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Pigments analysis in cartonages of an Egyptian mummy of the Roman Period using X-Ray Fluorescence Spectrometry

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Abstract

This work evaluates the chemical composition of pigments used in decorative paintings in the coffin cartonage fragments and linen wrappings of an Egyptian mummy, using X-ray microfluorescence with synchrotron radiation technique. The measures were obtained at the XRF beamline of the National Synchrotron Radiation Laboratory (LNLS). This Roman period female mummy is one of the most important mummies in the National Museum because of its unconventional embalming with disarticulated legs and arms. X-ray fluorescence analysis is a widely used spectroscopic technique in archaeometry for investigating the chemical composition of pigments in manuscripts, paintings, ceramics and other artifacts, metal alloys, and stones. Knowledge of composition allows pigment characterization through major or minor constituents, and makes it possible to establish the provenance, age, and consequently, the authenticity of the artifact.

Introduction

In the last years, scientific examination of artworks and archaeological objects has gained increasing consideration, due to positive development in the interaction between different and sometimes complementary sciences. It contributes to widening the knowledge of an object of artistic and historical value by giving information on its age, authenticity, place and technique of manufacture. On the other hand, it allows a diagnosis of the mechanisms of decay, necessary prior to any conservation treatment, and permits an evaluation of the effectiveness of such treatments (Mirti, 2000; Barone et al., 2003).

The X-Ray Fluorescence analysis (XRF) is a widely used spectroscopic technique in archaeometry to investigate the chemical composition of pigments (in manuscripts, paintings, ceramics and other artifacts), metal alloys and stones. This technique is based on the photoelectric effect, when x-rays photons with sufficient energy from a x-ray tube (or a radioisotope source) reach an atom in the sample, projecting an electron from an inner shell to the outside of this atom, producing an unstable electronic configuration. The atom suffers an electronic rearrangement, and the vacancy created by the ejection will be occupied by an electron from a more external shell. This transition is accompanied by emission of electromagnetic radiation. The energy of the emitted x-rays is equivalent to the difference between the potential energies of the orbitals involved, and it is characteristic of specific element and transition. Thus, is possible to identify (and to quantify) the elements that constitute a sample.

X-Ray Microfluorescence (μXRF) is the microscopic equivalent of XRF and it is a suitable analytical method for the analysis of cultural objects because, apart from its nondestructive character, it is a fast, accurate, sensitive, universal, versatile and multielemental analytical method. Its principal advantages are the minimization of sample preparation, the ability to operate in air and to perform a localized nondestructive analysis of microscopic areas over the surface of large objects (Papadopoulou and Zachariadis, 2004).

A pigment is characterized by its colour and by 1 to 5 different elements which, if detected in the correct proportions, allow the pigment to be identified. Nevertheless, this identification is not always easy and unambiguous, in many cases is necessary to use an additional investigative technique (Klockenkämper et al., 2000). Since the chronology of the use of most pigments is known, is possible to determine an approximate date of the artifact or of restored parts of it. Thus, the knowledge of its composition allows the pigment characterization through major or minor constituents and make possible to establish the provenance, age and, consequently, the authenticity of the artifact.

This work analyzed some fragments from sarcophagus cartonage of the mummy n.158, in order to establish its elemental composition and to verify if the pigments used in the decorative paintings are according to those used by

Egyptian craftsmen in the Roman period (1st century BC). The results were compared to those obtained for a linen wrapping fragment of which provenance was known. This female mummy is considered one of the most important pieces of the Egyptian Collection from the National Museum (Rio de Janeiro, Brazil), because it was embalmed with arms and legs swathed separately. This embalming procedure probably was used by a Theban family from the Roman period, whose tomb was recently discovered. The mummy, the linen wrapping and four cartonage fragments (samples A, B, D and I) are shown in figure 1.

