Conservation Techniques of an Archaeological Copper Tray in the Islamic Art Museum in Cairo

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Abstract
A copper tray dating back to the Mamluk era, kept in the stores of the Museum of Islamic Art in Cairo, registered under No. 9315. It was broken into six separate parts with several holes. Its edge is serrated by a line in the prominent Naskh script. The tray suffers from various deterioration phenomena, such as pits and holes in different places of the tray, and the wrong restoration, as it was welded incorrectly with the aim of assembling some of its separate parts. Various examinations and analyses were carried out. The results of the X-ray diffraction analysis showed the presence of Cuprite (Cu_2O), Atacamite and Paratacamite. Treatment and conservation of the tray was carried out, including mechanical cleaning and chemical cleaning. The assembly process was carried out for the separate parts. The holes were completed using mixture of epoxy with natural oxides and calcium carbonate with microballoon as filler. The tray was also isolated using 3% benzotriazole to protect it from exposure to corrosion.

Key Words:
Conservation, Corrosion, Archaeological Copper Tray, Deterioration, Islamic Art Museum in Cairo.

1. Introduction
The Museum of Islamic art is considered one of the most important museums that contain copper metal artifacts dating back to the Mamluk era, **(Russell, 1962).** An example of copper antiquities in the Museum of Islamic Art is a copper tray registered with No. 9315, preserved in the stores of the museum of islamic art, with a line in the prominent Naskh script reading from it (Al-Maliki al-Alami al-Amili al-Adly al-Fadi al-Mujahid al-Mujahid al-Murabati al-Azid al-Afdal al-Awda al-Amiri al-Kabir al-Mandi al-Saifi referred to by someone who looks like from presenter class). The Mamluk copper tray was executed in the style of grooving or engraving. The method of decoration by engraving or grooving is one of the methods of shaping inherited since antiquity in historical times in Egypt, **(Ward, R., 1998)** and this method is implemented using steel pens whose shapes vary according to the decorations to be formed **(Allam, N., 1989)**. In the Mamluk era in particular, this method reached the height of its prosperity in the decoration of small spaces **(Atil, 2002)** and fine bands such as ornamental

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frames, **(Geza, F., 1992)**. This method was used in a way that suggests the embodiment of some decorative elements by making precise lines and inscriptions **(Maher, S., 1986)** that cover a lot of vitality to show the subtle branches that make up the decorations and securitizations **(Geza, F., 1992).** This copper tray suffers from many deterioration signs, for example, thick corrosion layers, pits and holes containing copper corrosion compounds. In addition to prominent welds on the surface of the tray resulting from the wrong restoration of the tray parts assembly, also broken and separated parts amounting to six parts beside that missing parts in the outer serrated edge of the copper tray, fig. (1), A, B and C. This research aims to study the components of the Mamluk copper tray and its corrosion compounds, in addition to carry out treatment, restoration and conservation processes for it and protects it from being deteriorated again.

A B C

Fig. (1) , A,B and C, The Mamluk copper tray, kept in the stores of the Museum of Islamic Art in Cairo, registered under No. 9315.

