Recent Studies of Cartheginian Era Tyrian Purple Artifacts
Tijani KARMOUS, Housam BINOUS and Naceur AYED*
Laboratory of Natural Colorants and Additives
National Institute of Applied Sciences and Technology
BP 676, 1080 Tunis, Tunisia
Naceur.Ayed@insat.rnu.tn
Housam.Binous@insat.rnu.tn
* Author to whom correspondence should be sent

ABSTRACT

CONCLUSION

The colorant is the real purple used by the Phoenicians and the Romans. This colorant was found in a clayed support. The reason for this fact remains unclear. Maya blue is similar to Zembra Punic purple both in usage and preparation. Studies concerning Maya blue can provide clues to the understanding of the Punic colorant.

A sample of purple clay earth dating back to the third century BC is analyzed by several techniques such as HPLC,

Picture courtesy of the Man and Mollusc Site and Paul Monfils
X-ray fluorescence, X-ray diffraction, FTIR spectroscopy, scanning electron microscopy....

The precious colorant turn out to be true animal purple, which was, among other things, used in dyeing by the Phoenicians and the Romans.

The support of the colorant was found to be essentially clay containing titanium, phosphorus, calcium, iron, sodium, potassium....

Several interesting questions remain to be elucidated. For instance, it is not clear why the colorant was mixed with clay. We hope that other techniques such as Synchrotron Radiation analysis can bring a new insight to this exciting problem. In particular, we hope to find out more about the possible link between Maya blue and Punic Zembra purple.

INTRODUCTION

During excavations done at the island of Zembra in Tunisia, we discovered a sample of purple clay earth in a stratigraphic layer dating back to the third century BC.

Belonging to an archeological collection and unique in its kind, this material was studied by several methods of observation and analysis. The slightly destructive and non-destructive methods allowed us to have information as thorough as possible on the coloring matter as well as the support on which it is fixed. Among the analytical techniques used, we can mention HPLC, x-ray fluorescence, x-ray diffraction, FTIR spectroscopy, scanning electron microscopy.

HISTORICAL BACKGROUND OF PURPLE AT CARTHAGE & ARCHEOLOGICAL DATA OF THE SAMPLE FROM ZEMBRA

Purple dyeing is one of the main industries at the Phoenician and Roman Carthage. Traces in the form of piles of shells, testifying the importance of the purple workshops of Carthage, were pointed out in several sites: Kerkouane, Kram, Carthage, Utique, Mininx...

Carthage revealed also some signs concerning the purple craft: a shell of Murex Trunculus was drawn on a Punic seal, a container filled with broken shell of Murex Trunculus was found and fragments of shells were found in tombs. All these facts show the importance of this shell in Carthaginian way of life. Purple industry
has such a scale that Pliny considered that Mininx purple was among the most beautiful ones.

The archeological matter, that was subject to analysis, was discovered at the island of Zembra, during excavations conducted by a team of the National Institute of Patrimony of Tunis, in a stratum dating back to the third century BC. It is constituted of purple clay earth, conical shells with an elliptical base of the Patella genus and granules of wood coal.

CHEMISTRY OF PURPLE

Purple's origins are marine gastropods of the Murex and Purpura kinds, which contain several precursors of this precious colorant: indoxyl sulfate esters non-substituted (scheme 1) and indoxyl sulfate esters substituted in the position 2 by thiomethyl and sulfonyl methyl groups.

By enzymatic hydrolysis followed by the action of oxygen and light, these precursors give rise to the purple colorant. The nature and composition of the pigments of this colorant depend on the nature of the mollusk species used; this explains the wide range of shades obtained. In fact, the colorant of Murex Trunculus is a mixture of indigotin and 6,6'-dibromoindigotin giving purple and blue colorations while Murex Brandaris and Purpura produce exclusively a purple red colorant which is 6,6'-dibromoindigotin.

IDENTIFICATION OF THE COLORING MATTER

Several methods were used to identify the colorant of Zembra.

