ANALYSIS OF IBERIAN WALL PAINTINGS FROM “TOS PELAT” (4th century B.C.)

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Abstract

The wall paintings used in the decoration of domestic buildings are uncommon at the Iron Age in Spain and the archaeological site of “Tos Pelat” located in Moncada (Valencia, Spain) is a singular case. We aim with this work to carry out an identification of pigments from these Iberian wall paintings (beginning of the 4th century B.C.) that conserves remains of red, and blue colors.

Small wall fragments with pigment decoration and red lumps found in ceramic vessels were analyzed by non destructive Energy Dispersive X-Ray Fluorescence spectrometry (EDXRF) in order to characterize the inorganic elements of the pigments. Additionally, small size samples scraped off from the paint surface were analyzed by Scanning Electron Microscopy with coupled X-ray microanalysis (SEM-EDS), Optical Microscopy (OM) and X-Ray powder diffraction (XRD) to identify the crystalline phases. The results of the analysis have led to the identification of the blue pigment as Egyptian blue and the red pigments as hematite and vermilion, all of them applied over a preparation layer of calcium carbonate and quartz.
These analyses are very important to compare the materials used in domestic wall painting with the pigments used in sculptures, temples or tombs.
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Summary

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analyses are very important to compare the materials used in domestic wall painting with the pigments used in sculptures, temples or tombs.

1. Introduction.

The archaeological site of Tos Pelat with an extension of 20,000 m² is located near Moncada (Valencia, Spain). Figure 1 shows a map with the geographical situation and a plan of the archaeological site. The occupation of Tos Pelat began in the 6th century and finished in the 4th century B.C. Most of the archaeological remains correspond to the 5th century and the beginning of the 4th century B.C. (Mata & Burriel, 2000).

During the 2002-2004 excavation campaign at Tos Pelat remains of a defensive system integrated by a fortification with a double rampart and a tower were found. Inside the oppidum, six rooms belonging to two incomplete buildings and part of a street, parallel to the rampart, have been excavated. The domestic walls of Tos Pelat were made with stone and adobe and covered with a lime mortar layer on which an ornamental pigment was applied (figure 2).

Most of the studies about the use of pigments in the Iberian Culture during the Iron Age in Spain are associated with pottery and sculpture. The most frequent pigments used in the decoration of Iberian ceramics were ochre, red, black, and white (Sánchez Real, 1954, 1979; Martín Bueno, 1981). Rare pottery samples with blue decoration are some vessels found in the tombs of the "Dama de Baza" (4th century B.C.; Presedo, 1982) and "El Boverot" (beginning of the 2nd century B.C.; Clausell, 1999). Pigments from Iberian polychrome sculptures, dated in the 4th century B.C., have been analyzed in previous works (Cabrera, 1971; Ferrero, 1999, 2002). In the decoration of polychrome sculpture the artisans used black, red, ochre, white and blue pigments. Remains of wall paintings are unusual in the archaeological excavations of the Iberian Culture during the Iron Age in Spain; therefore the analyses of the pigments used in Tos Pelat wall paintings are of great interest both to increase our knowledge of the materials and techniques used by the pre-roman civilizations of the Iberian Peninsula.

The aim of this work is to characterise the painting materials used in the mural decoration of the archaeological site of “Tos Pelat”. A preliminary non destructive analysis of the samples was performed by portable EDXRF spectrometry to identify the inorganic elements presents in the wall paintings. Afterwards, OM, SEM-EDX and XRD of small
samples for the identification of the crystalline phases, were used. Our study represents the first analysis of wall paintings from the Iberian Culture in Spain.

2. Material and methods.

Wall fragments with paint remains and ceramic vessels containing red lumps were found in the rubble of two rooms excavated at the oppidum of “Tos Pelat”. The surviving fragments represent only a very small part of the original paintings and include representations of geometrical motifs with red and blue lines. A white levelling layer, in contact with the adobe wall, is used as a base under the red and blue pigments. Several samples of wall fragments with red and blue decoration on a white levelling layer, and reddish lumps are shown in figure 2.