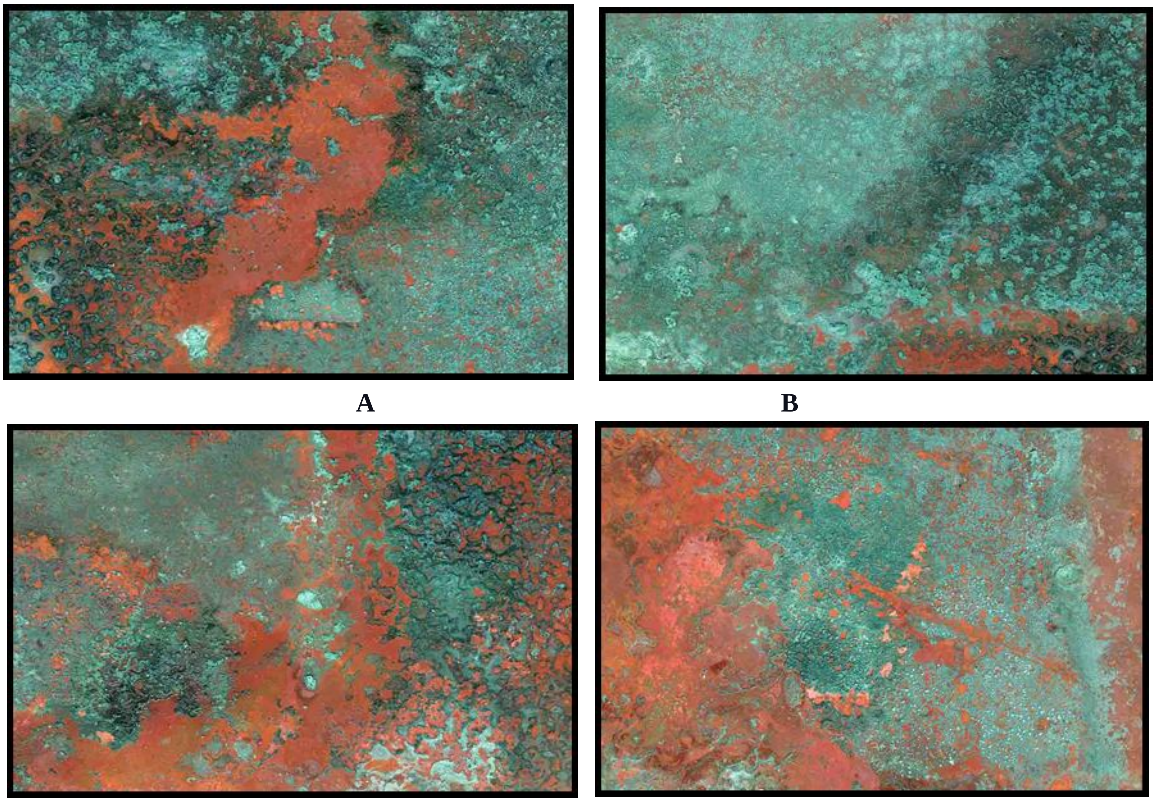
2. Materials and Methods

Examinations and analysis have been performed to know components of the copper tray and to diagnose the deterioration phenomena. Light Optical microscopy (LOM) was used to investigate samples from the copper tray. Samples were observed by a Wild M8 stereomicroscope, an Olympus BX51 optical microscope. Inverted research metallurgical microscope system [PMG3-F2]**,** Olympus Company was also used. This microscope system is used to inspect the crystals and inclusions for the acquisition of information on material composition and sizes by photomicrography. Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray analysis (EDX). Samples were analyzed by Philips (XL30) microscopy, equipped with EDX micro analytical system to carry out the total element content qualitatively and quantitatively by EDX unit. The beam voltage for the quantitative determination of elements was set to 25 kV, to obtain better excitation of the low-energy and low-concentration compounds. X-ray diffraction analysis carried out with Phillips X-ray diffraction equipment model pw/1840 with Ni filter, Cu radiation 1.54056 A° at 40 KV, 25mA, 0.05 /sec. Measurements were carried out on powders of the samples, in the range $0° < 2\theta < 60°$ with a step of 0.02°.

3. Results

3.1 Light Optical microscopy (LOM)

The light optical microscope was used for the corrosion layers on the surface. The optical microscopic for examination of the corrosion layers showed that it differs in color, from green to chalky green and in thickness, from thin to thick. The surface of the copper tray was appeared in a reddish-brown color, Examination of the nature and shape of the surface revealed the presence of some irregularities and regular surface erosion with the presence of some pits. It was also found that there is a color gradation of the corrosion products, which ranges from dark green, to a light green color with a chalky appearance due to the presence of different corrosion compounds. Fig. (2), A, B, C and D.



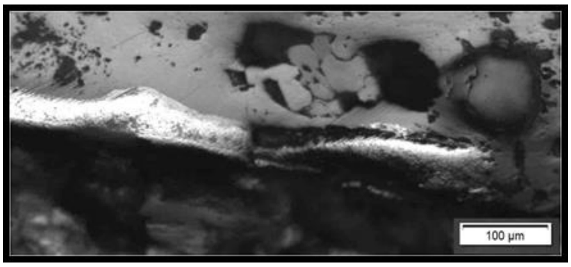
A **B**

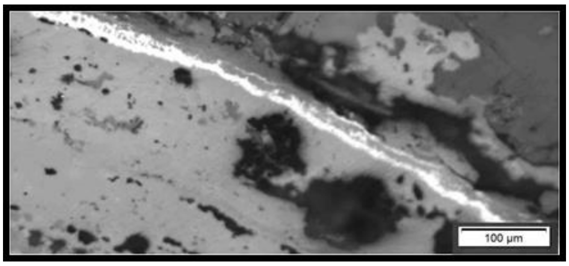
C **D**

Fig. (2) A, B, C and D corrosion products with green and reddish brown colors on the copper tray surface, (40X).

