BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
09-01A (2021) 01-10

Analysis of Victor Meirelles' painting "*Passagem de Humaitá*" by XRF

Felix[a] V.S., Pereira[b] M.O., Oliveira[a] A.L.C., Pimenta[a] A.R., Silva[a] M.C., Silva[a] M.L., Gonçalves[a] B.L.O., Pereira[a] L.O., Gonçalves[a] E.A.S., Freitas[a] R.P.

[a]*Laboratório de Instrumentação e Simulação Computacional.*
LISCOMP/IFRJ-CPAR, 26600-000, Paracambi, Brasil.
[b]*Centro Federal de Educação Tecnológica Celso Suckow da Fonseca.*
Campus Nova Iguaçu, 26041-271, Nova Iguaçu, Brasil
renato.freitas@ifrj.edu.br

ABSTRACT

Analysis of historical artifacts, it's a multidisciplinary field of research known as archaeometry, has expanded greatly in recent years. One of the reasons for this expansion was the great effort of physicists and engineers, who focused on the development of portable instruments, that allow analyses *in situ* and non-destructive of these artifacts. The X-Ray Fluorescence (XRF) technique is the most used in this field of study. In this work the XRF was used to analyse the artwork "*Passagem de Humaitá*", by the Brazilian painter Victor Meirelles, dated 1872. The painting, which has dimensions of 268 cm x 405 cm, is exhibited at National Historical Museum located in Rio de Janeiro. The analyses were carried out in situ with portable XRF system model TRACER IV from Bruker, which has Rh anode and can operate with maximum voltage and current of 40 kV and 200 µA. Spectra of more than 80 points of the painting were obtained, with the tube operating at voltage of 40 kV and a current of 10 µA, and the spectra were collected during 60 seconds. The results allowed to conclude that the painter used pigments such as vermilion and/or cinnabar [HgS], calcite [$CaCO_3$], zinc white [ZnO], lead white [$(PbCO_3)_2 \cdot Pb(OH)_2$], red ocher [$Fe_2O_3$], brown umbra [$Fe_2O_3.MnO_2$].

Keywords: **XRF, historical pigments, archeometry.**

ISSN: 2319-0612
Accepted: 2020-11-16

1. INTRODUCTION

Since prehistoric times, humans mark their environment in the form of images, ranging from simple fingerprints to wall paintings. For this reason, the analysis of materials used in cultural and historical artifacts, such as paintings and polychrome artifacts, occupies a prominent place in archeometry. The identification of the inorganic pigments and materials used to paint these artifacts are fundamental to promote a better understanding of the history of the object and the technique used by the artist, as well as assisting in the resolution of problems related to conservation, restoration and dating of artworks [1].

Different analytical spectroscopy techniques can be employed, with the purpose of analyzing pigments in works of art. However, due to the peculiarities of the artifacts analyzed in this field of study, which in most cases are single pieces, which add historical and cultural value and often monetary value, it is preferable that these artifacts are subjected to preferably non-destructive examinations. Following this requirement, the elemental characterization by X-Ray Fluorescence (XRF), has a great prominence in the analysis of historical cultural heritage artifacts. In addition to allowing non-destructive examinations, there are currently different types of portable XRF systems, easily operation, which allow in situ analysis [2–10].

In this work, the XRF was employed to investigate, the painting "*Passagem de Humaitá*" of the painter Victor Meirelles. The obtained results allowed to verify the pigments used by the artist in the creative process of the artwork, as well as possible restorations suffered by the painting.

2. MATERIALS AND METHODS

2.1. The painting "*Passagem de Humaitá*"

The canvas "*Passagem de Humaitá*" was painted in 1872 by the Brazilian artist Victor Meirelles and is exhibited at the National Historical Museum (MHN), located in the city of Rio de Janeiro, Brazil. The painting, seen in Figure 1, which has dimensions 268 cm x 405 cm, depicts a historical

moment related to the Paraguayan War, which was the largest armed confrontation in South America.

Figure 1: The canvas "*Passagem de Humaitá*", with the points and where were registered, the spectra by XRF.

Source: Authors.

2.2. XRF analyzes

The analyzes were carried in the MHN, being recorded spectra of XRF in 83 points indicated in Figure 1.

