2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-04-5**

ANALYSIS OF ARTIFACTS FROM ANCIENT EGYPT USING AN EDXRF PORTABLE SYSTEM

Cristiane Calza[1], Renato P. Freitas[1,2], Antonio Brancaglion Jr.[3] and Ricardo T. Lopes[1]

[1] Laboratório de Instrumentação Nuclear. COPPE.
Universidade Federal do Rio de Janeiro
Caixa Postal 68509
21941-972 Rio de Janeiro, RJ
ccalza@lin.ufrj.br
rfreitas@lin.ufrj.br
ricardo@lin.ufrj.br

[2] CEFETEQ
Rio de Janeiro, RJ.

[3]Museu Nacional/UFRJ
Rio de Janeiro, RJ

ABSTRACT

In this work, XRF technique was used to analyze some artifacts from the Egyptian Collection of the National Museum (Rio de Janeiro, Brazil), which is probably the oldest in the Americas. Most pieces of this collection were acquired in 1826, when the Italian trader Nicolau 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, which donated them to the Royal Museum, established in 1818. The analyzed samples include: a wooden polychrome funerary mask and different kind of sculptures (portraying the god *Bes*, a priest, female and macrophallic figurines and an *ushabti*). The analyses were carried out with an EDXRF portable system developed in the Nuclear Instrumentation Laboratory, consisting of an X-ray tube Oxford TF3005 with W anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. In each sample were obtained several spectra, with an acquisition time of 300 s and a beam collimation of 1.5 and 2 mm. The spectra were analyzed using the software QXAS-AXIL from IAEA. The results revealed the elemental composition of the material employed to execute the sculptures and the original pigments used in the mask and also in the decoration of some sculptures (Egyptian blue, malachite, realgar, red and yellow ochre, black iron oxide, etc.).

1. INTRODUCTION

The scientific examination of archaeological objects, belonging to museum collections, has gained increasing interest in the last years [1-8]. It can supply important information that makes possible to identify past technologies, migration of peoples, possible trade routes, and also to date an artifact, identifying modern forgeries [9]. However, the fact that every artifact is an unique piece emphasizes the necessity of working with non-destructive techniques. Among the techniques used more often for these purposes are the following: X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Particle-Induced X-ray Emission (PIXE), Raman Spectroscopy, Infrared Spectroscopy, Laser-induced Breakdown Spectroscopy (LIBS), Scanning Electron Microscopy (SEM), etc. [5]. XRF is the most widely used investigative technique in the field of archeometry due to a number of favorable analytical characteristics, such as multielemental and nondestructive analysis, high sensitivity and applicability to a wide range of samples [10].

In this work, XRF technique was used to analyze some ancient Egyptian artifacts belonging to the National Museum (Rio de Janeiro, Brazil), which houses probably the oldest Egyptian collection in the Americas. Most pieces of this collection were acquired in 1826, when the Italian trader Nicolau 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, advised by the counselor José Bonifácio de Andrada e Silva, and donated to the Royal Museum (established in 1818). Some years later, the collection was increased by the addition of the coffin of Sha-Amun-em-su ("the singer of Amun") – an offer of the Khedive Ismail to D. Pedro II, which was visiting Egypt. Nowadays, the collection comprises 700 objects like human and animal mummies, coffins, funerary masks and stelae, statues, canopic vases, necklaces, etc.

In case of sculptures, the scientific analysis allows to identify the composition of materials employed in its execution (clay, metallic alloys, rocks, etc.); the pigments used in the polychromy; the presence of retouchings and later additions; evaluate the conservation state (internal damages, crackings, etc.); establish the historical period of the artifact; identify forgeries; etc. The identification of a pigment is based on its color and composition. The knowledge of the composition allows pigment characterization through major or minor constituents and makes possible the establishment of the provenance, age and, consequently, the authenticity of the artifact. Nevertheless, this identification is not always easy and unambiguous and, in many cases, it is necessary to use an additional investigative technique. Since the chronology of use of most pigments is known, is possible to determine an approximate date of an artifact or its restored parts [11].

The analysis of artworks and artifacts belonging to museum collections presents a lot of difficulties regarding its transportation to a laboratory. Some of them are related to the dimensions, sometimes considerable. It also requires expensive infrastructure to avoid physical damages and an efficient security scheme due to the great artistic and cultural values involved. In other cases, the artworks are on public exhibition and cannot be removed from the galleries. Therefore, the use of a portable system is of crucial importance and enables to perform the analyses *in situ*, without removing artworks from pedestals and walls, as the system is connected to a tripod [1,2, 5-10].

