IMEKO International Conference on
Metrology for Archaeology and Cultural Heritage
Torino, Italy, October 19-21, 2016

# Analysis of Ancient Egypt artifacts using X-Ray Fluorescence

L.N.C. Castro[1], C. Calza[1], R.P. Freitas[2], A. Brancaglion Jr.[3], R.T. Lopes[1]

[1] *Nuclear Instrumentation Laboratory, COPPE/UFRJ, P.O. Box 68509, 21941-972 Rio de Janeiro, Brazil, ricardo@lin.ufrj.br*
[2] *IFRJ, Paracambi, Rio de Janeiro, Brazil*
[3] *National Museum/UFRJ, Rio de Janeiro, Brazil*

***Abstract* – In this work, X-Ray Fluorescence technique (XRF) was applied in the analysis of the pigments used in decorative paintings that adorn Ancient Egypt artifacts. The analyzed objects were four coffins, a coffin fragment and a funerary mask - belonging to the Egyptian Collection of the National Museum (Rio de Janeiro, Brazil). The analyses were performed using an EDXRF portable system, consisting of an X-ray tube Mini-X with W anode, operating at 30 kV and 40 µA, and a detector X-123 SDD, both from Amptek. The possible pigments employed in the artifacts decoration were identified by the presence of key elements in the spectra associated with the color of the analyzed region. The results revealed the use of red and yellow ochre, realgar, orpiment, Egyptian blue, Egyptian green, malachite, bone black, calcite and gypsum.**

## I. INTRODUCTION

In the last years, the scientific examination of archaeological objects, belonging to museum collections, has reached a remarkable development, allowing the interaction between different fields of science. This kind of analysis can provide information about the chemical or elemental composition of the artifacts, manufacturing techniques and production centers - that makes possible to reveal past technologies, migration of peoples, possible trade routes - and also allows to associate these artifacts to a historical period, assisting in the identification of forgeries and in the evaluation of conservation and restoration procedures. There is also an increasing trend for non-destructive investigations since most of the samples are unique and precious objects that represent the culture and history of a civilization [1-8].

The X-Ray Fluorescence technique (XRF) is one of the most used non-destructive techniques in the analysis of museum collections, providing the elemental composition of pigments, ceramics, coins, metals, gemstones, rocks, etc. [1-7].

The analysis of the pigments used in paintings is extremely important for restoration procedures, since it can help to distinguish the original regions from retouching or later added ones. With regard to conservation, it allows to identify pigments that may suffer degradation, in order to adopt specific practices for storage and/or exhibition of paintings and decorated artifacts, and in the choice of the most suitable treatments to reverse or to stop these deterioration processes [9].

The analytical identification of a pigment by means of XRF technique involves its color and composition (presence of specific key elements). Since the chronology of pigments use is well stablished in the literature, is possible to determine in some cases - based on the analysis of XRF spectra - the provenance, historical period and, consequently, the authenticity of a painting or artifact. However, organic pigments, or pigments composed only by light elements (low atomic number), cannot be directly detected by this technique. Furthermore, the use of mixtures of various pigments as well as the superposition of several paint layers can be hampered the analysis [3, 9].

The National Museum houses probably the oldest Egyptian collection in the Americas. Most pieces of this collection were acquired in 1826, when the Italian trader Nicola Fiengo brought from Marseille (France) to Rio de Janeiro various antiquities excavated by Giovanni Battista Belzoni in the necropolis of Thebes, at Karnak Temple. The artifacts were bought by the Brazilian Emperor Dom Pedro I and donated to the Royal Museum (established in 1818). In 1892, after the Brazilian Republic Proclamation, the museum changed its name to National Museum. Nowadays the museum belongs to the Federal University of Rio de Janeiro (UFRJ) and the

Egyptian collection - that contains more than 500 objects - is under the curatorial direction of the Department of Anthropology, Section of Archaeology [10].

The objective of this work was to identify the pigments employed by the ancient craftsmen in decorative paintings that adorn some artifacts belonging to the Egyptian Collection: four coffins, a coffin fragment and a funerary mask.