The XRF was performed using a Bruker, commercial, portable system TRACER IV, which has a X-ray tube with an anode Rh, that can operate at a voltage and maximum current of 40 kV e 100 μA, respectively. The system is equipped with X-ray detector, model XFlash® (10 mm²) SDD,

thermoelectrically refrigerated to –15°C with an energy resolution for Mn-Kα of 145 eV and is capable of performing up to 10 kcps. The XRF spectra were acquired directly from the selected points, with the tube operating at 40 kV and 10 μA over 60 seconds.

The spectra obtained were analyzed using software ARTAX version 7.4 from Bruker and PyMca [11].

XRF is an elemental analysis technique, so the characterization of pigments is performed by associating the elements detected in the spectrum with the visible hue. Table 1 reports some of the pigments widely used in the period in which the painting was produced.

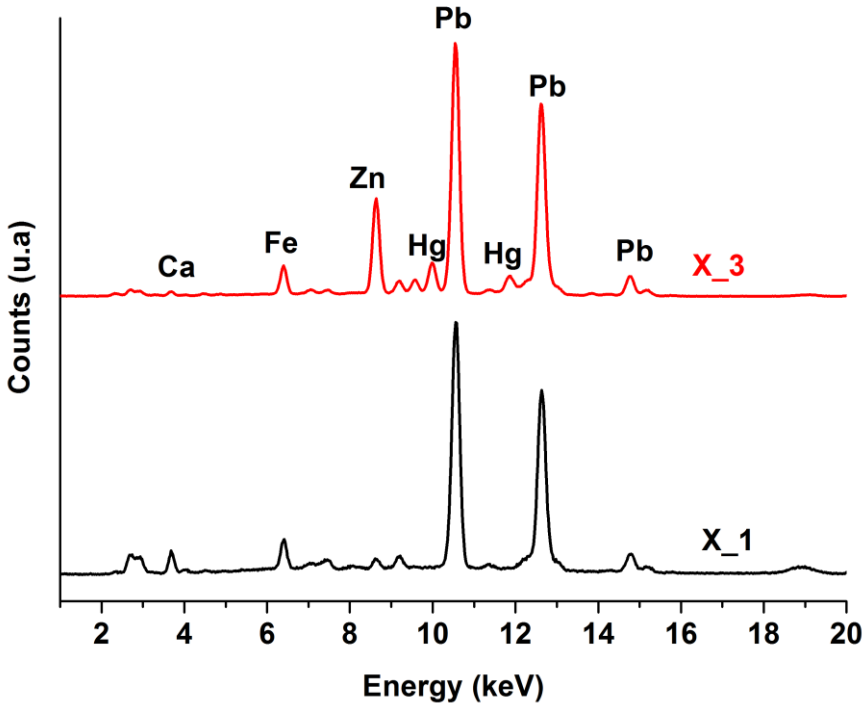
Table 1. Some pigments, used in the 19th century, with the chemical composition formula [12].

Pigment	Chemical Composition	Color
Cinnabar and/or Vermilion	HgS	Red
Red ocher	Fe_2O_3	Red
Umbra	$Fe_2O_3.MnO_2$	Brown
Chromium Óxide	Cr_2O_3	Green
Viridian	$Cr_2O_3.2H_2O$	Green
Lead white	$2PbCO_3.Pb(OH)_2$	White

3. **RESULTS AND DISCUSSION**

With the exception of point 83, which was analyzed in the frame. The results of the other points show that all the recorded spectra are very similar, presenting practically the same elements characterized in all the points, indicating a homogeneity in the pigments. The main difference between the recorded spectra is in spite of the intensity of the elements, which indicate that the shade variations are due to differences in the proportions of the mixed pigments.

Figure 2: Points X_1, collected at the edge, and the point X_3 collected in a region distant from the edge.

