Scientific insights of electrochemical replacement approach to describe the origin of Pre-Columbian Peruvian gilded copper-based objects

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Abstract. Pre-Columbian Peruvian goldsmiths developed gilded copper-based objects by ancient techniques that require identification to propose conservation strategies. Lechtman H, conducted experiments to suggest that the electrochemical replacement was the gilding technique used by the Moche and Vicus cultural groups. Despite her remarkable achievement, the quantitative data provided by her is still open to discussion. This work focused on obtaining experimental data to recreate her protocol by introducing less gold precursor. Polished copper pieces were plated with an adherent gold film of up to 7.5 µm after immersing them into an electrolytic solution for 3 min and 6 min at 80 ºC. Our results demonstrated that the electrochemical replacement technique gives rise to anodic regions in the plated objects. Further studies around the corrosion process that undergoes these heritage objects in burial and environmental conditions are suggested to determine their deterioration rate. Moreover, electroless and galvanic techniques should be explored in order to improve current approaches.

1. Introduction

Through the centuries that preceded the Spanish conquest, ancient Peruvian metalworkers developed various gilding techniques to change the metal surfaces of an object into different hues of gold and silver [1]. Those gilded objects were part of elite costumes and took part in the ritual paraphernalia that expressed and consolidated the power of rulers and priests. Most of the gilded copper objects were recovered from burial sites and are now part of museum collections. Despite their care, they are still undergoing severe corrosion processes that put their integrity at risk. Therefore, understanding the gilding techniques is not only essential to enrich our knowledge of the Andean metallurgy development, but more importantly, it provides scientific grounds to the practice of adequate conservation strategies that ensure the preservation of our metal cultural heritage [2].

Among the limited research done in this field, Lechtman H [3-5] was the first to identify and recreate the use of electrochemical replacement as a gilding technique, shared by the Moche and Vicus cultural groups from the north coast of Peru during the early intermediate period (100-500 AD). In her experimental work, she proposed using a mixture of KNO₃, KAl(SO₄)₂·12H₂O, and NaCl to dissolve the gold. Then, the solution was neutralized with NaHCO₃ until a pH of 9 to gently deposit gold on copper objects. However, her published experimental results lacked the quantitative data related to the exact temperature and concentration of NaHCO₃. She reported a thin and brittle layer of gold formed on
a cleaned copper substrate after dipping it into the bath for a few minutes. Thus, further annealing was required to create a strong bond between the layer and substrate. Therefore, this research work focused on obtaining the missing experimental data to recreate Lechtman’s protocol; for this, we studied the deposited gold on the copper substrate by X-ray fluorescence (XRF) while the uniformity of the layer was evaluated by optical microscopy. In addition, scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) was included to argue about the plating technique used by the Pre-Columbian goldsmiths from Dos Cabezas, North coast of Perú.

2. Methodology
An electrolytic replacement technique was developed based on Lechtman’s work [3]. The methodological steps introduced are described below.

2.1. Copper coupons preparation
Copper coupons were cut in rectangles of 5.0 cm length x 2.5 cm height x 0.1 cm width, sanded sequentially with the silicon carbide (SiC) grit sizes of 500 µm, 800 µm, 1200 µm, and 2000 µm, and polished to a mirror-like finish through a 1.0 µm alumina powder slurry. Before deposition, each copper coupon was cleaned using ethanol (99.9%, Merck) and acetone (99.8%, Merck) in an ultrasonic bath (WUC-A01H, Witeg) for 5 min, respectively.

2.2. Electrolytic bath and gold deposition
The electrolytic bath was prepared in a 150 mL beaker containing 0.01 M of HAuCl₄ (99.995%, Sigma-Aldrich) as the gold precursor, 0.046 M of KNO₃ (99%, EMSURE), 0.01 M of KAl(SO₄)₂·12H₂O (A.C.S. Reagent, J.T. Baker), and 0.08 M of NaCl (100%, J.T. Baker) in 60 mL of distilled water. Then, 0.13 M of NaHCO₃ (99%, Merck) was added to reach a pH level above 9 (between 9.1 and 9.3). The prepared bath was stirred with a magnetic pill for 1.5 h at 80 °C. Finally, half of the copper specimen was dipped in the electrolytic bath. The copper coupon was lifted 1.5 cm after 3 min of reaction and removed from the solution after 6 min of testing.

