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Non Destructive Study of Gilded Copper Artifacts from the Chichén-Itza Cenote

J. Contreras[(a)], J.L. Ruvalcaba Sil[(b)], J. Arenas Alatorre[(b)]

[(a)] *Esc. Nal. de Restauración, Conservación y Museografía, Inst. Nal. de Antropología e Historia, MEXICO*
[(b)]*Instituto de Física, Universidad Nacional Autónoma de México, MEXICO.*

Abstract. The studied collection comes from the sacred Chichen-Itzá Cenote, one of the major Mayan archaeological zones. These artifacts are soles of sandals and other pieces of the costumes dressed by the ones sacrificed in this. Some artifacts showed a gilded heterogeneous surface; polished and rough, in different colors: copper, golden and black. This alteration was due not only to the long burial period, but to an inadequate method of extraction that included the use of a dragger, and an acid and mechanical "cleaning" method done in the 60's. In order to identify the artifacts materials and production process, the pieces of the collection were analyzed by X-ray fluorescence (XRF), Particle Induce X-rays emission (PIXE) and Rutherford Backscattering (RBS), and some fragments isolated before the conservation processes were kept for its analysis with Scanning Electron Microscope with an electron microprobe (SEM-EDS). First, XRF was used at the conservation laboratory to determine the metal compositions and homogeneity of the gilding of all the artifacts. From this analysis, few artifacts were selected to carry out a more fine analysis by PIXE and RBS in order to measure the gilding thickness, the elemental depth profile of Au, Ag and Cu and to identify the gilding procedures. Then, microscopic studies were performed to refine the gilding thickness measurements and its homogeneity. From the results, it was determined that the metallic support is mainly copper while the platting is a rich Au-Ag alloy. The measurements pointed out to an electrochemical deposition gilding. Since this technology was not developed in the Yucatan area, we conclude that these pieces were obtained by commercial exchange with Central and South America. The methodology applied was suitable for the characterization of the materials and the manufacturing of the artifacts.

Keywords: Maya, Gilding, Non destructive analysis, XRF, PIXE, RBS, LV-SEM, EDS

INTRODUCTION

The collection studied comes from the sacred Chichen-Itzá Cenote, one of the major Mayan archaeological zones in Mexico. This site is famous among other reasons because of its Sacred Cenote, a large flooded cavity formed in the calcareous ground typical of the Yucatan Peninsula, mainly used for ritual objectives [1].

The first reference about the objects in the Cenote comes from the XVI century, of Diego de Landa, a monk who became bishop of Yucatan, who mentions: "in this Cenote they have had and they have the tradition to throw alive men in sacrifice to the Gods in the days of drought, it was thought that they did not die, although they weren't seen anymore. Many other things were also thrown: valued stones, which they had appraised. And thus, if this earth had had gold, this well will be the one that had more part of it, as has been told by devoted Indians."

After such panorama there were many people interested in extracting objects from the Cenote, the first try was done by the French Desiré Charnay in 1882, using Toselli automatic sounding machines, as it didn't worked he desisted, so the first was Edward Thompson using two techniques, from 1904 to 1907 using a dredge, that caused enormous damage to the objects, and from 1909 to 1911 employing the diving technique. Part of the materials extracted were sent to the Peabody Museum, of the Harvard University, and to the Chicago's Museum Field. In 1959 during the 58th Congress of American Anthropologists, the Peabody Museum gave back a number of, apparently, gold pieces to the Mexican State.

The Mexican exploration began until the decade of 60's under the direction of archaeologist Roman Piña Chan; it was divided in two phases. In the first, and air lift device was used, which caused a vacuum that impelled the object upwards, but it was abandoned because of the damage caused to the pieces. In the second phase the water level was lowered so it could be used a normal earth excavation technique.

The analyzed artifacts are soles of sandals and other pieces of the costumes dressed by the ones sacrificed in this, its constituent material is rich in copper The set of artifacts was composed of nine artifacts among them, axes, sole sandals, a stamped sheet, earrings and a disk (Fig. 1). Only the axes were not gilded. Representative images of the gilded surface conditions of the artifacts are shown in Fig. 2 (stamped sheet). Because of the characteristics of the gilded objects, and analyzing the commercial exchanges of Chichen Itza, the archaeologists propose that were obtained by means of commerce with Panama.