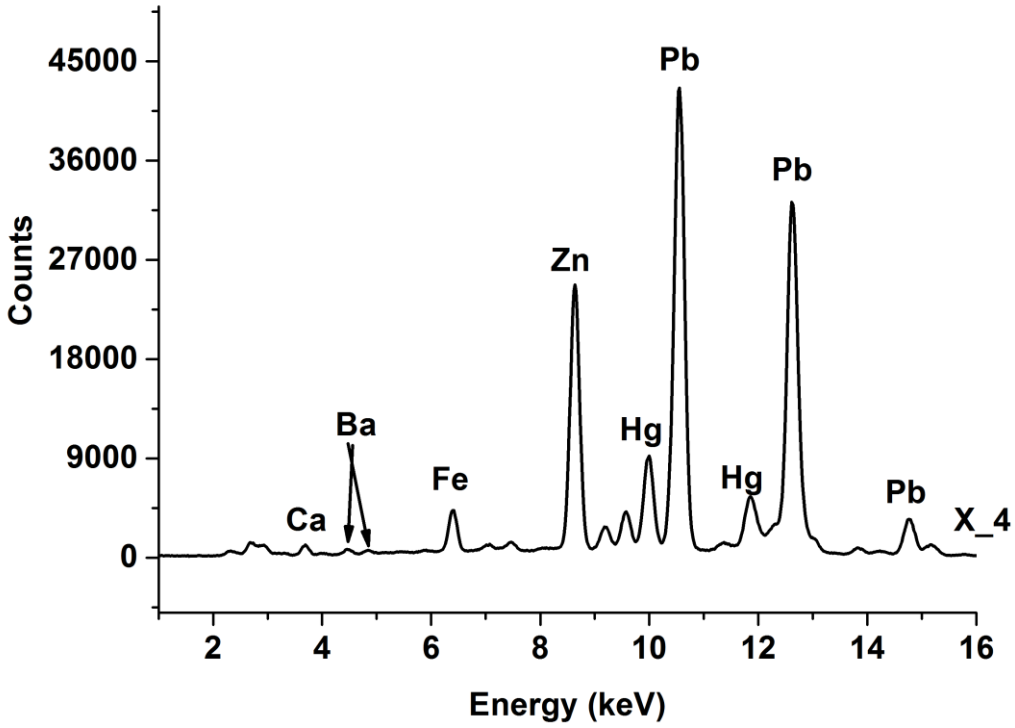


Source: Authors.

The similarity between the spectra can be visualized in Figure 2, which shows the spectra of points X_1, collected at the edge, and the point X_3 collected in a region distant from the edge. The Ca, Fe, Zn and Pb elements, which may be related respectively to the calcite ($CaCO_3$), red ocher (Fe_2O_3), zinc white (ZnO) pigments and lead-based pigments as lead white ($2PbCO_3.Pb(OH)_2$), and/or yellow massicot (PbO) [8,13].

In all spectra the Pb was characterized as a majority element, being the presence of this element due to by the use of pigments with Pb, such as lead white ($2PbCO_3.Pb(OH)_2$), yellow massicot (PbO) and red litharge (PbO). These pigments are also known for their secant properties from Pb, so by the end of the 19th century they were commonly used as the layer of preparation for polychromy in artworks [6,14,15].

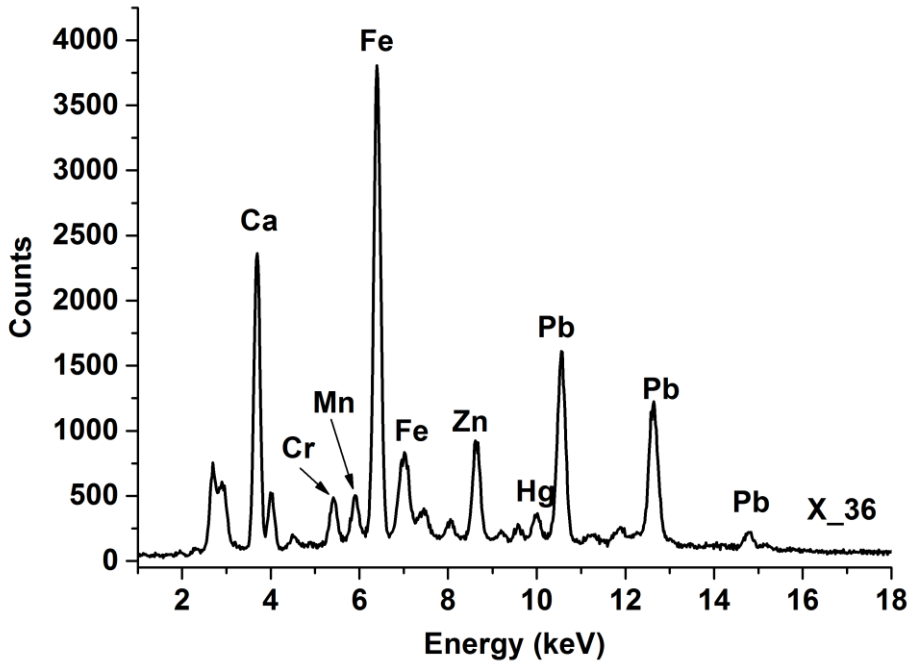
Figure 3: XRF spectrum, collected at point X_4.