2.3. Characterization of samples
The characterization of gilded copper coupons was performed through XRF and optical microscopy; besides, SEM-EDS analysis aimed to complement the results obtained in the lab by comparing them with the data provided by an archaeological Moche sample from Dos Cabezas, North of Perú.

2.3.1. X-ray fluorescence spectroscopy. These measurements were made through the Hitachi X-MET 8000 Expert equipment. The gilded copper was placed in the spot region of the equipment -avoiding anodic zones- for 20 s of measuring time in the alloy mode. The resulting spectra were reviewed to confirm the presence of gold in the sample. The obtained results correspond to the average of the two measurements made in both frontal faces of the coupons.

2.3.2. Scanning electron microscopy with energy-dispersive x-ray spectroscopy. This characterization was performed using a TESCAN second-generation SEM, VEGA/XMU model. The gilded copper samples were mounted in resin (TramsOptic) for metallographic samples (ZXQ-5A, LYRICTEST) and polished until mirror finishing before characterization.

2.3.3. Optical microscopy. The microscopic features of the sample were characterized after the gilding process through a continuous zoom trinocular stereo microscope (Alpha Optics, GL6545TI). The images were taken by a trinocular camera of 18 megapixels (Amscope software).
3. Results and discussion

Heather Lechtman proposed an effective method for gilding copper with a corrosive bath rich in reagents possible known and available for ancient Peruvian Piura Valley citizens [3-5]. We took the same 1:1:1 mass ratio of potassium aluminum sulfate, potassium nitrate, and sodium chloride that she reported. The mass required per reagent in the solution was set based on the sodium chloride molecular weight -the lowest-. Then, according to a similar study [6], we selected the specific concentration of 0.08 M for the sodium chloride. Meanwhile, for the gold precursor -chloroauric acid-, the concentration of 0.01 M was fixed to evaluate a lesser value than the one used by Lechtman and other authors [3,6,7]. Moreover, in order to reach the optimum pH level of the electrolyte bath, we found that 0.13 M of sodium bicarbonate was enough to obtain a pH of 9.

Lechtman described the deposition temperature by associating it with a gentle boiling of the solution. However, to determine the exact temperature value in our experiments, previous studies that pointed out 80 °C and 90 °C for outstanding results were taken into consideration [8]. Here, 80 °C was taken as an optimal condition to avoid the faster evaporation of water at higher temperatures, which leads to nonuniform gilding processes. In this way, we were able to evaluate the amount of gold deposited in the copper coupon by XRF after 3 min and 6 min of reaction.

As shown in Figure 1, the plating process is not uniform in the whole sample due to the presence of several anodic regions on it (dark zones in the specimen). This phenomenon is caused by the oxidation of copper that rises because of the electrochemical replacement reaction. Copper behaves as an anode, transferring ions to the gold to be reduced at the solid-liquid interface. Equation (1) and Equation (2) show the half-reactions of copper and gold, respectively, and Equation (3) shows the balanced overall reaction in the cell. A similar replacement reaction was provided previously by Lechtman [3].

![Figure 1](image-url)

**Figure 1.** (a) Image of the gilded copper sample after 3 min and 6 min of dipping time in the bath and (b) optical microscope image indicating the presence of an anodic region on the sample’s surface.

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\begin{align*}
\text{Cu}(s) & \rightarrow \text{Cu}^{2+} _(aq) + 2e^-, \\
\text{Au}^{3+} _(aq) & + 3e^- \rightarrow \text{Au}(s), \\
2\text{Au}^{3+} _(aq) + 3 \text{Cu}(s) & \rightarrow 2\text{Au}(s) + 3\text{Cu}^{2+} _(aq),
\end{align*}
\]

The plating of the copper sample was uniform and adherent throughout the immersed piece. On the other hand, at the bath-air interface, the water vapor released from the boiling solution generated an external anodic and nonuniform zone on the coupon (Figure 1). The electrochemical replacement reaction runs until the copper potential is uniform throughout the coupon. Thus, the anodic zones get covered at the maximum deposition time [9]. Figure 2 shows that after 6 min of deposition, the gold
mass amount on the copper doubles its value regarding the 3 min test. Then, under our experimental conditions, the dipping time required to stop the electrochemical reactions goes beyond 6 min.