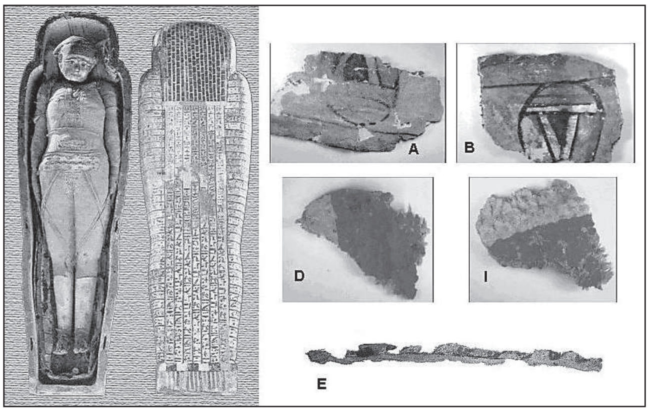

Fig. 1 - The mummy n.158, some cartonage fragments (samples A, B, D, I) and the linen wrapping fragment (sample E).

Experimental

The mXRF analysis of the samples was performed at the XRF beamline D09B of the Brazilian Synchrotron Light Laboratory (LNLS), using white beam and a Si(Li) detector with resolution of 165 eV at 5.9 keV. The samples of cartonage and linen wrapping fragments were fixed in an acrylic support and moved through the beam by means of a motorized stage (in the XYZ directions), so that specific regions on the surface were irradiated. In each selected region an EDXRF spectrum were acquired during 300 s. The results obtained were analyzed by means of a software package QXAS –AXIL, from IAEA. The elemental concentrations were calculated using WinIrrad, a software developed by the Nuclear Instrumentation Laboratory.

Results and discussion

The elements found in the samples were: Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Hg and Pb. Based on the elements that exhibited the highest concentrations, possible pigments were established. All of them are according to the pigments used by Egyptian craftsmen in the Roman Period. In addition, were performed correlation tests that revealed strong correlation among all cartonage samples and the linen wrapping fragment.

The principal red pigments in Egypt are of two main types, red iron oxide (hematite) and red ochre (hydrated iron oxide, perhaps partially dehydrated goethite). Red lead (minium) and red sulfide of arsenic (realgar) are also reported (Uda et al., 1993). Natural iron oxides occur plentifully in Egypt and then anhydrous and hydrated oxides could be used as red pigments without any heat treatment (Uda et al., 2000). In the red pigments, from the cartonage samples D and I, the elements that presented the highest concentrations were: Fe and Ca. This result indicates the red ochre pigment ($Fe_2O_3.H_2O$ + clay + silica). The use of red ochre in ancient Egypt was reported by Uda et al. (2000), David et al. (2001), Olsson et al. (2001) and Edwards et al. (2004). In the figure 2 is shown a mXRF spectrum of the red pigment.

In the pink pigments, from the samples A, B (cartonage fragments) and E (linen wrapping fragment), the highest concentrations were exhibited by: Fe, Ca and As. The possibilities, in this case, are realgar (arsenic sulfide, As_4S_4) and red ochre pigment. This result indicates a mixture of red and white pigments (gypsum or chalk) as reported by Uda et al. (1993) and Edwards et al. (2004).

In the dark green pigments, from the samples A, B and C, the elements that showed the highest concentrations were: Ca, Cu, K and Fe. The presence of Fe and K suggests the

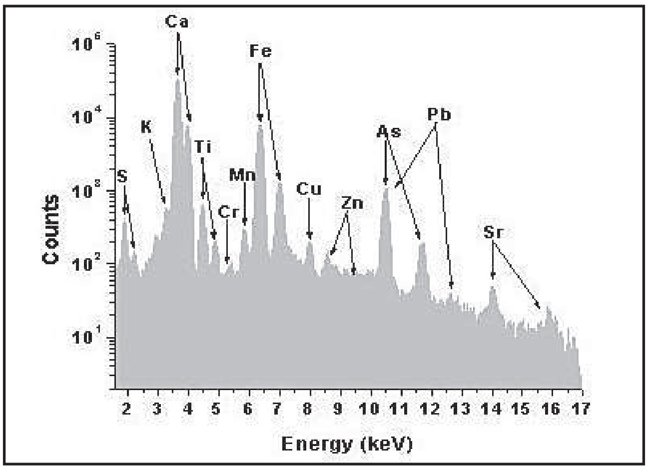

Fig. 2 - mXRF spectrum of the red pigment.

possibility of green earth, a mixture of celadonite and glauconite, $K[(Al^{III}, Fe^{III})(Fe^{II},Mg^{II})],(AlSi_3,Si_4)O_{10}(OH)_2$. In addition, the presence of Cu also could indicate verdigris, $Cu(CH_3COO)_2.2Cu(OH)_2$, or malachite, $CuCO_3Cu(OH)_2$. In this case, there are three possibilities of pigments, because XRF technique is unable to determine the chemical form of the analyzed samples, but only the elemental composition. The use of green earth, malachite and verdigris was reported, respectively, by David et al. (2001), Olsson et al. (2001) and Mazzochin et al. (2003a).

