ANALYSIS OF THE PAINTING “THE FIRST MASS IN BRAZIL” (VITOR MEIRELES) USING A PORTABLE XRF SYSTEM

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ABSTRACT

Energy Dispersive X-Ray Fluorescence was used to analyze the painting “The First Mass in Brazil”, identifying the pigments used by the artist, areas that revealed signs of previous retouchings and visible alterations in the paint layer, in order to settle the best procedures to its recovery. This painting, executed by Vitor Meireles in 1860, is one of the most powerful and definitive images ever created by a Brazilian artist. The measurements were carried out with a portable EDXRF system consisting of a TF3005 x-ray tube from Oxford with W anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. The results revealed that the drawings were made over a preparatory layer of zinc and lead white pigments. Some pigments used by the artist were: ochre, umbra, vermilion, Prussian blue, chromium oxide and cobalt blue.

1. INTRODUCTION

This work used Energy Dispersive X-Ray Fluorescence (EDXRF) to characterize one of the most famous Brazilian paintings from the XIX century, belonging to the National Museum of Fine Arts Collection. “The First Mass in Brazil” (“Primeira Missa no Brasil”) was executed by Vitor Meireles, in 1860, with academic rigor involving a documentary research developed at the Sainte Geneviève Library, in Paris, and dozens of preliminary studies. To get inspiration the artist read the historic letter written by Pero Vaz de Caminha, describing the arrival of Portuguese navigators in Brazil and their first contact with the Indians. Soon this work becomes one of the most powerful and definitive images ever created by a Brazilian artist. Vitor Meireles de Lima born as a poor child, son of Portuguese immigrants, in Nossa Senhora do Desterro (Florianópolis) in August 18, 1832. Discovered by the Imperial Counselor Jerônimo Francisco Coelho, at about 14 years old, he was sent to Rio de Janeiro in February 1847 to attend the drawing classes at the Imperial Academy of Fine Arts. At 20 years old, he won the 7th Europe Travel Prize, with the painting “St John Baptist in Prison”, and traveled to improve his skill in Europe. During the second half of the XIX century he shared with Pedro Américo the distinction of being the most popular artists in Brazil. He died in Rio de Janeiro, in February 22, 1903.
EDXRF and CR corresponded to the first part of a meticulous restoration process, recently performed. These techniques were used to evaluate the general conditions of the painting, identifying problems, areas that revealed signs of previous retouchings and materials employed by the artist in order to settle the best procedures to its recovery. In the figure 1 is shown the painting before restoration. XRF analysis is a widely used spectroscopic technique in archaeometry to investigate the composition of pigments (in manuscripts, paintings, ceramics and other artifacts), metal alloys, coins and statuary. It is a non-destructive technique to make possible qualitative and quantitative multielemental analysis with good precision and accuracy [1]. The analysis of the pigments used in a painting is important for many reasons. The first is the possibility of evaluate the artist’s working method, which pigments were used by him, in such way they were mixed to create a specific colouring, and also, which pigments were used in the preparatory layer. This analysis is also an extremely important aid for restoration, since it can help to distinguish the original sections of a painting from restored or later added ones. Thus, pigment characterization may be crucial to important decisions such as those regarding the removal of spurious layers or the choice of the most closely matching pigment for retouchings. A third purpose is related to conservation. Because, depending on their nature, pigments may be sensitive to light, humidity, gaseous atmospheric pollutants or heat, which may require specific storage or display conditions. Additionally, can be necessary the pigments identification before apply any chemical treatment to reverse or to stop a deterioration process. Finally, a characterization of the pigments can help to assigns a probable date to the painting, reconstructing its restoration and conservation history and also detecting forgeries [2,3].

The identification of a pigment is based on its colour and composition. The knowledge of the composition allows the pigment characterization through major or minor constituents and make possible to establish the provenance, age and, consequently, the authenticity of the artifact [4]. Nevertheless, this identification is not always easy and unambiguous and, in many cases, is necessary to use an additional investigative technique. Organic pigments, such as lakes or blacks, or pigments composed of light elements only, e.g. lapis lazuli, cannot be directly detected by the XRF technique. However, their presence may, in some cases, be implied by the absence of certain characteristic heavy element associated with the particular colour under investigation. For blue colours an absence of copper would exclude azurite, verditer blue, etc.; an absence of cobalt would exclude cobalt blue, cerulean blue, smalt, etc.; and an absence of iron would exclude Prussian blue, for example [5].