2. EXPERIMENTAL

2.1. Analyzed samples

In this work were analyzed, by means of XRF technique, seven artifacts belonging to the Egyptian Collection:

(i) *Face of Woman Coffin* (Inventory number: 2061. Third Intermediate Period, 21st dynasty, c. 1100-1000 BC.). A funerary mask, sculpted in wood, covered with a thin layer of gypsum, exhibiting geometric colored motifs in the head ornament.

(ii) *Statue of a woman* (Inventory number: 98. New Kingdom, 18^{th} dynasty, c. 1388-1348 BC.). This statuette represents a noble Egyptian lady wearing a folded linen dress. She holds a lotus flower in her hands – symbol of rebirth – and exhibits a cone of aromatic animal fat in her head. This kind of female representation shows the sophistication and magnificence characteristic of this period.
(iii) *Shabti of Penmennefer* (Inventory number: 197. New Kingdom, 19^{th} dynasty). Mummyform figurine wearing blue glazed tripartite wig, red and yellow necklace, exhibiting a central band with yellow background and red lines containing a black inscription. The colors and the necklace are typical of the region of Deir el-Medina. The *shabtis, shawabtis* or *ushabtis* are funerary figurines which act as servants of the deceased or as personal substitutes for its master, performing agricultural labor in order to pay tribute to the gods.
(iv) *High priest of Amun* (Inventory number: 81. Third Intermediate Period, 21^{st} dynasty, c. 990-969 BC.). This bronze statue represents the High Priest of Amun, Menkheperre.
(v) *Statue of the god Bes* (Inventory number: 1968. Late Period, c. 380 BC.). The god Bes is portrayed as a nude bearded dwarf with long arms, bowed legs and a face combining leonine and human characteristics, sticking out his tongue. This god was extremely popular and his most important role was to watch over woman throughout their entire pregnancies and during childbirth. Consequently, it was always present at the rich and poor Egyptian homes.
(vi) *Figurine of the god Bes playing tambourine* (Inventory number 201/2. New Kingdom, 18^{th}-19^{th} dynasties, c. 1330-1279 BC.). This statuette, in green Egyptian faience, also represents the god Bes and was used as an amulet.
(vii) *Macrophallic figurine* (Inventory number: 846, Third Intermediate Period, c. 770 BC.). This figurine in blue Egyptian faience, representing a man playing tambourine, was used as a fertility amulet.

2.2. EDXRF measurements

The EDXRF measurements were carried out with a portable system developed in the Nuclear Instrumentation Laboratory, consisting of an Oxford TF3005 x-ray tube and a Si-PIN XR-100CR detector from Amptek (with 6 mm^2 active area and a 25 μm Be window). The X-ray tube presents a tungsten (W) anode, a 127 μm Be window and maximum operating current and voltage of 0.5 mA and 30 kV respectively. The angle between the x-ray tube and the detector window is 60°, the source–sample and the detector–sample distances are 4 cm. A metallic device was developed in order to indicate the exact point of analysis and to maintain the same distance between the system and the sample for all sampling points, ensuring the reproducibility of the measurements. Another device makes possible a fine adjustment of the system: approaching or moving away with regard to the sample. The use of external collimators of aluminum allows analyses near the frames of paintings, in concave or convex areas, in statues and vessels, etc. Furthermore, the system is connected to a tripod, which makes it possible to reach higher regions during the analysis of paintings and statues. The tripod is light to carry and can be easily disassembled for transport [5-8]. In each sample were obtained several spectra, with an acquisition time of 300 s and a beam collimation of 1.5 and 2 mm. The spectra were analyzed using the software QXAS-AXIL from IAEA. In the figure 1 is shown the EDXRF portable system used in this work.