The studied objects form part of the Yucatan's Museum of Anthropology collection, showed heterogeneous surface; polished and rough, in different colors: copper, golden and black and were sent to the conservation laboratory in order to eliminate corrosion products and stabilize its materials. It is evident that the alteration was due not only to the long burial period, but to an aggressive extraction method, and a very inadequate "cleaning" that presumably included the use of sulphuric acid, due to the lack of calcareous patina expected from a rich calcium environments such as the cenote's waters and soil, the presence of sulphides and an evident chemical attack indicated by metal dissolution. Even of these incorrect treatments, the pieces conserve a large amount of gild which points to a gilding technique that allowed a strong binding to the artifact alloy.

FIGURE 1. Some of the studied gilded artifacts.

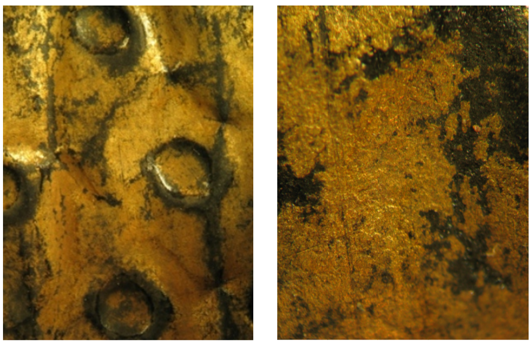

FIGURE 2. Detail of the gilding surfaces (40X).

Pre-Columbian Gilding Techniques

In Center and South America the work of metals reached a notable development, obtaining not only complex alloys like tumbagas, but also surface finishing and plating techniques [2-3].

Foil gilding is obtained by means of mechanical union of gold sheets; eventually the heat reinforced the bonding and caused some diffusion. This gilding is quite thick (35-90 μm) does not cover all the details of the substrate, and it is not the best option for thin sheets like the ones from the Sacred Cenote of Chichen Itzá.

Fusion gilding requires frequently the application of molten gold or gold alloy to a supporting metal with a higher melting point, like copper or copper alloys. This plating is thick also (up to 0.75 mm) and neither suitable for artifacts like the ones analyzed in this case.

Depletion gilding, probably the most famous of all gilding techniques of Central and South American, is done commonly from tumbaga, corroding the copper and silver and then cleaning its corrosion products and leaving on surface only a porous layer of gold. The gold enriched surface may range from 3 to 35 μm.

Electrochemical replacement plating implies the use of previously heated and acidic gold solutions. As it has been proposed by Lechtman [4], the electrochemical reactions are due to the interactions between the ions of the metal to be plated and the gold in solution, the bonding need also heating. The gilding layers obtained in this way are very thin, their mean thickness is of 0.5 to 2 μm, and they are relatively uniform. There is a solid state diffusion zone between the gold and the core metal, because of the heating necessary to the finish the process, and there is no trace of flushing of the molten gold.

METHODOLOGY

In order to identify the artifacts' constituent materials and production process, the pieces were analyzed by means of X-ray fluorescence (XRF), Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometries (RBS), and those fragments isolated before the conservation processes were kept for its analysis with Low Vacuum Scanning Electron Microscopy with a microprobe (LVSEM-EDS).

Portable XRF was used at the conservation laboratory to determine the homogeneity of the gilding of nine artifacts and to get a mean surface composition by a portable system with a Mo X-rays tube and a CZT detector on a 1.5 mm dia. spot. From this analysis, few artifacts were selected to carry out a more fine analysis by PIXE and RBS at the Pelletron accelerator of the IF-UNAM.

Two artifacts, one sole sandal and one earring, were selected to PIXE-RBS analysis due to better gilding conditions and their more homogeneous gilding. At first place, a 3 MeV proton beam was used with an external beam setup. Nevertheless, the thickness of the artifacts was too thin (lower than 2 μm) to be measured by differential PIXE with a proton beam. Then, PIXE and RBS were applied simultaneously using a 3.1 MeV alpha beam in vacuum with 1.5 mm dia. beam spot [5-6]. The particle detection angle was 138° from the beam direction. In this case, the depth resolution was enough to measure the elemental depth profile on both artifacts. The elemental depth profile was determined by the RUMP code using PIXE data.

