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Pigments Elementary Chemical Composition Study of a Gainsborough Attributed Painting Employing a Portable X-Rays Fluorescence System

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Abstract. The investigated painting, identified with the title "The woodman", is attributed to Thomas Gainsborough (XVIII century) and is under investigation at the Laboratory of Conservation Science (LACICOR), CECOR/EBA/UFMG. The measurements were carried out 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 special designed mechanical system for the detector and X-ray tube positioning, that enables angular and XYZ movements of the excitation-detection system. The employed voltage and current intensity 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 corresponding to the same colors were absent in the analyzed spectra.

Keywords: pigments; EDXRF; chemical elementary composition; authenticity
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1. Introduction

Energy-dispersive X-ray fluorescence (EDXRF) is a well-established analysis technique for the identification of key elements in applications where the integrity of the samples is a basic requirement of the measurement. Because of the non-destructive feature of X-ray fluorescence analysis, over the past few years, a number of valuable studies have appeared focused on its use and analytical applications as a sensitive technique in archaeometry [1]. Analysis of works of art by EDXRF spectrometry has rapidly increased an shows the importance of this analytical technique in the study of the cultural heritage.

Energy Dispersion X-Ray Fluorescence Technique (EDXRF) was employed to investigate the painting, identified with the title "The woodman", attributed to Thomas Gainsborough (XVIII century) which is under investigation at the Laboratory of Conservation Science (LACICOR), CECOR/EBA/UFMG. The authentication is still in course.

2. Materials and Methods

The measurements were carried out with a portable X-rays fluorescence (XRF) system constituted of a X-rays tube with Ag Anode (operated at 17 kV and 3μA), a Si-PIN detector (221 eV FWHM for the 5.9 keV line of Fe), nuclear electronic chain and a special designed mechanical system for the detector and X-ray tube positioning, that enables 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. The Figure 1 show the points measured in the painting.

The excitation and detection time was 500 seconds for all measurements.

The data were analyzed at the Laboratory of Applied Nuclear Physics of the State University of Londrina, Paraná, using the AXIL-WinQXAS software [2]. As the measures were accomplished in air, the line of Ar will always be present. On the other hand, due to the anode of the tube to be of Ag, the line L-lines will be overlap with K of the Ar, what is not problem, because the presented analysis doesn't involve the lines of these elements.

3. Results and Discussion

Figs. 2-6 present the X-rays spectra for each measured area shown in Figure 1, and the table 1 presents the net areas and standard deviations of the face region.

All the investigated regions presented a clear and strong line of the Lead (Pb), indicating a base of Lead white (Carbonate of Lead - $2PbCO_3.Pb(OH)_2$), as well as, some Calcium Sulfate (CaSO4), due to the presence of Sulfur (S) and of Calcium (Ca), under the layers of the colored pigments and/or mixed with them. Part of the

Sulfur can also be originated from atmospheric pollution deposited on the painting along the time.

In a recent work about a collection of Gainsborough paint bladders, Burnstock.A, et al (3) analyzed bladders with white pigments and the results indicated the presence of lead carbonate.

The blue pigment in the "Sky" region should be the Blue of Prussia ($Fe_4[Fe(CNO_9)_6]_3$), due to the presence of the Fe and for the absence of key elements of another blue pigments, more recent than the Blue of Prussia.

Prussian blue became very popular for painting and was widely used soon after its introduction, and has been found in several paintings by Thomas Gainsborough [3].

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.

In the "leaves" region the dominant elements are Ca, Fe and Pb. Lead appears here with a larger plenty amount than in all the other regions, with exception of the "face" region. These areas indicate that the green pigment has been obtained by a mixture of Blue of Prussia with yellow pigments based on Pb and Calcium Sulfate.

In the "Face" region the elements S and Hg indicate the use of HgS (Vermilion) mixed with other pigments. The area of the peak of Hg was extracted employing the sofware AXIL , it doesn't appear clearly in the spectrum of the figure 5 due to the background of the spectrum, but it can be verified in the Table 1 that the net area of this element was determined with just 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 brown pigment based on Fe and Mn oxides.

Brown pigments (umber) were also analyzed in the work of Burnstock. A, et al [3] and they agree with the brown pigments characterization of our work.

4. Conclusions

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 corresponding to the same colors were absent in the analyzed spectra.

The pigments found in our analysis are in agreement with the data presented by Burnstock.A, et al (3), in a recent work about a rare collection of Gainsborough paint bladders.

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3. A. Burnstock, K. J. Berg, R. Bubb, *Proceedings of the 8th International Conference on "Non-Destructive Investigations and Microanalysis for Diagnostics and Conservation of the Cultural and Environmental Heritage"*, Lecce, May 15–19, 2005.