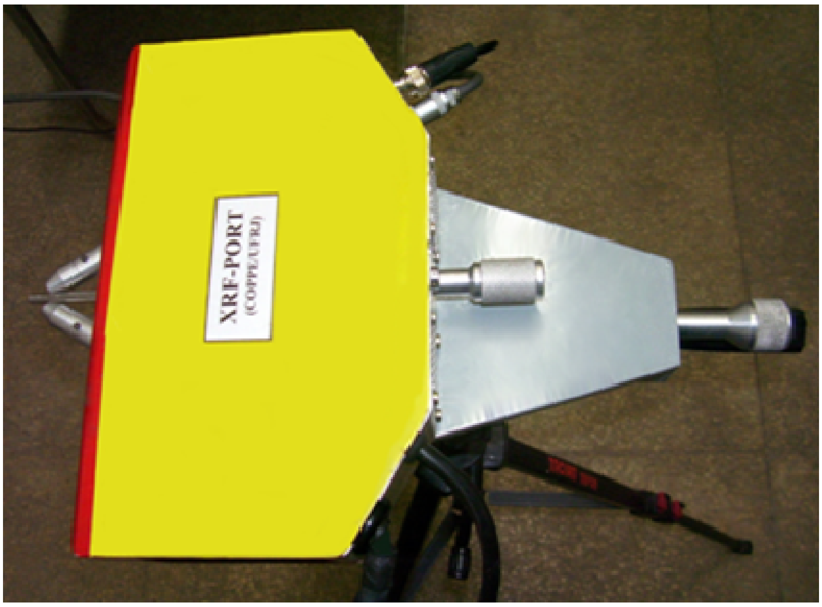

Figure 1. EDXRF portable system.

3. RESULTS AND DISCUSSION

3.1. Funerary mask

The XRF results revealed a presence of a thin layer of gypsum ($CaSO_4$), deposited over the wood, as a preparation base for painting. In the green color, the presence of Cu indicates the use of malachite ($CuCO_3.Cu(OH)_2$). Malachite is probably the oldest known green pigment and is chemically similar to azurite ($2CuCO_3.Cu(OH)_2$), a greenish blue pigment. They are chemically similar, comprising basic copper carbonate, and occur as natural minerals in Egypt. The pigments are obtained by crushing and washing the minerals, appearing in Egyptian tomb paintings from the 4th Dynasty. Egyptian women also used malachite to paint their eyelids [12].

In the yellow color, the presence of Fe indicated the use of yellow ochre ($Fe_2O_3.H_2O$); whereas in the black region, the presence of the same element indicated the use of black iron oxide (Fe_3O_4). Ochre pigments were used since prehistoric times and the word ‘‘ochre’’ comes from the Greek *ochros*, meaning yellow. The chemical responsible for the color is ferric oxide monohydrate ($Fe_2O_3.H_2O$), found mixed with silica and clay. The pigment is produced by grinding and washing and is essentially yellow clay [12].

In the red color, the presence of S, As and Fe indicates the use of a mixture of realgar (As_4S_4) and red ochre (Fe_2O_3) pigments. Realgar (αAs_4S_4) was used to obtain bright reds and begun to be used in Egypt from New Kingdom. In the mineral form can be found in volcanic and geothermal regions although it is also found with limestone and dolomite. However, the red color of the pigment is not permanent and can easily fade on exposure to light, originating pararealgar (γAs_4S_4) that exhibits orange/yellow color. Another possible reaction with oxygen leads to the white pigment As_2O_3. These changes are accompanied with an expansion of crystallites lattice and the colored layers might flake off. Red ochre can be produced by heating the yellow ochre ($Fe_2O_3.H_2O$) to drive off the water and produce anhydrous ferric oxide (Fe_2O_3). By controlling the heating it is possible to produce a range of warm yellows to bright red. Nevertheless, red ochre also occurs naturally as hematite (αFe_2O_3), which was very common in Ancient Egypt [12, 13]. In the figure 2 is shown the funerary mask.

Figure 2. Funerary mask.

3.2. Statue of a woman

In this case, the composition of the rock used to make the sculpture presents: Ca, Fe and traces of Ti and Mn. In the green color, the presence of Cu indicates the use of malachite ($CuCO_3.Cu(OH)_2$), which use in Ancient Egypt was discussed above. In the yellow and black regions, the presence of Fe indicated the use, respectively, of yellow ochre ($Fe_2O_3.H_2O$) and black iron oxide (Fe_3O_4). In the white areas, the presence of Ca indicates the use of calcite ($CaCO_3$).