EDXRF non destructive analyses were performed without sampling. For XRD, SEM-EDS and OM analyses, sub-samples were scraped off the wall paintings fragments with a scalpel. In the samples we can observed up to two layers of colours, and each was carefully scrapped off in order to minimize inter-contamination between layers. Mortar layers, used as a base under the pigments, and reddish powder collected from the red lumps were also examined.

The pigments were analyzed directly on the samples by means of a portable and easily operated EDXRF spectrometer that allows non-destructive and non-aggressive analyses. The spectrometer is integrated by an X-Ray tube (EIS, s.r.l., Italy) with wolfram anode, variable voltage between 0 and 35 kV and variable intensity current between 0 and 1 mA. The detection system consists of a Peltier cooled Si-PIN 5 mm² 500 µm thick detector (AMPTEK Inc.) with beryllium window of 13 µm and resolution of 180 eV (FWHM @ 5.9 keV). The analyses were carried out operating the X-ray tube with a potential of 30 kV and an intensity of 0.3 mA. The irradiation time was 200 s.

The EDXRF spectrum of a fragment of the wall simultaneously includes information from the pigment layers, the preparation layer that coats the wall and the adobe wall. The discrimination of the characteristic elements of the pigment and preparation layer has been made by comparing the EDXRF spectra of an area with pigment, preparation layer and adobe, and an area with only preparation layer and adobe.

Sub-samples scraped off from the paint surface and the powder collected from the red lumps were ground in an agate mortar and exposed to the Cu-Kα filtered radiation from a Seifert XRD 3003 TT diffractometer to identify the crystalline phases present in the pigments.
A primary monochromator on the diffracted beam and a positional detector MBraun PSD-500 were used. The measurements were taken with a current of 40 mA and a potential of 40 kV in a 2-90° (2θ) range with a step size of 0.08°. The identification of the crystalline phases was carried out from the comparison between the sample spectrum and a JCPDS pattern data base.

EDS microanalysis of the powdered samples were taken using an environmental Philips XL-30 ESEM microscope equipped with an EDAX PV 9760 system.

3. Results and discussion.

A total of six samples of the blue and red pigments, six samples of the preparation layer applied over the wall and four samples from the reddish lumps were analyzed.

3.1. Preparation layer.

Six samples of the preparation layers were analyzed where white appear in wall fragments as a basic background color. Figure 3a shows the EDXRF spectrum of a preparation layer sample that was analyzed jointly with the adobe substrate and therefore we detect fluorescence peaks that come from the substrate and the preparation layer. In this figure we can see that calcium and iron are the main components in the substrate and calcium is the main element in the preparation layer. XRD analyses (figure 4) shown that a mixture of calcite and quartz were used in the preparation layers.

3.2. Blue pigments.

Two wall fragments with blue pigment over the white preparation layer were analyzed without sampling by EDXRF spectrometry. In figure 3b we can see the comparison of three spectra obtained from the wall fragment: the adobe spectrum, the preparation layer spectrum and the blue pigment spectrum. As can be observed in this figure, copper it is the dominant element in the blue color. The fluorescent peaks of iron and calcium are presents in the blue pigment, preparation layer and adobe.

Microscopic examination of the scraped blue sub-samples shows the presence of blue crystals and transparent crystals that, in many cases, are separated by a fracture line. This visual description of this pigment agrees with the identification of the Egyptian blue made by other authors (Riederer, 1997). The microanalysis reveals that in the blue crystal the predominant elements are copper, calcium and silicon with traces of iron, while in the transparent ones the predominant elements are silicon, calcium and aluminum.
The fragments of blue decoration analyzed by XRD contain the characteristic diffraction pattern of *Egyptian blue*, a synthetic pigment first prepared in ancient Egypt made from calcareous rocks, quartz sand, a compound of copper and sodium as melting product, ground together and fired between 850°C and 1100°C. The resulting compound is a heterogeneous material constituted by a crystalline phase and an amorphous phase. The crystalline phase is predominant and is made up of blue crystals of *cuprorivaite* (CaCuSi$_4$O$_{10}$) and colorless crystals of *quartz* (SiO$_2$) (Riederer, 1997). In figure 4 we present the XRD spectrum of this blue pigment where we have identified the diffraction patterns of the cuprorivaite, quartz and calcite.