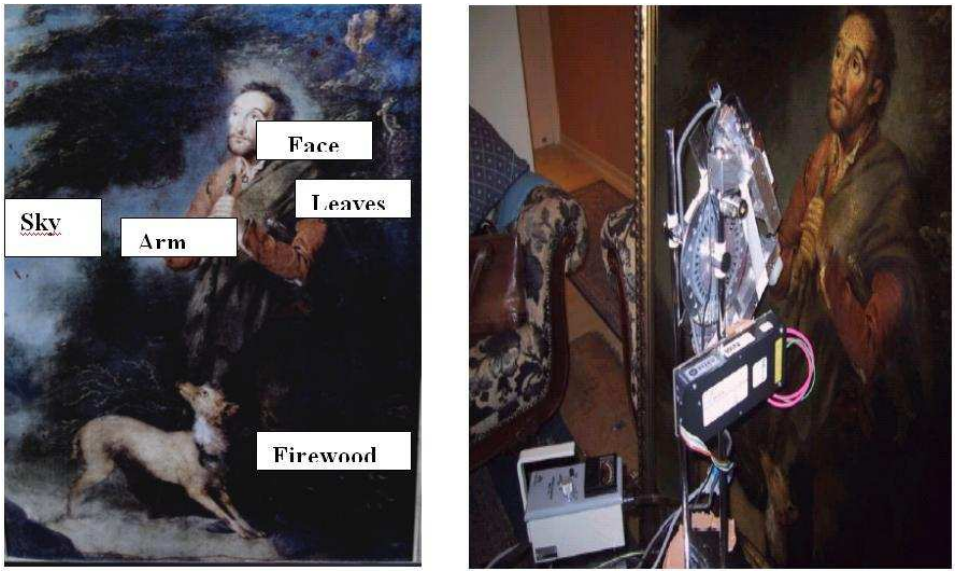

Fig. 1. The points measured in the painting (left) and the portable equipment EDXRF positioned for the measure of an region of the painting (right).

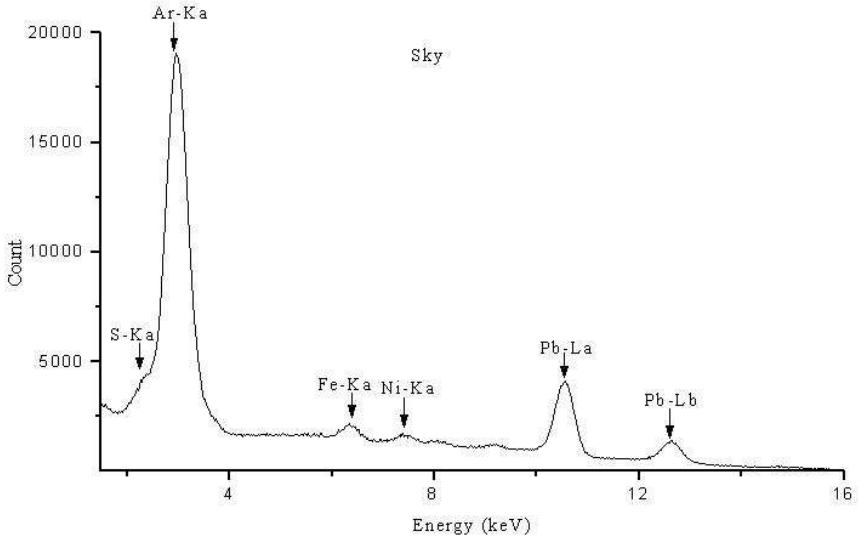

Fig. 2. Spectrum of X-rays of the sky region. Time of excitation and detection was 500 s.

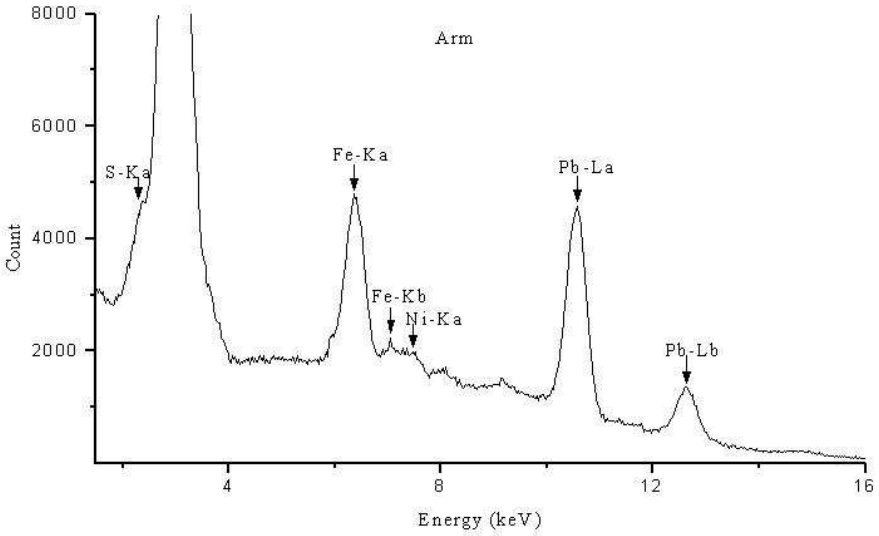

Fig. 3. Spectrum of X-rays of the arm region.Time of excitation and detection was 500 s.