Source: Authors.

The Zn is another element with remarkable presence in the spectra including, in regions of red hue, as can be seen to the side in the spectrum of point X_4, showing in Figure 3. This result indicates that the zinc white pigment (ZnO) may have been intentionally mixed, with the other pigment for the purpose of obtaining lighter shades. In some points the presence of Ba, which associated with Zn, was detected, can be correlated to the white pigment lithopone ($BaSO_4$ + ZnS), whose usage record began in 1878 [1,12]. As the beginning of use of said pigment is close to the date of the painting. There is a possibility that the lithopone may have been used by the author himself instead of being correlated to a restoration point.

Figure 4: XRF spectrum, collected at point X_36.



Source: Authors.

The painting shows in majority a reddish tonality, where the Hg and Fe elements were detected in these regions, which are correlated to cinnabar and/or vermilion (HgS) and red ocher (Fe_2O_3) pigments [16], indicating a mixture of these two pigments in the reddish regions. Already in the regions of brown hues was predominant the presence of Fe, where it was also detected the presence of Mn, reminding the presence of the brown pigment umbra ($Fe_2O_3.MnO_2$) [17].

In the point X_36, of brown hue, whose elemental spectrum can be seen in Figure 4, besides Fe and Mn, was detected Cr, which may be related to the green pigment chromium oxide (Cr_2O_3) and/or Viridian ($Cr_2O_3.2H_2O$). A mixture between the brown pigments based on Fe and greens based on Cr was detected in the work of Calza [8], during the analysis of brown regions of the artwork "*Primeira Missa do Brasil"*, also attribuited to the painter Victor Meirelles. This result indicates that this is a mark of the author, which allows him to achieve specific shades of brown in his artworks.

4. CONCLUSION

The results indicated the presence of pigments, which were identified in other paintings by Victor Meirelles, as in the "*Primeira Missa do Brasil*".

It was detected elements that refer to the use of the lithopone pigment, which was used after the date of the artwork. In addition, some points presented results a little different from the others, such as the majority characterization of Zn instead of Pb. This results indicate that the artwork has undergone small interventions, however it maintains its originality to a large extent.

It is also possible to conclude that the artwork is very homogeneous with practically the same pigments in all parts like vermilion, red ocher and umbra. Therefore, the differences in shades observed throughout the artwork, they are due to variations in the proportions of the mixed pigments.

Being the main difference between the points in relation of the intensity of the mixture of pigments used at the each point. This result indicates that the differences in shades, come from the technique used by the artist during the creation process and not specifically from pigments.

ACKNOWLEDGMENT

We thank IFRJ's Pro-rectory of Research, Innovation and Graduate Studies (PROPPI – Pró-reitoria de Pesquisa, Inovação e Pós-Graduação) for financial support from grant number 01/2018. We also thank the Foundation for Research Support of the State of Rio de Janeiro (FAPERJ - Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro), for financial support through project grant numbers E-26/290.066/2018, E-26/202.672/2018 and E-26.201.867/2018. The staff of the National Historical Museum (MHN).

REFERENCES

1. M.L. Franquelo, A. Duran, J. Castaing, D. Arquillo, J.L. Perez-Rodriguez, XRF, μ-XRD and μ-spectroscopic techniques for revealing the composition and structure of paint layers on polychrome sculptures after multiple restorations, *Talanta*. (2012).

doi:10.1016/j.talanta.2011.12.063.