Test of vat and mordant dyeing

Mordant colorants can be extracted in acid medium at 100°C for 10 minutes. While vat colorant develops a yellow-greenish coloration accompanied by a solubilization of the colorant under the action of alkali reducing medium (sodium bisulfate and sodium carbonate).

The acid hydrolysate, analyzed by TLC (run on a silica plate with the eluent toluene-ethanoic acid 9/1), did not show any spot. This result indicates that the sample does not contain mordant colorant. On the other hand, the redox test with bisulfite is positive. This is an argument in favor of the presence of indigoic derivatives.

Selective solubility test
We contemplated isolating the pigments constituting the tinctorial form of the colorant and identifying them by TLC. We isolated indirubin with ether and indigotin with dichloromethane or dimethylformamide. Dibromoindigotin is extracted with quinoline.

Alteration reaction of dibromoindigotin test

The alkali medium in the presence of a reducing agent degrades the dibromoindigotin by transforming it into indigotin if the medium is heated or exposed to UV radiation. This type of reactions was led on the Zembra sample after elimination of indigotin and indirubin by solvents. The sample treated this way developed a blue coloration indicating the formation of indigotin. This result indicates the presence of dibromoindigotin among the pigments of the colorant of Zembra. Bromide is analyzed by TLC using a cellulose plate with the eluent pyridine-distilled water-isoamylol-ethanoic acid (40/25/20/5).

High performance liquid chromatography analysis

The equipment used in the HPLC analysis consists of a diode array detector and a C18 inversed phase column. The analysis of the acid hydrolysate of the Zembra sample gave no peak, excluding the presence of any mordant colorant. The chromatogram of the extract with DMSO made at ebullition showed 3 peaks (detected at 288nm) which correspond to indirubin (1.4%), indigotin (65%) and 6,6'-dibromoindigotin (34%). This composition shows the animal origin of the colorant. This colorant is a true purple, which originates from purple mollusks. The strong percentage of indigotin suggests that it is mainly Murex Brandaris and Murex Trunculus which were used by the Phoenicians.

ANALYSIS OF THE SUPPORT

Analysis of the support by x-ray fluorescence

We sorted an ensemble of samples rich in colorant. The spectra of this ensemble showed profiles that plead in favor of a clayed matter (Si, Al) more or less rich in iron oxide accompanied by titanium and salts of potassium, sodium, calcium essentially.

The fact that we did not detect bromine by x-ray fluorescence in our samples prompted us to look for a mean to enrich our sample in colorant. This is possible by a pyridine extraction made at ebullition after pertinent washing of the sample in
order to eliminate bromide ions due to inorganic mineral salts. Filtration of the pyridine extract gave a clayed earth residue in the filtrate, which fixes the colorant. The x-ray fluorescence spectrum of this residue reveals intense bromide rays. We compared this spectrum with the one obtained from purple powder from Monaco.

Analysis of the support by Scanning electron microscopy

The analysis by scanning electron microscopy of the image shown in the figure and the spectra obtained for the ensemble of samples rich in colorant indicate the presence of iron, silicon, aluminium and oxygen. It did not show the presence of carbon and bromide. The corresponding elemental analysis point out the following results:

- presence of clay (due to aluminium and silicon).
- presence of iron oxides probably hematite because of the red color of the earth sample (due to iron and oxygen)
- presence of silica grains (due to silicon and oxygen).
- it is difficult to link the presence of titanium to anyone of the minerals mentioned above because no correlation appears with the other elements. It may be impurities in iron oxide.

Potassium, sodium and magnesium are detected only in the presence of chlorine. Thus they are chlorides due to seawater.

Limestone found in very small amounts suggests that the sample originates from a dyeing vat, which contained fragments of shells rich in limestone. This indicates that our purple was man made. Further excavations are needed to confirm this supposition.

Analysis of the support by x-ray diffraction

The diffractogram of the Zembra earth rich in colorant shows rays attributable on one side to kaolin and on the other side to silica. The same holds for the light gray sample with no colorant. The ferruginous pigments were not detected by this technique. This is explained by the fact that they are present in minute amounts or not properly crystallized.