This pigment could have been imported from Egypt, but its raw materials (calcite, quartz and copper) were also found in Spain, suggesting local production since the technique for preparing Egyptian blue was widespread throughout the Mediterranean area during the Hellenistic period (Chase, 1971). However, at the present time, there is not documental evidence about the local production of Egyptian blue in Spain.

### 3.3. Red pigments.

Two different pigments were identified by EDXRF spectrometry: a red pigment in which iron is the main element detected and a red pigment in which the fluorescent peaks of mercury are presents (figure 3c and 3d).

The microscopic examination of the samples from the iron based red pigments shows a red matrix of granular structure with dispersed white grains. The fluorescence microanalysis carried out by SEM-EDS microanalysis identifies calcium, iron, silicon, and aluminum as the main elements. This composition agrees with the XRD pattern of the red earth (figure 4) where we have identified a mixture of compounds formed by *hematite* ($\alpha$-Fe$_2$O$_3$) responsible for the red color, calcite, and quartz. The intense peaks of calcite in the XRD spectrum can be due to the presence of the compounds from the white layer, on which the red pigment was applied, when the sample was scraped for XRD analysis. The mercury based red pigments analyzed by XRD contain cinnabar, calcite, and quartz (figure 4). The most important deposits of cinnabar in the ancient world were the Spanish mines of Almadén and their mineral was probably the raw material of the vermilion pigment used at “Tos Pelat”, but further studies and analyses are need to confirm this hypothesis.
3.4. Reddish lumps.

Iron is the predominant element in the red lump as we can see in the EDXRF spectrum shown in figure 3. Their XRD spectrum contains the hematite and quartz diffractions patterns (figure 4). Probably, these red lumps were used in the manufacture of the red pigments.


Red, ochre, black, white and blue were the main pigments used in the artistic manifestations of the Iberian Culture. Analyses of these pigments have been made in ceramic (Sánchez Real, 1954, 1979; Martín Bueno, 1981) and sculpture (Cabrera, 1971; Ferrero, 1999, 2002) but not in wall paintings because the discoveries of mural painting are rarely found in archaeological sites of the Iberian Culture. Now, for the first time it has been possible to analyze the pigments used in the wall decoration.

The analytical methods used in this work permitted the identification of pigments used in the samples from Tos Pelat wall paintings (beginning of the 4th century B.C.). The artisans gave the wall a coating of lime mortar on which the red and blue pigments were applied. The material of these preparation layers were identified as a mixture of quartz and calcite, as shown the EDXRF and XRD analyses. The blue pigment of the analyzed wall paintings contains calcite, quartz and cuprorivaite. According to this composition, the pigment is Egyptian blue, a synthetic material made from quartz, calcium carbonate and a compound of copper, ground together and fired. Two red pigments were identified in wall paintings: red ochre and cinnabar. Hematite is present in the red ochre pigment that probably was produced from raw materials which can be locally found. The red pigment with cinnabar is vermilion and, evidently, the raw material is not local.

The comparison between the results from this work and the results obtained in previous analysis of polychrome sculpture reveals the use of a similar pigment palette: Egyptian blue for the blue pigments, red ochre and vermilion for the red pigments. However, while the preparation layer in the sculptures was made of gypsum, a preparation layer made of calcite and quartz was identified in the wall paintings of Tos Pelat.

The identification of pigments such as the Egyptian blue and the vermilion contribute new topics in the context of the Iberian Culture as the trade of pigments or preparation procedures. However, a good knowledge of these topics should be based in the extensive analysis of pigments in a wider geographical context.
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Figure 1. Map and a plan view of the archaeological site of Tos Pelat (Moncada, Spain).
Figure 2. (a), (b) UE 1050, fragments of wall paintings with blue and red pigments and preparation layer; c) UE 1041 fragment of wall paintings with red pigment and preparation layer; (d) UE 1041 reddish lumps.
Figure 3. EDXRF spectra from the fragments of wall paintings; (a) preparation layer; (b) blue pigment; (c) red-iron oxide pigment; (d) red-vernilion pigment; (e) reddish lump. (In all spectra, the Ni peak comes from the spectrometer)
Figure 4. XRD spectra of the powdered samples scrapped of the wall painting fragments. (H: hematite; V: vermilion; E: Egyptian blue; Q: quartz; C: calcite).