## II. MATERIALS AND METHODS

### *A. Analyzed Artifacts*

The artifacts analyzed in this work were: the coffins of Sha-Amun-Em-Su (750 BC), Hori (1070-767 BC), Pestjef (1070-767 BC) and Harsiese (650-600 BC); a coffin fragment (1100-1050 BC) and a golden funerary mask (250 BC).

The choice of XRF technique for this analysis was based on the fact that each artifact is a unique piece, with great historical and cultural value, which emphasizes the need to work with a non-destructive method. Furthermore, were also considered aspects such as direct, fast and simple analysis; measurements performed *in situ*, with the analyzed objects at its own exhibition site, without the requirement of transport them to a laboratory.

### *B. EDXRF Analysis*

The analyses were performed with a portable EDXRF system, consisting of an X-Ray tube Mini-X, with W anode, operating at 30 kV and 40 μA, and a detector 123-SDD (12.5 μm Be window) - both from Amptek. The system is fixed in a support with an angle of 60° between the detector and the tube. For each different color analyzed in the paintings, several spectra were obtained, with an acquisition time of 120 s.

## III. RESULTS AND DISCUSSION

The possible pigments used in the decorative paintings were identified by the presence of key elements in the spectra associated with the color of the analyzed region. The following elements were identified in all spectra: S, Ca, W and Sr.

The presence of tungsten (W) is related to the X-ray tube anode, which is constituted by this material.

The presence of strontium (Sr) is related to the high intensities observed for Ca (due to the use of gypsum in the preparatory layer of the paintings). Since these elements present high chemical similarity, strontium can replace calcium atoms in the crystal lattices of various minerals found in nature.

Finally, the presence of calcium (Ca) indicates the use of gypsum ($CaSO_4.2H_2O$) or calcite ($CaCO_3$) in a preparatory layer, under the decorative paintings. Sulphur (S) was also identified in all spectra, although in low intensities, due to the fact of this element present low atomic number, which makes its detection more difficult at the experimental conditions mentioned above. The use of gypsum in the manufacturing of Egyptian cartonnage and calcite (with smaller amounts of gypsum) in preparatory layers of decorated artifacts has been reported [2, 11].

Most of the trace elements identified in the spectra - as the case of K, Ti, Mn, Cu and Zn - can be considered as impurities from the raw materials employed in the manufacture of the pigments by the Egyptian craftsmen. The presence of traces of K, Ti, Mn, Cu and Zn were identified in pigments of the Roman Age [12] and in Egyptian pigments from the Roman Period [2], both analyzed by μXRF. The presence of Ti, usually associated with modern paintings, has been reported in ancient Egyptian and Roman age pigments by some authors [2, 12, 13]. Ti, Mn, Zn, and other elements considered "moderns", can be found as common impurities in earth colours like red and brown. In addition, the minerals hematite and goethite, used to obtain ochre pigments, can be found associated to anatase or rutile ($TiO_2$), cuprite ($Cu_2O$), microcline ($KAlSi_3O_8$) and other minerals [2].

In the regions showing white color, the presence of Ca, in high intensities, suggests calcite ($CaCO_3$) or gypsum ($CaSO_4.2H_2O$) as possible pigments.

Calcium carbonate is commonly found in nature in its mineral forms aragonite and calcite. Natural calcium sulphates were also widely available in Egypt. Both were extensively used, either as the grounds of paintings to be made on cartonnage or wood, or as pigments used for the final paintings themselves [2, 14-18].

In the regions presenting yellow color, high intensities of Fe could be observed in the spectra, characterizing the use of yellow ochre ($Fe_2O_3.H_2O$) as also reported in various works [2, 18-20]. In some cases, a mixture of pigments was employed, indicated by the presence of Fe, As and S in the spectra. This result suggests mixture of yellow ochre with orpiment ($As_2S_3$), as also reported in a work describing an investigation in the tomb of Menna, located on the Theban Necropolis in Luxor [17].