Analysis of the support by FTIR

The colorant support gives a spectrum similar to washed kaolin. This result confirms that we are dealing with a kaolinitic clay.
An ochre sample taken from the Zembra samples gave absorption bands in IR which were located at the same wave numbers as those obtained from a reference ochre sample. This analysis confirms the abundant presence of iron, which was found in elemental analysis.

Analysis of the support with Raman spectroscopy

This method did not allow the identification of the coloring matter of the Zembra earth because colorant percentage is very small. The spectra obtained enabled us to identify mineral components such as iron oxide and titanium oxide. In addition, Raman analysis showed the presence of carbon originating from the coal used as a source of energy in the preparation of purple by the Phoenicians.

Multi-element analysis of the support

This technique was applied on many samples rich and poor in colorant. The results plead in favor of a clayed earth containing SiO2 (50 to 60%) and Al2O3 (16 to 20%). Other elements were present such as calcium (4.5%), iron (3.2%), sodium (1.3%), potassium (1.4%), titanium (5000 ppm) and phosphorus (1350 ppm).

Analysis of the support by x-ray spectrometry induced by proton beam (PIXE)

This analysis concerned three samples chosen according to their colors: brick red, yellow and purple. The results obtained for the three samples confirm those obtained by other techniques. The analysis of the three samples showed that they are rich in Si (SiO2 : 50 to 60%) and Al (Al2O3 : 23 to 27%). The results showed that we are dealing with a clayed earth containing Titanium, calcium, sodium, magnesium as well as other elements at trace levels such as Sr, Zn, As, Ga...

The different tints of the samples is explained by the abundance of iron in the brick red sample (Fe2O3 : 19.67%) while the yellow sample has a smaller content of the iron oxide (Fe2O3 : 2.72%). Bromide is found with highest percentage in the purple sample (Br : 822 ppm). In the brick red and yellow samples, the bromide content is around 420 ppm. These results support the fact that the purple colorant has a strong coloring power and participate with iron in giving the purple shade to the third sample.

**Tyrian Purple**

Variously known as Royal purple, Tyrian purple, purple of the ancients, this ancient dyestuff, mentioned in texts dating about 1600 BC, was produced from the mucus of
the hypobranchial gland of various species of marine molluscs, notably Murex. Although originating in Tyre (hence the name), man's first large scale chemical industry spread throughout the world. With the decline of the Roman Empire, the use of the dye also declined and large scale production ceased with the fall of Constantinople in 1453 (29 May, actually). It was replaced by other cheaper dyes like lichen purple and madder. William Cole in 1685 described in some detail how to use Nucella lapillus (his drawing) to obtain the purple dye.

He "found this species on the shores of the Bristol Channel, which on cracking and picking off the shell, exhibited a white vein lying transversely in a little furrow or cleft next the head of the fish; which must be dug out with the stiff point of a horse hair pencil being made short and tapering; which must be so formed by reason of the viscous claminess of that white liquor in the vein so that by its stiffness it may drive in the matter into the fine linen or white silk ...... if placed in the Sun will change into the following colours, i.e., if in the winter about noon, if in the summer an hour or two after sunrise and so much before setting (for in the heat of the day the colours will come on so fast, that the succession of each colour will scarce be distinguishable) next to the first light green will appear a deep green; and in a few minutes this will change into a dull sea green; after which, in a few minutes more, it will alter into a watchet blue; from that in a little time more it will be purplish red; after which, lying an hour or two (supposing the Sun still shining) it will be of a very deep purple red; beyond which the Sun can do no more."

The major component of the dye is 6,6'-dibromoindigo. Paul Friedlander was the first to determine the composition of the dye from Murex brandaris in 1909. 6,6'-Dibromoindigo in solution is blue, but when used as a dye on wool the colour is purple. Below are spectra of the absorption in solution, tetrachloroethane, showing a maximum absorption at 590 nm and of the wool-dyed reflectance spectrum showing a maximum absorption at 520 nm.