In the red line at the pectoral adornment of the lady, the presence of S and As indicates the use of realgar (αAs_4S_4). There are some regions of orange color in this red line that presented the same elements in the XRF analysis. This result revealed an example of the photochemical degradation of this pigment, which changes into the orange pararealgar (γAs_4S_4). In the figure 3 is shown the statue of a woman and, in the figure 4, a characteristic XRF spectrum of the orange region.

Figure 3. Statue of a woman.

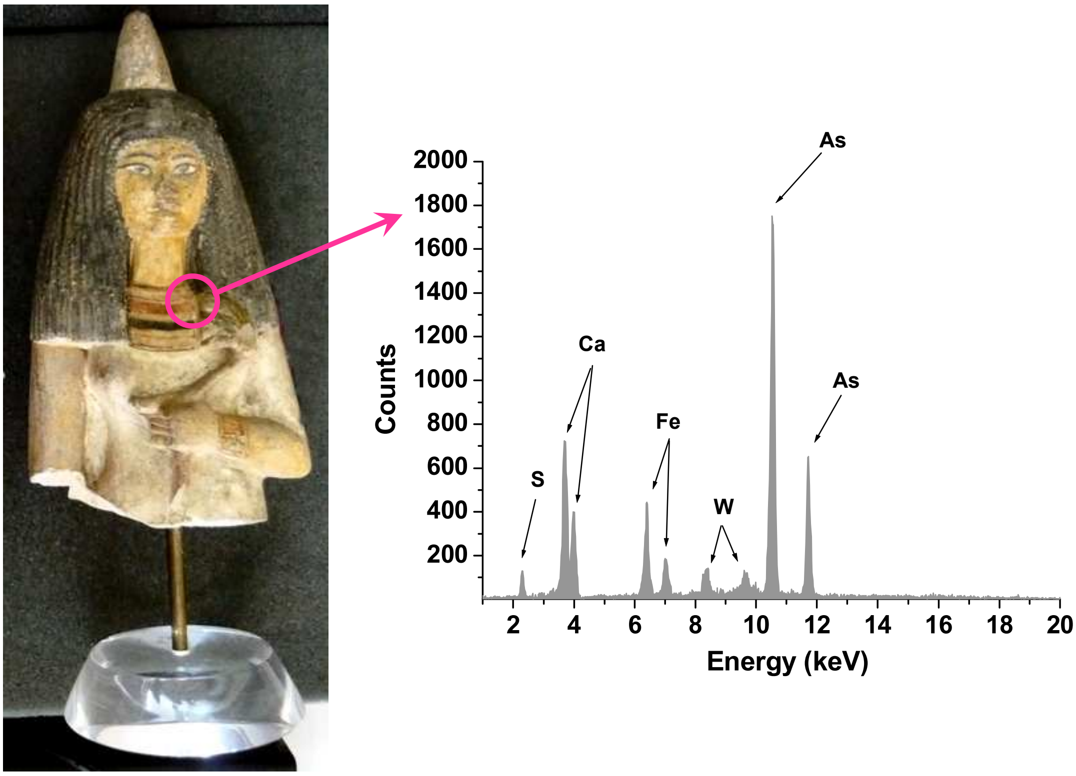

Figure 4. Characteristic XRF spectrum of the orange color.

3.3. Shabti of Penmennefer

In the blue region, the presence of Ca and Cu in the spectra indicates the use of Egyptian blue pigment ($CaO.CuO.4SiO_2$). This pigment was the first synthetic pigment produced by man, in ca. 3000 BC. It was widely used during antiquity, spreading all around the Mediterranean basin until the VII century AD. After this time, the pigment was no longer used, probably due to the loss of the chemical and technological knowledge required for its synthesis [14-17].

In the regions of red, yellow and black colors, the presence of Fe indicates, respectively, the use of red ochre (Fe_2O_3), yellow ochre ($Fe_2O_3.H_2O$) and black iron oxide (Fe_3O_4). In the white area, the presence of Ca indicates the use of calcite ($CaCO_3$). In the figure 5 is shown the shabti of Penmennefer.

Figure 5. Shabti of Penmennefer.