Earth pigments varying from dull yellow to red and brown are commonly called ochres. Their use as artistic pigments has started in pre-historic times and soon became very common in all over world. Its color is given by a presence of different iron oxides, mainly goethite and hematite; sometimes the colour is brownish due to manganese oxides. The word ‘‘ochre’’ comes from the Greek word *ochros*, meaning yellow. The chemical responsible for the yellow color is ferric oxide monohydrate ($Fe_2O_3$.H2O), and it is found mixed with silica and clay. The pigment, which is essentially yellow clay, is produced by grinding and washing [21, 22].

Orpiment, yellow sulfide of arsenic ($As_2S_3$), was employed in order to obtain bright yellow or gold shades. The mineral is found in volcanic and geothermal regions, although it is also found with limestone and dolomite [21]. The use of this pigment in Ancient Egypt was reported since the 16th century BC by several authors [11, 17, 19, 20, 23, 24]

In the regions of red color, in all analyzed artifacts, was identified the use of red ochre ($Fe_2O_3$), characterized by the presence of Fe in the espectra. In some cases, this pigment was found mixed with realgar ($As_4S_4$), identified by the presence of As and S in the spectra.

Red ochre is produced by heating the yellow ochre to drive off the water and produce anhydrous ferric oxide. By controlling the heating it is possible to produce a range of warm yellows to bright red. Red ochre occurs naturally in volcanic regions where thermal activity has caused the dehydration [21].

Realgar began to be used as pigment in Egypt during the New Kingdom (1570-1080 BC) [16]. The use of red ochre [2, 14, 17, 19, 20, 24] and realgar [2, 17] in the ancient Egypt have been widely reported.

In the regions of orange color, the presence of high intensities of Fe in the spectra suggests the use of ochre pigments based on iron oxides. It could be a mixture of yellow ($Fe_2O_3.H_2O$) and red ochre ($Fe_2O_3$) or a unique compound presenting orange color. Ochre pigments can be found in the nature in a great variety of shades from yellow to red, including brown.

In the blue regions, the spectra exhibited high intensities of Cu. As mentioned previously, Ca was also present in these regions as well in all analyzed spectra, due to its use in the preparatory layer of the paintings. Therefore, the possibilities in this case are Egyptian blue ($CaO.CuO.4SiO_2$) or azurite ($2CuCO_3.Cu(OH)_2$). Since XRF technique is able to determine only the elemental composition of the analyzed samples, besides the fact that Si could not be detected by the equipment, it was not possible to establish which pigment was used. Anyway, the most likely choice would be Egyptian blue; taking into account that azurite was rarely employed as a blue pigment in Egypt [18, 25].

In ca. 3000 BC, Egyptian craftsmen created the first synthetic pigment produced by man, Egyptian blue, which was widely used during the antiquity, spreading all around the Mediterranean basin until the 7th century AD. The Egyptian green pigment, also called green frit, appeared shortly after, presenting the same chemical elements and a turquoise colour. These two pigments have been confused for a long time [26, 27]. The use of Egyptian blue has been reported in several works [2, 11, 17, 19].

Azurite and malachite are chemically similar, comprising basic copper carbonate, and occur as natural minerals which were converted to pigment by crushing and washing. Both appear in Egyptian tomb paintings from the 4th dynasty [21].

In the same way as occurred with the blue regions, the green ones presented high intensities of Cu and also lower intensities of Ca in the spectra (as seen in the figure 1). The possibilities in this case are Egyptian green ($(Ca,Cu)_3Si_3O_9$) or malachite ($CuCO_3.Cu(OH)_2$). The use of malachite as pigment in Egyptian artifacts has been reported in some works [2, 20, 24, 28].

