Abstract

The investigated painting, named as “The woodman” by its owners, is in process of authenticity verification as a Thomas Gainsborough (XVIII century) painting and is under investigation at the Laboratory of Conservation Science (LACICOR), CECOR/EBA/UFMG. The authentication process is still in course. The measurements were carried out in the place where the painting was on custody, with a portable X-rays fluorescence (XRF) system constituted of a X-rays tube with Ag anode, a Si-PIN diode detector, nuclear electronic chain and a specially designed mechanical system for the detector and X-rays tube positioning, that enables angular and XYZ movements of the excitation-detection system. The employed voltage and current intensity of the X-rays tube were 17 kV and 3 mA, respectively. The time of acquisition for each measurement was 500 s. XRF spectra were analyzed using the AXIL-WinQXAS software. Three measurements in each of the following regions of the painting were done: face, leaves, arm, sky and firewood. The carried out analysis indicated the following pigments: White (lead white and calcium sulfate, identified by the elements Pb, Ca and S), Blue (Prussian blue, identified by the key element Fe), Red (Vermilion, identified by the elements Hg and S) and Brown (mixture of Fe and Mn oxides, identified by the elements Fe and Mn). Elements belonging to modern pigments (after XVIII century) corresponding to the same colors were absent in the analyzed spectra.

Keywords: Elementar chemical composition; X-rays fluorescence; Portable EDXRF; Pigments; Painting; Gainsborough

1. Introduction

Energy dispersive X-rays fluorescence (EDXRF) is a well established analysis technique for the identification of key elements in applications where the integrity of samples is a basic requirement of the measurement. Because of the nondestructive feature of X-rays fluorescence (XRF) analysis and the recent development of noncriogenic detectors, suitable for portable systems, over the past few years, a number of valuable studies have appeared focused on the use of portable EDXRF and analytical applications as a sensitive technique in art, archaeometry and conservation sciences [1–3]. Analysis of works of art by EDXRF spectrometry has rapidly increased and it shows the importance of this analytical technique in the study of the cultural heritage.

Portable EDXRF technique was employed to investigate the painting identified by the owner with the title “The woodman”, in process of attribution to the famous English painter Thomas Gainsborough (XVIII), which is under investigation at Laboratory of Conservation Science (LACICOR), CECOR/EBA, Federal University of Minas Gerais, MG, Brazil. The authentication process is still in course.

2. Materials and methods

Measurements were carried out at the place where the painting was guarded. The portable XRF system employed...
was constituted by a X-rays tube with Ag anode (operated at 17 kV and 3 mA), a Si-PIN diode detector (221 eV FWHM for the 5.9 keV line), standard X-rays spectrometry nuclear electronic chain, a 8 K multichannel card, a HP200LX palm top and a specially designed mechanical system for the detector and X-rays tube positioning, which enabled angular and XYZ movements of the excitation-detection system.

Three measurements in each of the following regions of the painting were done: face, leaves, arm, sky and firewood. Fig. 1 shows the painting and the portable EDXRF equipment positioned for data acquisition.

The excitation and detection time was 500 s for all reported measurements.

During the measurements, a qualitative analysis of the X-rays spectra was done in loco, with the aid of the data acquisition system PMCA software, allowing the identification of the pigments main elements. Later, the spectra were analyzed at the Laboratory of Applied Nuclear Physics of the State University of Londrina, using the AXIL-WinQXAS software [4], for the final data reduction.

As the measures were accomplished in air, the Ar line is always present. On the other hand, due to the Ag tube anode, the Ag L-lines overlap with the Ar K-lines, what is not a problem because this analysis does not involve the lines of these elements.

3. Results and discussion

Figs. 2–6 present one of the three X-rays spectra obtained for each measured area shown in Fig. 1.

Table 1 presents the average net areas and standard deviations of the identified elements at face region (flesh color pigment).