On the other hand, fragments that could not have been reintegrated to the artifacts were selected for SEM analysis. The microscopic studies were performed to observe the gilding layer homogeneity and the surface morphology of the corrosion layers. A LV-SEM, JSM 5600LV microscope with resolution of 5 nm in LV mode, fitted with an energy dispersive X-ray spectrometer (Noran, model Voyager 4.2.3). Before the analysis, samples were fixed on the specimen holder with a carbon tape and mounted on an aluminum specimen holder. The LV-SEM was operated to 20 kV acceleration voltage and 15-20 Pa of pressure in the specimen chamber, obtaining the images with the backscattering electron signal (BSE).

RESULTS

The XRF results indicate that the core metal of the artifacts is mainly copper with As traces. In some cases such as the axes, they have Pb traces as well. This elemental profile fits the features of artifacts from west and central regions of Mesoamerica. On the othe hand, the gilded objects present a non-uniform thickness but Au and Ag were detected in all the cases.

Figures 3 show the typical PIXE and RBS spectra using the alpha beam of the gilded and eroded -gild lost- surfaces. It is evident from the spectra that in the gilded region Au and Ag are in the main elements in the surface layer while in the eroded region the amount of both elements decreases, but still few amounts remain. PIXE spectra showed a strong diminution of gold in the eroded surface.

RBS measurements indicate that the gilded thickness ranges 0.4-0.5 . μm. Using the PIXE composition, the elemental depth profile was determined by the RUMP program (Fig. 4). Ag was observed diffused in the interface while Cu was detected mainly in the artifact core. Considering the thickness of the gilding and the diffusion observed at the interface between the gilding layer and the copper support, we may consider that an electrochemical plating method and a rich Au-Ag alloy were used.

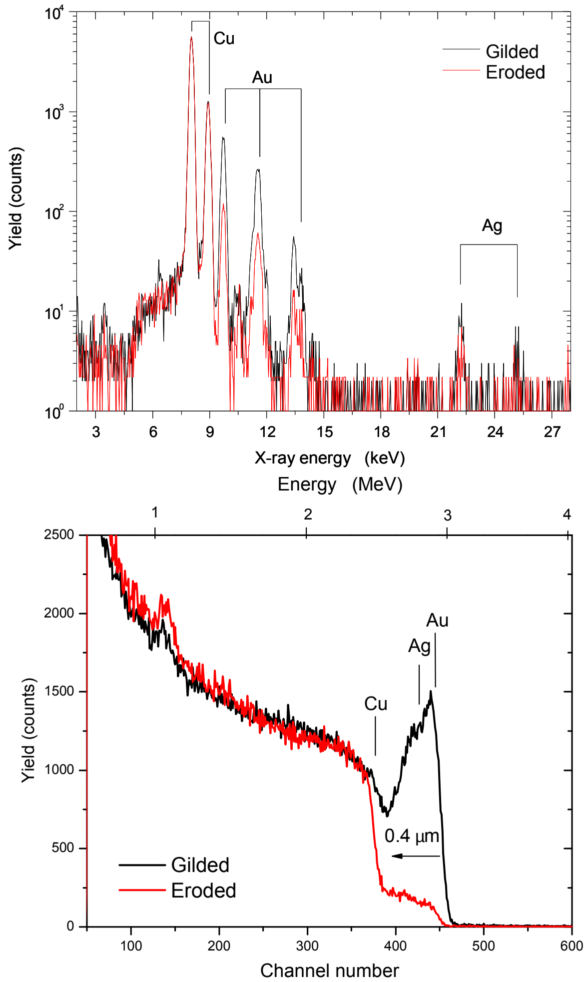

FIGURE 3. PIXE and RBS spectra of the gilded and eroded -gild lost- surfaces using a 3.1 MeV alpha particle beam.

Similar results were observed for the ear-artifact, but the thickness is slightly thinner (0.3-0.4 μm) and the amount of Au is lower (about 20%).