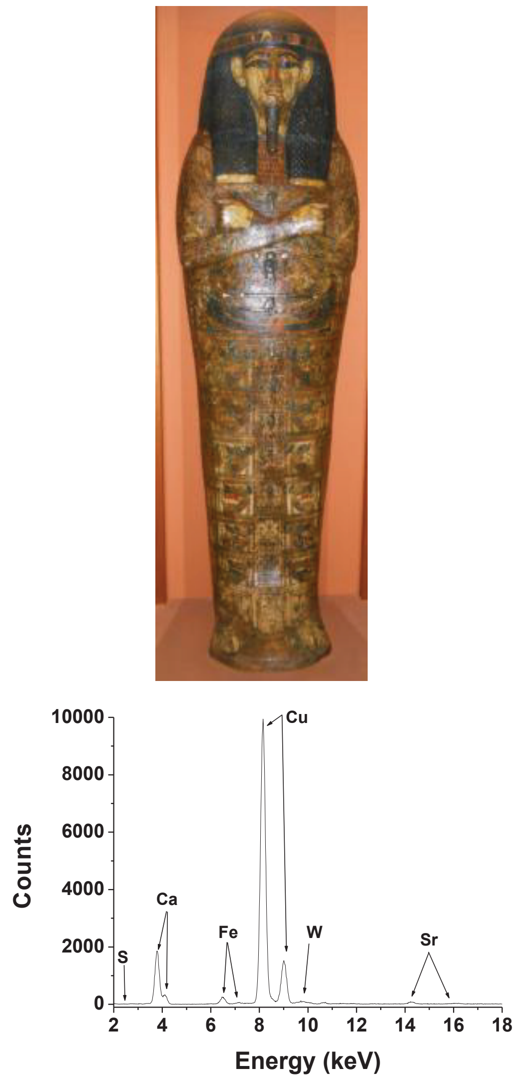


*Fig. 1. (A) Coffin of Hori, 1070-767 BC, 2.15 m. National Museum/UFRJ. Rio de Janeiro, Brazil. (B) XRF characteristic spectrum of the green color.*

The black regions presented high intensities of Ca in the spectra, which suggests the use of bone black pigment ($Ca_3(PO_4)_2 + C + MgSO_4$).

The spectra obtained for the golden region of the funerary mask revealed high intensities of Au, which indicates the use of a gold leaf in the face of the mask, as can be observed in the figure 2. This figure also shows a characteristic XRF spectrum of the golden area. The presence of Fe in the spectrum is related to red ochre pigment applied under the gold layer. The traces of K, Ti and Mn probably are related to impurities present in the red pigment. The presence of Cu is related to Au.

## IV. CONCLUSIONS

This work used XRF technique to identify the the pigments used in decorative paintings that adorn four coffins, a coffin fragment and a funerary mask - belonging to the Egyptian Collection of the National Museum (Rio de Janeiro, Brazil).

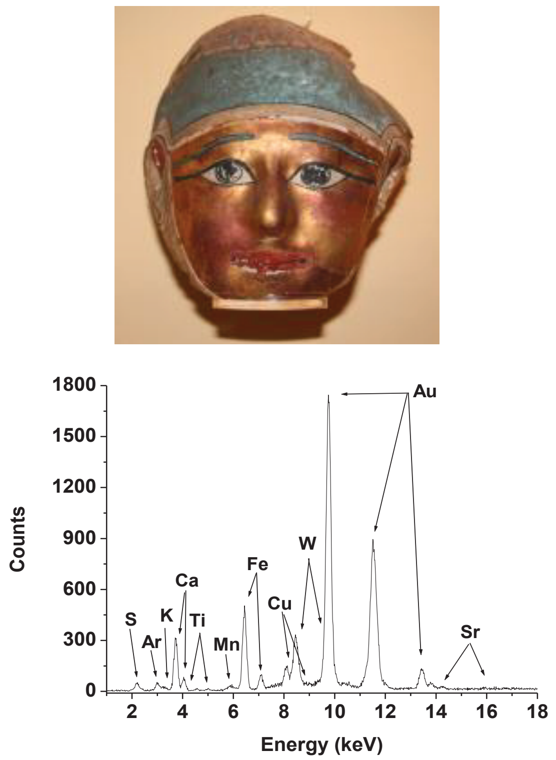


*Fig. 2. (A) Golden funerary mask, 250 BC. National Museum/UFRJ. Rio de Janeiro, Brazil. (B) XRF characteristic spectrum of the golden region.*