![XRF spectra](image1)

**Figure 2.** (a) XRF spectra after 3 min of reaction time, (b) XRF spectra after 6 min of reaction time, and (c) XRF mass percentage of gold deposited on copper for each testing time.

According to Lechtman, a good electrochemical replacement process should be characterized by tiny anodic zones surrounded by large cathodic areas. Those anodic regions are invisible to the human eye but big enough to sustain the electrons interchange between the substrate and the bath until they get completely covered [3]. She also believes that the presence of multiple pits on the copper surface could stimulate the conformation of the anodic regions. However, when searching for evidence in different excavated samples from Loma Negra, Piura valley, the current corroded state of the objects obstructed her scientific discussion.

The research work of Lechtman suggested that the electrochemical replacement process limits the thickness of the deposited gold to 2 µm and that temperatures from 500 ºC to 800 ºC are required to develop a diffusion zone at the copper interface to obtain a good adherence of the gold’s film [3]. However, as shown in Figure 3, our results showed that it is feasible to obtain up to 7.5 µm of thickness for the deposited layer after 6 min in the electrolytic bath. The thicker plating layers developed in this work -even for 3 min of reaction (5.17 µm)- could be related to the introduction of higher temperatures in our experiments compared to Lechtman’s protocol. In addition, the temperature of the process was enough to develop diffusion zones in the copper sample, almost doubling their length from 3 min to 6 min of reaction. This confirms the good adherence of the gilded layer obtained after the electrochemical replacement. It differs from Lechtman’s argument even though further experimentation is lacking to evaluate this, and other issues associated with the thermal treatment, such as the grain size of the copper substrate.
Lechtman’s approaches to the techniques and methods used by Moche and Vicus goldsmiths are helpful to reconstruct their plating objects. However, the corrosion process that undergoes these pieces under environmental conditions could start with less difficulty when the thickness of gold is thinner. Besides, the corrosion processes could be accelerated by the humid and saline environments found on the northern coast of Peru [10,11]. As a result, some gilded objects would have been required to be replated with some frequency. Likewise, the presence of diverse corrosive agents such as chlorine in the burial environment enhances the diffusion of copper through gold, troublesome its conservation to the

Figure 3. Backscattered images of the cross-section of the copper substrate after (a) 3 min and (b) 6 min in the electrolytic solution.
present [12]. As shown in Figure 4(a) and Figure 4(c), in burial environments, the solid diffusion of copper through gold is so important that it scratches the gold layer and erupts from it. Once the copper diffusion overpasses the cathodic protection, the degradation of the substrate accelerates, spreading transversely and underneath the layer of gold.

On the other hand, Figure 4(b) and Figure 4(d) show that the thickness of the gold layer reaches a value around 10 µm in Moches’s gilded objects, thicker than those shown in Figure 3. Therefore, extended reaction times should be used to explore the possibility of higher thicknesses with the electrochemical replacement technique. Furthermore, we suggest that Moches and Vicus could have also used electroless or galvanic gilding techniques. But to sustain this statement, new experimental data associated with materials that these cultures could have used are missing.

4. Conclusions
This research work provides scientific insights into the electrochemical replacement technique for plating copper objects with gold. We deposited adherent gold layers with thicknesses of 5.17 µm and 7.50 µm after dipping a copper sample for 3 min and 6 min into an electrolytic solution, respectively. However, several anodic regions were as well found in the copper substrate. This issue points out that the maximum deposition of gold on copper is beyond 6 min of reaction time. However, the thickness of gold observed in some archaeological samples exceeds the ones achieved in our trials. Futures studies should focus on extended reaction times as much as on assessing the corrosion rate of gilded coppers in burial and atmospheric environments. These arguments would reinforce the electrochemical replacement technique as the one used by Pre-Columbian goldsmiths. Also, plating techniques such as electroless and galvanic should be considered to enrich the scientific discussion. These research initiatives are essential for the development of conservation strategies to preserve our historical heritage.
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