2. EXPERIMENTAL

The EDXRF analysis of the painting “The First Mass in Brazil” was carried out with a portable system developed by the Nuclear Instrumentation Laboratory, consisting of an Oxford TF3005 x-ray tube, with tungsten (W) anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. The system was placed in a tripod, which made possible to reach higher regions in the painting. In each colour and presumed alteration in the painting were obtained 553 spectra with an acquisition time of 300 seconds and a beam collimation of 2 mm. The spectra were processed and analyzed using the software QXAS-AXIL, from IAEA. To perform the analysis, the painting (2.68 x 3.56 m) was divided in 108 square regions, which were photographed and radiographed.
3. RESULTS AND DISCUSSION

The pigments identified in the painting are shown in table 1. Tungsten (W), found in all spectra, is due to the x-ray tube anode. Calcium (Ca) was identified in several spectra, in low intensities, and seems to be used in small portions, mixed to other pigments, probably as whitening. The results revealed that the drawings were made over a preparatory layer of zinc (ZnO) and lead white (2PbCO₃.Pb(OH)₂) pigments. Lead white is one of the oldest manufactured pigments. Like cinnabar, it was used as a cosmetic by Greco-Roman ladies (as face powder) and its cosmetic use continued during the Middle Age. Zinc white was first produced, in small quantities, as an artificial pigment by Courtois, in Dijon (1780). Due to its price, it was not widely used as a pigment prior to 1835 [6,7].

In the regions of blue sky, were identified: Fe, Co, Zn and Pb. This result indicates the use of Prussian blue (Fe₄[Fe(CN)₆]₃.14-16H₂O) and cobalt blue (CoO.Al₂O₃), mixed with lead white. Zinc appeared in the spectra with very low intensities and seemed to be present only in the preparatory layer. In the regions of cloudy sky it was not found Co, indicating the use of Prussian blue and lead white only. Prussian blue was the first modern artificial pigment. It was discovered accidentally in 1704 by Diesbach, in Germany, and was available to artists in 1724. Cobalt blue was developed in 1802 by Thenard, partly as a result of studying the production of Sévres porcelain, and replaced smalt [7,8,9].
In the analysis of the leaves from the tree located at the right side of the painting, with two Indians over its branches, we can find meaningful differences among its colourings. In the green and dark green leaves the elements identified were: Ca, Cr, Fe, Co, Zn and Pb; indicating the use of viridian (Cr₂O₃.H₂O) or chromium oxide (Cr₂O₃), cobalt green (CoOₙZnO), ochre (Fe₂O₃.H₂O + clay + silica), zinc and lead white. The figure 2 shows the XRF spectra of green, brown and orange leaves. In the spectrum of the dark green leaves it can be observed an increase in the Cr intensities in respect to the green ones, which demonstrates an increase in the quantities of green pigment added to the mixture. In the spectrum of the brown leaves were found the same elements and, consequently, the same pigments, differentiating only in the proportions of pigments used to prepare a specific colouring. Fe shown higher intensities than Cr and Co, which indicates a major use of brown ochre. Finally, in the orange leaves, it was identified mercury (Hg), which indicates the use of vermilion (HgS) mixed to the other pigments. The presence of Cr could be related to some possibilities: a green layer under the orange pigment; contamination from adjacent regions that contained green colour; or already the use of chromium orange (PbCrO₄.Pb(OH)₂) or zinc yellow (ZnCrO₄). In a closer observation, it is possible to note that the artist initially painted all leaves with green pigment and, later, he added other colours (like orange and brown) over the first layer. Therefore, the presence of Cr is related to the pigments viridian/chromium oxide identified in the other leaves. Chromium oxide green was first produced in 1809 and was used on a limited basis until 1820, when a substantial source of Cr ore was found in North America and a large scale production began. Viridian green was discovered as a pigment in 1838 and the process of its manufacturing was patented by Guignet in 1859 [6]. The name “viridian” comes from Latin viridis (green). Cobalt green was developed by Rinmann, a Swedish chemist in 1780. The ochre pigments were used since prehistoric times. The word “ochre” comes from the Greek word ochros (yellow). The chemical responsible for the colour is ferric oxide monohydrated, found mixed with silica and clay. Vermilion was developed by the Chinese around 2000 years before the Romans used it. In the Roman age, cinnabar was mined at Almaden (Spain) and was extensively used in wall decorations and statues at the nobility houses, and also by Roman ladies as lipstick [7].

In the white clothes of the priest and his acolyte, at the main scene of the painting, the elements identified were: Zn and Pb, indicating the use of lead white (Zn presented very low intensities). In the blue clothes, were found: Ca, Fe, Zn and Pb, characterizing the use of Prussian blue. The elements identified in the red clothes of the knights and noblemen were: Ca, Fe, Zn, Hg and Pb, which denotes the use of red ochre and vermilion. Finally, in the yellow clothes, were found: Ca, Fe, Zn and Pb, characterizing the use of yellow ochre. White pigments were mixed to the coloured ones in order to create specific colourings.