3.4. High priest of Amun

The statuette of the High priest of Amun, Menkheperre, was executed in bronze alloy, characterized by XRF analysis: Cu (93.7 %), Sn (3.4 %), Fe (2.1 %), Pb (0.8 %). The majority of Egyptian bronzes have up to around 10% Sn, as is generally typical in antiquity. These levels show chronological variations as the decrease in average tin content presented in Third Intermediate Period objects [18], as could be observed in this case. In this same period, copper alloy lead levels are still usually under 5 %. High lead content is typically a Late Period phenomenon that continued into the Ptolemaic Period, when over 20 % is not unusual and over 30 % is reported in some instances [18]. Therefore, this composition seems to corroborate the historical period assigned for this statue.

An important discovery was that in specific regions (kilt and headband of the priest) the XRF spectra revealed the presence of Au. This result indicates the use of gold leaf application over these regions, which was almost completely vanished and cannot be perceived at naked eye.

In the figures 6 and 7 are shown the analyzed statuette and the XRF spectrum of the skirt.

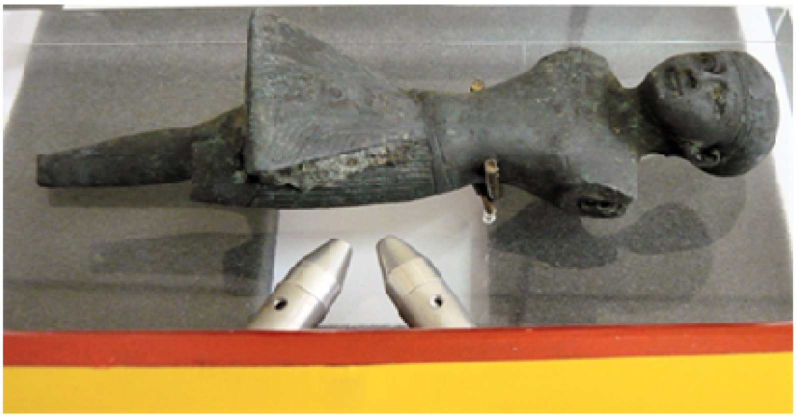

Figure 6. High Priest of Amun, Menkheperre.

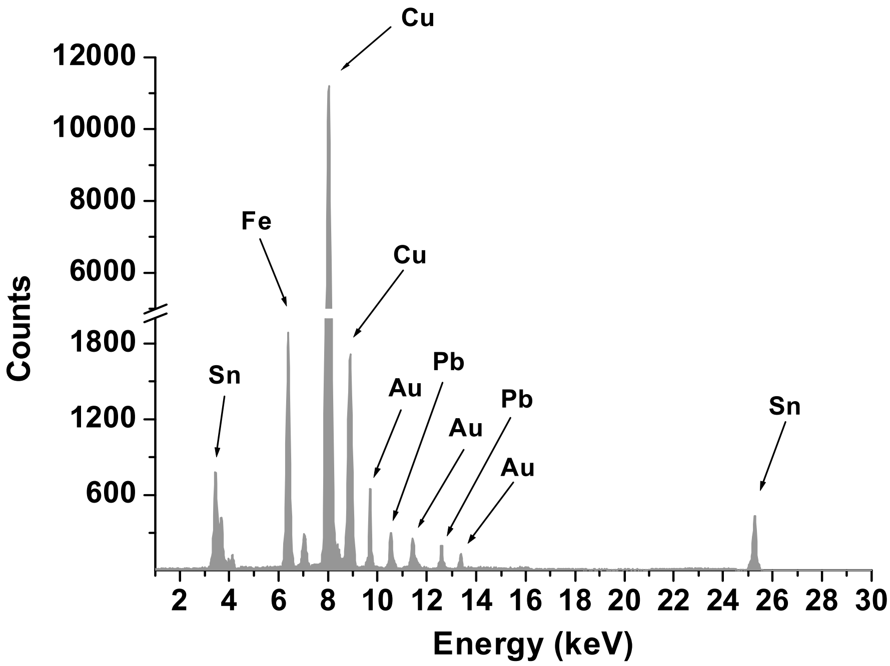

Figure 7. XRF spectrum of the skirt.

3.5. Statue of the god Bes

The XRF analysis of the black pigment used in this statuette revealed the presence of Fe, indicating the use of black iron oxide (Fe_3O_4). The white color – in the eyes – presented Ca in the spectra, characterizing the use of calcite ($CaCO_3$). In the red tongue, exhibiting a glazing appearance, the presence of Cu and Pb suggests the use of a red opaque glass containing Cu_2O and PbO [19].