The results revealed the use of red and yellow ochre, realgar, orpiment, Egyptian blue, Egyptian green, malachite, bone black, gypsum and calcite. In some cases, a mixture of pigments were employed in order to obtain a distinct hue. A preparation layer of gypsum was applied under the paintings and a thin layer of gold was applied in the funerary mask. Since XRF is an elemental technique, it cannot provide the chemical composition of the analyzed region, but only the chemical elements that are present therein. Due to this characteristic, some pigments could not be identified with precision as in the case of copper-based pigments. Nevertless, the results supplied important information to the archaeologists, which will assist in the study of ancient manufacturing techniques and also in the preservation of these artifacts, attending the demand of the museum staff for a non-destructive, fast and *in situ* analysis.

## ACKNOWLEDGMENTS

The authors thank the Rio de Janeiro State Research Foundation (FAPERJ) and the Brazilian Research Council (CNPq) for the financial support. K.N. Suzuki thanks a grant from the Brazilian Ministry of Science (PNPD/CAPES).

## REFERENCES

[1] C. Calza, M.J. Anjos, M.I.M.S. Bueno et al., "EDXRF analysis of Marajoara pubic covers", Nuclear Instruments and Methods in Physics Research B, vol. 263, 2007, pp. 245–248.
[2] C. Calza, M.J. Anjos, S.M.F. Mendonça de Souza et al., "X-ray microfluorescence with synchrotron radiation applied in the analysis of pigments from ancient Egypt", Applied Physics A, vol. 90, 2008, pp. 75-79.
[3] C. Calza, A. Pedreira, R.T. Lopes, "Analysis of paintings from the nineteenth century Brazilian painter Rodolfo Amoedo using EDXRF portable system", X-Ray Spectrometry, vol. 38, 2009, pp. 327–332.
[4] C. Calza, D.F. Oliveira, H.S. Rocha et al., "Analysis of the painting "Gioventù" (Eliseu Visconti) using EDXRF and computed radiography", Applied Radiation and Isotopes, vol. 68, 2010, pp. 861–865.
[5] R.P. Freitas, C. Calza, T.A. Lima et al., EDXRF and multivariate statistical analysis of fragments from Marajoara ceramics", X-Ray Spectrometry, vol. 39, 2010, pp. 307–310.
[6] R. Cesareo, C. Calza , M.J. Anjos et al., "Pre-Columbian alloys from the royal tombs of Sipan; energy dispersive X-ray fluorescence analysis with a portable equipment", Applied Radiation and Isotopes, vol. 68, 2010, pp. 525–528.
[7] C. Calza, D.F. Oliveira, R.P. Freitas et al.,

"Analysis of sculptures using XRF and X-ray radiography", Radiation Physics and Chemistry, vol. 116, 2015, pp. 326–33.

[8] R.P. Freitas, I.M. Ribeiro, C. Calza et al., "Analysis of clay smoking pipes from archeological sites in the region of the Guanabara Bay (Rio de Janeiro, Brazil) by FT-IR", Spectrochimica Acta A, vol. 163, 2016, 140–144.

[9] R. Klockenkämper, A. Von Bohlen, L. Moens, "Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection X-ray fluorescence spectrometry", X-Ray Spectrometry, vol. 29, 2000, pp. 119–129.

[10] A. Brancaglion Jr., "From Egypt To Brazil: An Egyptian Colletion In Rio de Janeiro". In: M. Eldamati, T. Mai (eds.). Egyptian Museum Collections Around the World. Studies for the Centennial of the Egyptian Museum, Cairo. Cairo: Supreme Council of Antiquities, 2002, pp. 155-162.

[11] D.A. Scott, S. Warmlander, J. Mazurek, S. Quirke, "Examination of some pigments, grounds and media from Egyptian cartonnage fragments in the Petrie Museum, University College London", Journal of Archaeological Science, vol. 36, 2009, pp. 923–932.