2. R.P. Freitas, Aplicações de Técnicas Nucleares e Espectroscopia Molecular em Arqueometria, Programa de Engenharia Nuclea, COPPE, Universidade Federal do Rio de Janeiro, 2014.
3. V.S. Felix, U.L. Mello, M.O. Pereira, A.L. Oliveira, D.S. Ferreira, C.S. Carvalho, F.L. Silva, A.R. Pimenta, M.G. Diniz, R.P. Freitas, Analysis of a European cupboard by XRF, Raman and FT-IR, *Radiat. Phys. Chem.* **151** (2018) 198–204. doi:10.1016/J.RADPHYSCHEM.2018.06.036.
4. P.H.O.V. Campos, E.A.M. Kajiya, M.A. Rizzutto, A.C. Neiva, H.P.F. Pinto, P.A.D. Almeida, X-ray fluorescence and imaging analyses of paintings by the Brazilian artist Oscar Pereira Da Silva, *Radiat. Phys. Chem.* **95** (2014) 362–367. doi:10.1016/J.RADPHYSCHEM.2013.05.029.
5. R.P. Freitas, C. Calza, T.A. Lima, A. Rabello, R.T. Lopes, EDXRF and multivariate statistical analysis of fragments from Marajoara ceramics, X-*Ray Spectrom.* **39** (2010). doi:10.1002/xrs.1200.
6. C. Calza, M.O. Pereira, A. Pedreira, R.T. Lopes, Characterization of Brazilian artists' palette from the XIX century using EDXRF portable system, *Appl. Radiat. Isot.* (2010). doi:10.1016/j.apradiso.2009.10.049.
7. P.H.O. V Campos, E.A.M. Kajiya, M.A. Rizzutto, A.C. Neiva, H.P.F. Pinto, P.A.D. Almeida, X-ray fluorescence and imaging analyses of paintings by the Brazilian artist Oscar Pereira Da Silva, *Radiat. Phys. Chem.* (2014). doi:10.1016/j.radphyschem.2013.05.029.
8. C.Calza, Desenvolvimento de sistema portátil de fluorescência de raios x com aplicações em arqueometria, Programa de Engenharia Nuclear, COPPE, Universidade Federal do Rio de Janeiro, 2007.
9. L.N.C. Castro, C. Calza, R.P. Freitas, A. Brancaglion, R.T. Lopes, Analysis of Ancient Egypt artifacts using X-Ray Fluorescence, i*n: IMEKO Int. Conf. Metrol. Archeol. Cult. Heritage, MetroArcheo* 2016, 2016.
10. C. Calza, D.F. Oliveira, R.P. Freitas, H.S. Rocha, J.R. Nascimento, R.T. Lopes, Analysis of sculptures using XRF and X-ray radiography, *Radiat. Phys. Chem.* **116** (2015). doi:10.1016/j.radphyschem.2015.04.012.

11. V.A. Solé, E. Papillon, M. Cotte, P. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, Spectrochim. Acta - Part B At. Spectrosc. (2007). doi:10.1016/j.sab.2006.12.002.

[12] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Raman spectroscopic library of natural and synthetic pigments (pre-∼ 1850 AD), *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* (1997). doi:10.1016/S1386-1425(97)00140-6.

13. P.H.O. V. Campos, Caracterização de pinturas da artista Anita Malfatti por meio de técnicas não destrutivas, Instituto de Física, Universidade de são Paulo., n.d.

14. S. Akyuz, T. Akyuz, G. Emre, A. Gulec, S. Basaran, Pigment analyses of a portrait and paint box of Turkish artist Feyhaman Duran (1886-1970): The EDXRF, FT-IR and micro Raman spectroscopic studies, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* (2012). doi:10.1016/j.saa.2011.12.046.

15. R.P. Freitas, I.M. Ribeiro, C. Calza, A.L. Oliveira, V.S. Felix, D.S. Ferreira, A.R. Pimenta, R. V. Pereira, M.O. Pereira, R.T. Lopes, Analysis of a Brazilian baroque sculpture using Raman spectroscopy and FT-IR, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **154** (2016) 67–71. doi:10.1016/j.saa.2015.10.013.

16. M.L. Franquelo, J.L. Perez-Rodriguez, A new approach to the determination of the synthetic or natural origin of red pigments through spectroscopic analysis, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **166** (2016) 103–111. doi:10.1016/J.SAA.2016.04.054.

17. F.A.C.R. de A. Sanches, R.C. Nardes, H.S.G. Filho, R.S. dos Santos, O.M.O. de Araújo, A.S. Machado, T. Calgam, R. Bueno, C. Canellas, E.A.S. Gonçalves, J.T. Assis, R.P. de Freitas, D.F. de Oliveira, R.T. Lopes, M.J. dos Anjos, Characterization of a sacred statuette replica of "Nossa Senhora da Conceição Aparecida" using X-ray spectrometry techniques, *Radiat. Phys. Chem.* (2019). doi:10.1016/J.RADPHYSCHEM.2019.04.016.