SEM results indicate that the samples showed an irregular surface with high roughness probably due to the corrosion occasioned by the environment in which the artifact was kept. The contrasts observed in the SEM images obtained by BSE indicate an inhomogeneous composition. In figure 5 we can observe a high contrast among the rich Au layer (region 1) and the rich Cu artifact core (region 2).

Table I shows the comparison of the elemental compositions obtained by EDS analysis for these regions. Since the analyzed depth of the 20 keV beam is around 1 μm, the elemental composition results show higher Cu contents due to the thin thickness of the gild layer. The region 1 contains more Ag (7.1%) than the region 2 richer in Cu (4.0%). In this region, S may be present (1%<), it maybe related to Ag and Cu sulphides while in the region 2, O may be linked to the presence of thin layers of copper oxides at the surface of this region.

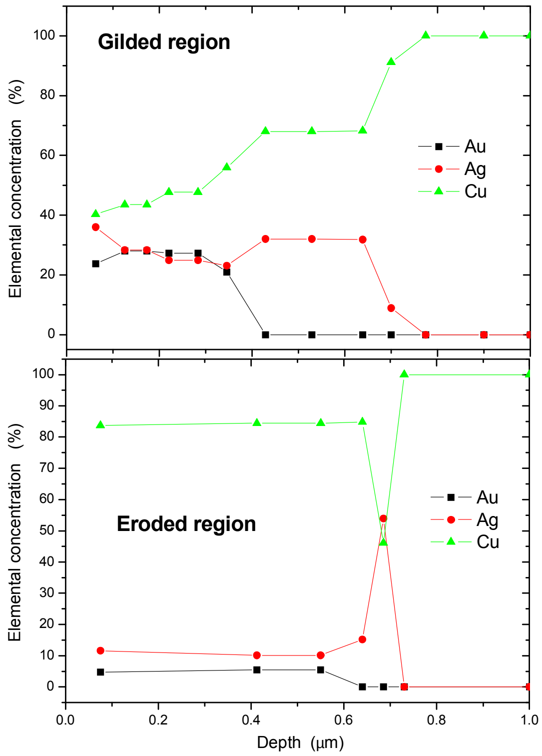

FIGURE 4. Elemental depth profile from PIXE-RBS.

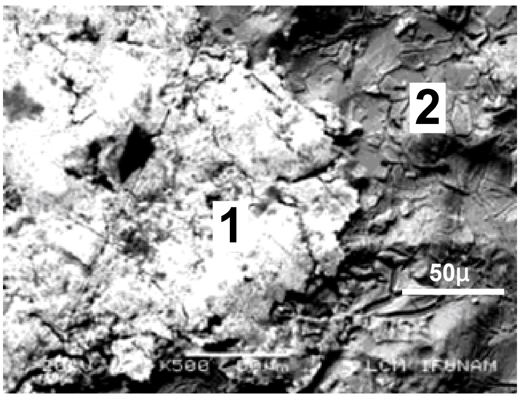

FIGURE 5. LV-SEM image of the stamped sheet (500X).

TABLE I. Elemental concentrations determined by EDS of the regions showed in figure 5.

Element	Elemental concentration (%)		
	Region		
	1	2	3
O	-	1<	1<
Cu	30.5	80.7	86.5
Ag	7.1	4.0	2.4
Au	62.3	14.8	9.6
S	1<	-	1<

CONCLUSIONS

For the gilded objects, it was determined that the artifacts core is copper, nevertheless the platting are a rich gold-silver alloys. The measurements pointed out to an electrochemical deposition gilding technique due to the uniform and thin gilding layer (0.3 up to 0.55 μm) and intermetallic diffusion at the interface. These results are consistent to the fact that the gilding layer remains despite the inadequate recovery from the Cenote and the cleaning methods used. From the XRF and PIXE-RBS measurements we may expect a similar gilding technique for the other artifacts since comparable relative elemental contents of Au and Ag were observed. Other studies showed similar results [7-8]. Since this technology was not used in Mesoamerica, our data agree with the proposal of long distance exchange from Central and South America.

The applied methodology was suitable for the characterization of the materials and the manufacturing techniques of the artifacts.

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