[12] G. Paternoster, R. Rinzivillo, F. Nunziata, et al., "Study on the technique of the Roman age mural paintings by micro-XRF with polycapillary conic collimator and micro-Raman analyses", Journal of Cultural Heritage, vol. 6, 2005, pp. 21–28.

[13] M. Uda, T. Tsunokami, R. Murai et al., "Quantitative analysis of ancient Egyptian pigments by external PIXE", Nuclear Instruments and Methods in Physics Research B, vol. 75, 1993, pp. 476.

[14] H.G. Wiedemann, E. Arpagaus, D. Muller et al., "Pigments of the bust of Nefertete compared with those of the Karnak Talat", Thermochimica Acta, vol. 382, 2002, pp. 239–247.

[15] J. Ambers, "Raman Analysis of Pigments from the Egyptian Old Kingdom", Journal of Raman Spectroscopy, vol. 35, 2004, pp. 768–73.

[16] K. Hühnerfuβ, A. Von Bohlen, D. Kurth. "Characterization of pigments and colors used in ancient Egyptian boat models", Spectrochimica Acta part B, vol. 61, 2006, pp.1224-1228.

[17] P. Vandenabeele, R. Garcia-Moreno, F. Mathis et al., "Multi-disciplinary investigation of the tomb of Menna (TT69), Theban Necropolis, Egypt", Spectrochimica Acta Part A, vol. 73, 2009, pp. 546–552.

[18] D.A. Scott, "A review of ancient Egyptian pigments and cosmetics", Studies in Conservation, vol. 61, No 4, 2016, pp. 185-202.

[19] M. Uda, S. Sassa, S. Yoshimura et al., "Yellow, red and blue pigments from ancient Egyptian palace painted walls", Nuclear Instruments and Methods in Physics Research B, vol. 161–163, 2000, pp. 758.

[20] H.G.M. Edwards, S.E.J. Villar, A.R. David, D.L.A. de Faria, "Nondestructive analysis of ancient Egyptian funerary relics by Raman spectroscopic techniques", Anal. Chim. Acta, vol. 503, 2004, pp. 223.

[21] J.R Barnett, S. Miller, E. Pearce. "Colour and art: A brief history of pigments", Optics & Laser Technology, vol. 38, 2006, pp. 445–453.

[22] D. Hradil, T. Grygar, J. Hradilova, et al. "Clay and iron oxide pigments in the history of painting", Applied Clay Science, vol. 22, 2003, pp. 223-236.

[23] M. Uda. "In situ characterization of ancient plaster and pigments on tomb walls in Egypt using energy dispersive X-ray diffraction and fluorescence*", Nuclear Instruments and Methods in Physics Research B, vol. 226, 2004, pp. 75-82.

[24] A.M.B. Olsson, T. Calligaro, S. Colonart, et al., "Micro-PIXE analysis of an ancient Egyptian papyrus: Identification of pigments used for the "Book of Dead", Nuclear Instruments and Methods in Physics Research B, vol. 181, 2001, pp. 707-714.

[25] L. Lee, S. Quirke, "Painting Materials". In: P.T. Nicholson, I. Shaw (eds.). Ancient Egyptian Materials and Technology. New York: Cambridge University Press, 2000, pp. 104-120.

[26] G.A. Mazzocchin, D. Rudello, C. Bragato, F. Agnoli, "A short note on Egyptian blue", J. Cult. Herit., v. 5, 2004, pp.129-133.

[27] S. Pagès-Camagna, S. Colinart, "The Egyptian green pigment: its manufacturing process and links to Egyptian blue", Archaeometry, vol. 45, 2003, pp. 637.

[28] S. Pagès-Camagna, "A Review of Pigment Research at the Louvre Egyptian Collections". In: C. Rozeik, J. Dawson, M. Wright (eds.). Decorated Surfaces on Ancient Egyptian Objects: Technology, Deterioration and Conservation. Cambridge: Fitzwilliam Museum: University of Cambridge, 2010.