In the brown hood of the man, kneeled near to the soldiers, the elements identified were: Ca, Fe, Mn, Zn and Pb, indicating the use of umbra (Fe₂O₃.Mn₂O). However, it cannot be discarded the possibility of a mixture with brown ochre, which also contains iron in its composition. The umber pigments first appeared in the late XV century. In its natural state it is known as raw umber and, when heated it, becomes a richer brown, known as burnt umber. Its original source was Umbria (Italy), although it is also mined in Devon and Cornwall. The word “umber” comes from Latin and means “shadow” [7,10].

In all analyzed regions that presented alterations in the paint layer were identified the same elements: Ca (in low intensities), Ba and Zn (in high intensities). The presence of Ba seems to be associated to lithopone (BaSO₄.ZnS). This white pigment began to be used around 1874 [3] as a substitute or supplement for lead white. This painting was executed in 1860;
consequently, this pigment was used in its first restoration in 1876. At this time, the painting participated in The Philadelphia Centennial Exhibition, which celebrated the 100th anniversary of the beginning of the American Revolution. During the return voyage to Brazil, had been occurred serious damages in the painting, like splits and holes in the canvas. In another alteration area, with apparent mortaring, the XRF spectra revealed the presence of the same elements mentioned above. The only difference was the presence of Ca in very high intensities, which is in accordance with the composition of the mortar used in repairs at this time: calcium sulphate (CaSO₄) or carbonate (CaCO₃) and animal glue (fish glue).

![Figure 2. EDXRF spectra of green (A), dark green (B), orange (C) and brown leaves (D).](image)

4. CONCLUSIONS

The present study reported the use of an EDXRF portable system to analyze a famous Brazilian painting from XIX century: “The First Mass in Brazil”. The XRF results characterized the pigments used by the artist and regions of apparent alterations in the painting, revealing that the drawings were made over a preparatory layer of zinc and lead white pigments. Some pigments used by the artist were: ochre, umbra, vermilion, Prussian blue, chromium oxide and cobalt blue.
REFERENCES


Table 1. Pigments, chemical compositions, colours and period of use.

<table>
<thead>
<tr>
<th>Pigments</th>
<th>Chemical Composition</th>
<th>Colour</th>
<th>Period of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prussian blue</td>
<td>Fe₃[Fe(CN)₆]₃.14-16H₂O</td>
<td>blue</td>
<td>1704 – still in use</td>
</tr>
<tr>
<td>Cobalt blue</td>
<td>CoO.Al₂O₃</td>
<td>blue</td>
<td>1775 or 1802 – still in use</td>
</tr>
<tr>
<td>Viridian</td>
<td>Cr₂O₃.2H₂O</td>
<td>green</td>
<td>1838 or 1850 – still in use</td>
</tr>
<tr>
<td>Chromium oxide</td>
<td>Cr₂O₃</td>
<td>green</td>
<td>Beginning XIX century – still in use</td>
</tr>
<tr>
<td>Cobalt green</td>
<td>CoO.nZnO</td>
<td>green</td>
<td>1780 – still in use</td>
</tr>
<tr>
<td>Green earth</td>
<td>K[(AlIII, FeIII)(FeII, MgII)], (AlSi₃, Si₄)O₁₀(OH)₂</td>
<td>green</td>
<td>Antiquity – still in use</td>
</tr>
<tr>
<td>Vermilion</td>
<td>HgS</td>
<td>red</td>
<td>Antiquity – XX century</td>
</tr>
<tr>
<td>Ochre</td>
<td>Fe₂O₃.H₂O + clay + silica</td>
<td>Red, orange, yellow, brown,</td>
<td>Prehistory – still in use</td>
</tr>
<tr>
<td>Umbra</td>
<td>Fe₂O₃.MnO₂</td>
<td>brown</td>
<td>Prehistory – still in use</td>
</tr>
<tr>
<td>Lead white</td>
<td>2PbCO₃.Pb(OH)₂</td>
<td>white</td>
<td>Antiquity – XIX century</td>
</tr>
<tr>
<td>Zinc white</td>
<td>ZnO</td>
<td>white</td>
<td>1834 – still in use</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO₃</td>
<td>white</td>
<td>Antiquity – still in use</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>CaSO₄.2H₂O</td>
<td>white</td>
<td>Antiquity – still in use</td>
</tr>
<tr>
<td>Lithopone</td>
<td>BaSO₄.ZnS</td>
<td>white</td>
<td>1874 – still in use</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>Fe₃O₄</td>
<td>black</td>
<td>Prehistory – still in use</td>
</tr>
</tbody>
</table>