Colored and opacified glass has been produced since ancient times. Glass color can be determined by the presence of metal ions dissolved within the glass matrix, which absorb visible light as a result of electronic transitions. The most common coloring agents present in ancient glass are: Fe(II), Fe(III), Mn(III), Cu(II), and Co(II) ions. The two ionic states of Cu produce two correspondingly different colors in Egyptian glasses: a turquoise-blue color when the cupric (Cu(II)) ion is present and a dull brown-red color when the cuprous (Cu(I)) ion is present. All Egyptian opaque red glasses which pre-date the XIX century BC contain lead oxide levels of less than 3%; after this date the lead oxide levels generally rise and a brighter (sealing-wax) red glass color is produced [18-20]. In the figure 8 is shown the statue of the god Bes.

Figure 8. Statue of the god Bes.

3.6. Figurine of the god Bes playing tambourine and Macrophallic figurine

These two figurines are made of Egyptian faience, which are glazed low-clay ceramic materials or silica, composed of crushed quartz or sand, with small amounts of lime, and either natron or plant ash. In the Near East and Egypt, vitreous materials in the form of glazed stones and faience were produced from about the 4^{th} millennium BC until the first century AD. The body of a typical faience, composed by a sintered quartz structure, was coated with a soda-lime-silica-glaze, most commonly having a bright blue-green color due to the use of

Cu(II) salts. When fired, probably at a temperature close to 1000 °C, the quartz body acquired its typical blue-green glassy surface. The typical color of faiences and their general visual aspect were quite similar to turquoise and the idea of substituting the semi-precious stone with a synthetic material could have played an important role in the success of the widespread production of these kinds of artifacts in the ancient world [21].

The material was used to produce bowls and tiles as well as small objects such as amulets, beads, rings and scarabs. Initially the principal colorants were copper and manganese producing turquoise and black glazes, respectively. Then, with the beginning of glass production around 1500 BC, the glaze colors were extended to include cobalt blue, manganese purple and lead antimonate yellow [22].

In the first case, the figurine made of green faience (god Bes) presented the following elements in the spectra: K, Ca, Ti, Fe, Zn and Cu. The macrophallic one, made in blue faience, presented: Ca, Ti, Mn, Fe and Cu. The intensities of Fe are highest in the case of the green faience. In the figures 9 and 10 are shown the faience figurines.

Figure 9. Figurine of the god Bes playing tambourine.

Figure 10. Macrophallic figurine.

Table 1. Pigments identified by XRF, key elements, characteristic color, chemical composition and period of use.

ELEMENTS	PIGMENTS	CHEMICAL COMPOSITION	PERIOD OF USE
Ca, Cu	Egyptian blue	$CaO.CuO.4SiO_2$	3000 BC – VII century
Cu	Malachite	$CuCO_3.Cu(OH)_2$	Antiquity – XVI century
S, As	Realgar	αAS_4S_4	1500 BC – XIX century
S, As	Pararealgar	γAS_4S_4	1500 BC – XIX century
Fe	Yellow ochre	$Fe_2O_3.H_2O$	Prehistory – still in use
Ca	Calcite	$CaCO_3$	Antiquity – still in use
Fe	Black iron oxide	Fe_3O_4	Prehistory – still in use

4. CONCLUSIONS

The materials employed in some ancient Egyptian artifacts, belonging to the National Museum Collection, were characterized by means of a non-destructive analysis *in situ*, using an EDXRF portable system. The identification of pigments and techniques used by the Egyptian craftsmen during Antiquity will provide an important aid to the researchers about this period and, also, to the evaluation of conservation and restoration procedures. Works like this, which have been developed during the last years in the field of archaeometry, demonstrate the potential and applications of the XRF technique to the restoration, maintenance and preservation of the Cultural Heritage.

ACKNOWLEDGMENTS

FAPERJ (Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro) for postdoctoral fellowship.

REFERENCES

1. R. Cesareo, C. Calza, M.J. Anjos, R.T. Lopes, A. Bustamante, J. Fabian, W. Alva, L. Chero, "Pre-Columbian alloys from the royal tombs of Sipán: Energy dispersive X-ray fluorescence analysis with a portable equipment", *Applied Radiation and Isotopes*, **68**, pp. 525-528 (2009).