In ca. 3000 BC, Egyptian craftsmen created the first synthetic pigment produced by man, Egyptian blue, which was widely used during 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 (Pagès-Camagna and Colinart, 2003; Mazzochin et al., 2004). In the turquoise pigment, from the sample H, the highest concentrations were presented by the elements: Cu, Fe, Ca and K. The presence of Cu and Ca suggests the possibility of Egyptian blue, $CaO.CuO.4SiO_2$, or Egyptian green frit, $(Ca,Cu)_3Si_3O_9$. In the other hand, the presence of Fe and K suggests green earth pigment. In many cases, Egyptian blue was added in small

amounts to enhance the brilliance of other colours. The mixture of Egyptian blue and green earth to form green pigments was reported by Mazzochin et al. (2003a,b).
In the black pigments, from the samples A and B, calcium exhibited the highest concentrations. This result suggests the possibility of ivory black pigment, $Ca_3(PO_4)_2 + C + MgSO_4$.
In the brown pigment, from the linen wrapping fragment, the highest concentrations were found to Ca and Fe. The possibilities are a mixture of black (ivory black or magnetite, Fe_3O_4) and red pigments (red ochre). Other possibility is the brown ochre pigment (Fe_2O_3). The use of ochre as a brown pigment in ancient Egypt was reported by David et al. (2001).
In the white pigment, from samples A and B, Ca presented the highest concentration. The possible pigments in this case are: chalk ($CaCO_3$), gypsum ($CaSO_4.2H_2O$) or bone white ($Ca_3(PO_4)_2$). Calcium carbonate, calcium sulphate and calciferous clay are reported to have been used in ancient Egypt for white pigments (Uda et al., 1993; Mazzochin et al., 2003b).

Sample	Colour	Elements	Concentrations (mg.g-1)
A	pink	Fe	1395 ± 98
		Ca	88245 ± 2691
		As	1183 ± 86
	green	Ca	70736 ± 1757
		Cu	17135 ± 903
		K	5851 ± 237
		Fe	3100 ± 172
	white	Ca	132227 ± 4128
	black	Ca	102403 ± 5497
B	pink	Fe	2491 ± 157
		Ca	63678 ± 1933
		As	5013 ± 261
	dark green	Ca	57900 ± 2027
		Cu	22934 ± 986
		K	5079 ± 211
		Fe	2488 ± 164
	white	Ca	136485 ± 4581
	black	Ca	93262 ± 2964
C	dark green	Ca	127635 ± 4892
		Cu	45181 ± 2103
		K	5972 ± 306
		Fe	7444 ± 218
D	red	Fe	26326 ± 1049
		Ca	70090 ± 1784
E	pink	Fe	1281 ± 76
		Ca	94875 ± 3754
		As	1674 ± 90
	brown	Fe	28053 ± 1253
		Ca	75970 ± 1935
H	turquoise	Cu	36788 ± 1620
		Fe	5241 ± 301
		Ca	48614 ± 2158
		K	2789 ± 149
I	red	Fe	19584 ± 882
		Ca	57338 ± 1834

Table 1 - Mean concentrations (mg.g-1) of some elements found in the samples.

Conclusions

The present work characterized the elemental composition of the pigments used in decorative paintings in the cartonage fragments. In addition, it allows to conclude that all pigments found in the samples are according to those used by the Egyptian craftsmen during the Roman Period. Because XRF technique is capable of determining only the elemental composition and not the chemical or geochemical form of the materials analyzed, it would be necessary to use an additional investigative technique in order to obtain an unambiguous identification of the pigments.

Acknowledgments

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