt. The other two identified blue pigments are ultramarine and azurite.
- The identified palette contains two green pigments: green earth and copper resinate.

Table 1 shows all so far identified pigments in 15 investigated paintings and associated 28 samples analyzed at the RBI nuclear microprobe facility.

Table 1. Identified pigments in individual paintings.

[illegible]

5. Conclusion

The nuclear microprobe in combination with PIXE and RBS analysis is valuable tool that can help in identification of pigments used by artists to make paintings. Data bases of pigments are needed as a basis for restoration of valuable objects of cultural heritage. Since the technique preserves the sample integrity, the same samples may be reused for complementary analysis by some other technique.

In this particular case, the technique has been successfully used in combination with OM to identify a number of pigments in 15 paintings of the Master HGG. Further analysis of the measured data, in combination with the data obtained by the other techniques will help to get the overall picture and understanding of the full Master HGG opus.

5. Acknowledgment

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