All the investigated regions presented a clear and strong lead (Pb) line, indicating a base of “White of lead” pigment
as well as some calcium sulfate (CaSO₄), due to the presence of sulfur (S) and calcium (Ca), under the layers of the colored pigments and/or mixed with them. Part of the sulfur can also be originating from atmospheric pollution deposited on the painting along the time.

In a recent work about a collection of Gainsborough paint bladders, Burnstock et al. [5] analyzed bladders with white pigments and their results indicated the presence of lead carbonate.

The blue pigment in the “sky” region should be the “Prussian Blue” (Fe₄[Fe(CNO)₆]₃), due to the presence of Fe and the absence of key elements of another blue pigments, more recent than the Prussian Blue.

Prussian Blue became very popular for painting and was widely used soon after its introduction, and has been found in several Gainsborough paintings [5].

The largest amount of Fe in the “arm” region in relation, for example, to the “sky” region, indicates the existence of pigments on the base of Fe oxides.

The dominant elements in the “leaves” region are Ca, Fe and Pb. Lead appears here with a larger amount than in all other regions, with the exception of the “face” region. These areas indicate that the green pigment has been obtained by a mixture of Prussian Blue with yellow pigments based on lead and calcium sulfate.

The “natural” candidate for the yellow pigment would be the “Naples Yellow” (Pb₃(SbO₄)₂), very popular at that time, but the Lα line of the key element Sb was totally absent in the spectra. In order to verify the capability of the system to detect this line, which is very close to the Ar Kα line, a thin sample of this pigment was measured and the Sb Lα line was clear in the spectra. Its net area was measured with a 7% standard deviation.

The elements S and Hg in the “face” region indicate the use of HgS (Vermilion) mixed with other pigments. The area of the Hg Lα line was extracted with good precision by AXIL software. This line does not appear clearly in the spectrum of Fig. 5, due to the graphic scale and the background, but it can be seen in Table 1 that this element was determined with 2.7% of deviation, confirming its presence in the spectrum.

The “firewood” region was the only one that presented the element Mn, besides a big amount of Fe. This indicates the use of a brown pigment based on Fe and Mn oxides.

Brown pigments (Umber) were also analyzed in the paper of Burnstock et al. [5] and they agree with the brown pigment characterization of this work.

---

**Table 1**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Lines</th>
<th>Net areas</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Kα</td>
<td>89 067</td>
<td>912</td>
</tr>
<tr>
<td>Cl</td>
<td>Kα</td>
<td>50 293</td>
<td>1262</td>
</tr>
<tr>
<td>K</td>
<td>Kα</td>
<td>56 570</td>
<td>1200</td>
</tr>
<tr>
<td>Fe</td>
<td>Kα</td>
<td>77 957</td>
<td>536</td>
</tr>
<tr>
<td>Hg</td>
<td>Lα</td>
<td>12 761</td>
<td>341</td>
</tr>
<tr>
<td>Pb</td>
<td>Lα</td>
<td>118 621</td>
<td>452</td>
</tr>
</tbody>
</table>

---

**Fig. 4.** X-rays spectrum of the leaves region. Excitation and detection time was 500 s.

**Fig. 5.** X-rays spectrum of the face region. Excitation and detection time was 500 s.

**Fig. 6.** X-rays spectrum of the firewood region. Excitation and detection time was 500 s.

---

(carbonate of lead—2PbCO₃·Pb(OH)₂)
4. Conclusions

The carried out analysis indicated the following pigments: white—Lead White, identified by the elements Pb, Ca and S; blue—Prussian Blue, identified by the key element Fe; red—Vermillion, identified by the key elements Hg and S; brown—mixture of Fe and Mn oxides, identified by the elements Fe and Mn.

Elements belonging to modern pigments corresponding to the same colors were absent in the analyzed spectra.

The pigments found in this analysis are in agreement with the data presented by Burnstock et al. [5], in a recent work about a rare collection of Gainsborough paint bladders.

References