2. R. Cesareo, A. Bustamante, J. Fabian, C. Calza, M.J. Anjos, R.T. Lopes, C. Elera, I. Shimada, V. Curay, M.A. Rizzutto, "Energy dispersive X-ray fluorescence analysis of a pre-columbian funerary mask from the Museum of Sican, Peru", *X-Ray Spectrometry*, **39**, pp. 122-126 (2010).
3. C. Calza, M.J. Anjos, M.I.M.S. Bueno, S.M.F. Mendonça de Souza, A. Brancaglion Jr., T.A. Lima, R.T. Lopes, "XRF applications in archaeometry: analysis of Marajoara pubic covers and pigments from sarcophagus cartonnage of an Egyptian mummy", *X-Ray Spectrometry*, **36**, pp.348-354 (2007).
4. C. Calza, M.J. Anjos, S.M.F. Mendonça de Souza, A. Brancaglion Jr., R.T. Lopes, "X-ray microfluorescence with synchrotron applied in the analysis of pigments from ancient Egypt", *Applied Physics A*, **90**, pp.75-79 (2008).
5. 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*, **38**, pp.327-332 (2009).
6. C. Calza, M.O. Pereira, A. Pedreira, R.T. Lopes, "Characterization of Brazilian artists palette from the XIX century using EDXRF portable system", *Applied Radiation and Isotopes*, **68**, pp.866-870 (2010).
7. C. Calza, D.F. Oliveira, H.S. Rocha, A. Pedreira, R.T. Lopes, "Analysis of the painting "Gioventú" (Eliseu Visconti) using EDXRF and Computed Radiography", *Applied Radiation and Isotopes*, **68**, pp.861-865 (2010).
8. 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 Spectrometry*, **39**, pp.307-310 (2010).
9. M. Uda, A. Ishizaki, R. Satoh, K. Okada, Y. Nakajima, D. Yamashita, K. Ohashi, Y. Sakuraba, A. Shimono, D. Kojima, "Portable X-ray diffractometer equipped with XRF for archaeometry", *Nuclear Instruments and Methods in Physics Research B*, **239**, 77-84 (2005).
10. D. N. Papadopoulou, G. A. Zachariadis, N. A. Anthemidis, N. C. Tsirliganis, J. A. Stratis, "Development and optimisation of a portable micro-XRF method for in situ multi-element analysis of ancient ceramics", *Talanta,* **68**, 1692-1699 (2006).
11. 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*, **29**, 119-129 (2000).
12. J.R. Barnett, S. Miller, E. Pearce, "Colour and art: A brief history of pigments", *Optics & Laser Technology*, **38**, pp. 445–453 (2006).
13. K. Hühnerfuβ, A. Von Bohlen, D. Kurth, "Characterization of pigments and colors used in ancient Egyptian boat models", *Spectrochimica Acta Part B*, **61**, pp. 1224-1228 (2006).
14. G.A. Mazzochin, F. Agnoli, et al., "Analysis of pigments from Roman wall paintings found in Vicenza", *Talanta*, **61**, 565-572 (2003).
15. G.A. Mazzochin, D. Rudello, et al., "A short note on Egyptian blue", *Journal of Cultural Heritage*, **5**, 129-133 (2004).
16. S. Pagés-Camagna, S. Colinart, "The Egyptian green pigment: its manufacturing process and links to Egyptian blue", *Archaeometry*, **45**, 637-658 (2003).
17. G.A. Mazzochin, F. Agnoli, I. Colpo, "Investigation of roman age pigments found on pottery fragments", *Analytica Chimica Acta*, **478**, 147-161 (2003).
18. P.T. Nicholson, I. Shaw, *Ancient Egyptian Materials and Technology*, Cambridge University Press, Cambridge, England (2003).

19. P. Mirti, P. Davit, M. Gulmini, “Colourants and opacifiers in seventh and eighth century glass investigated by spectroscopic techniques”, *Analytical and Bioanalytical Chemistry*, **372**, 221–229 (2002).
20. M. Bimson, I.C. Freestone, *Early vitreous materials*, British Museum, London, England (1987).
21. S. La Delfa, V. Formisano, E. Ciliberto, “Laboratory production of Egyptian faiences and their characterization”, *Journal of Cultural Heritage*, **9**, 113-116 (2008).
22. M.S. Tite, P. Manti, A.J. Shortland, “A technological study of ancient faience from Egypt”, *Journal of Archaeological Science*, **34**, 1568-1583 (2007).