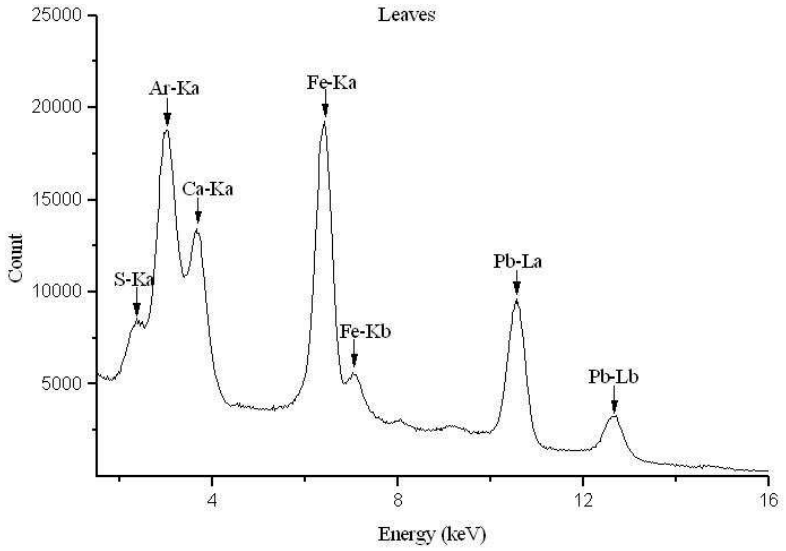

Fig. 4. Spectrum of X-rays of the leaves region. Time of excitation and detection was 500 s.

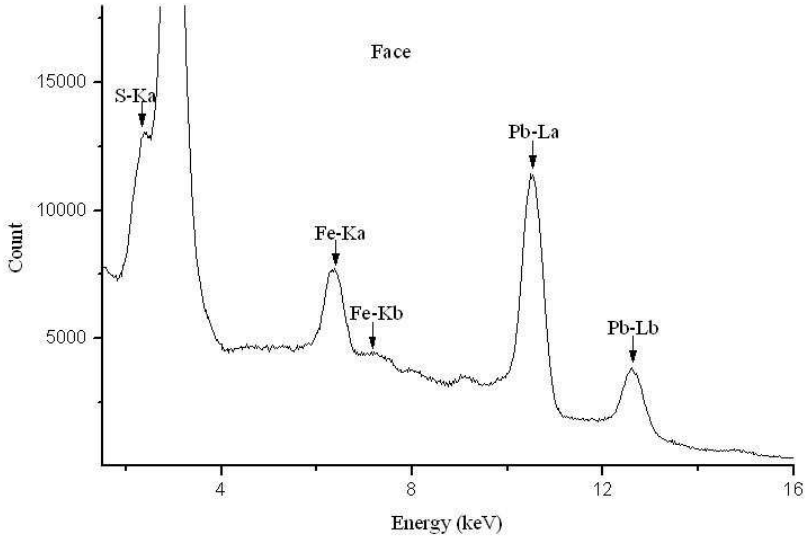

Fig. 5. Spectrum of X-rays of the face region. Time of excitation and detection was 500 s.

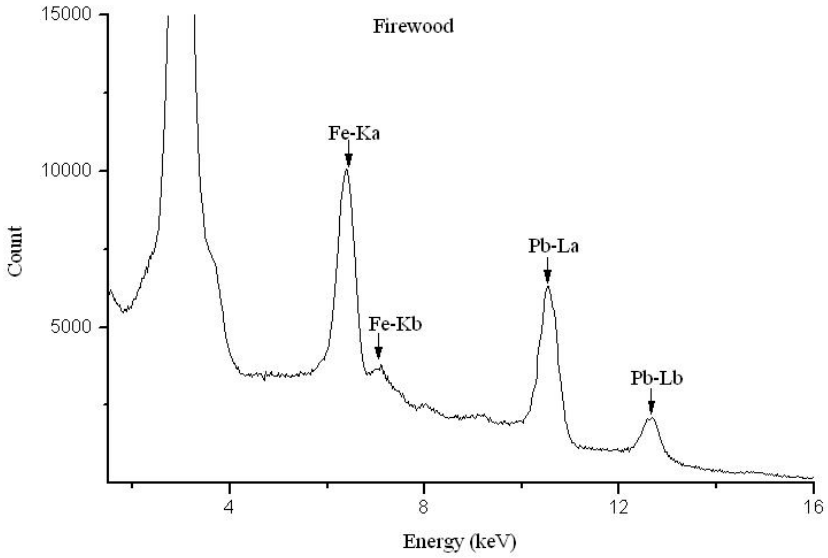

Fig. 6. Spectrum of X-rays of the firewood region. Time of excitation and detection was 500 s.

Table 1-Net areas and standard deviations of the face region (flesh color pigment)

	Face		
Elements	Lines	Net areas	Standard deviation
S	Kα	89067	±912
Cl	Kα	50293	±1262
K	Kα	56570	±1200
Fe	Kα	77957	±536
Hg	Lα	12761	±341
Pb	Lα	118621	±452