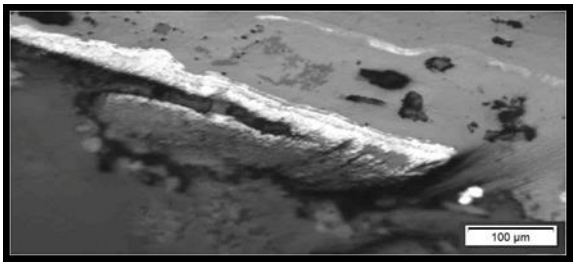
3.2 Examination using Inverted research metallurgical microscope system

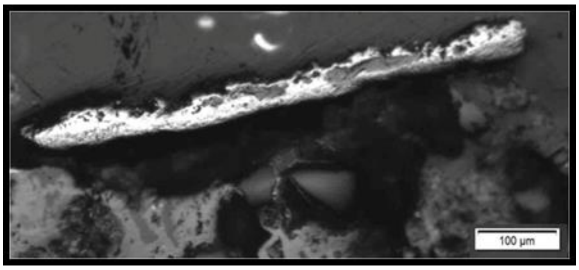
Inverted research metallurgical microscope system [PMG3-F2] was used to investigate samples from the copper tray. It shows that, erosion of copper metal of the tray, corrosion compounds, clay minerals and grains of quartz as impurities. The examination revealed the presence of corrosion, roughness and irregularity in the surface due to the transformation of some metal components into corrosion compounds fig. (3), A, B, C and D.





A B





C D

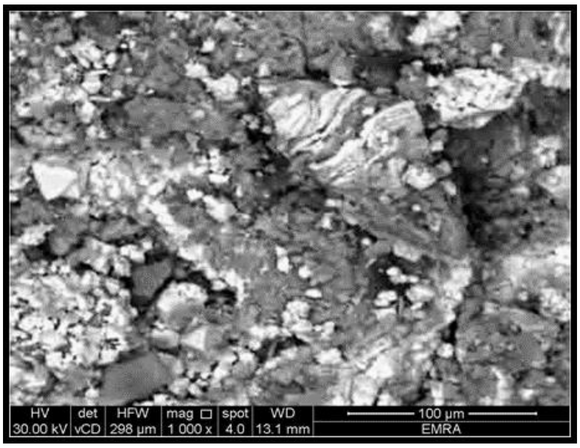
Fig. (3) A, B, C and D metallographic photomicrographs of the copper tray samples show corrosion layers and erosion of copper with clay and quartz minerals.

3.3.3 Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray analysis (EDX)

Investigations of the copper tray samples by Scanning electron microscope showed that the presence of erosion, voids, micro-cracks, and pits, Fig. (4), A, B, C and D.

3.4 Analysis by (EDX) unit of the gilding layer

Corrosion samples were analyzed by the (EDX) unit attached to the scanning electron microscope (SEM). It showed that, the presence of Cu by 49.69 %, Ca by 8.3 %, Sn by 0.72 % . Ratios of other elements have been found and the results are complete shown in fig. (5).



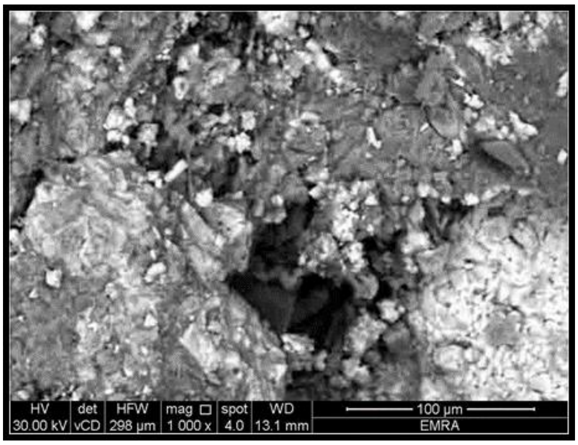
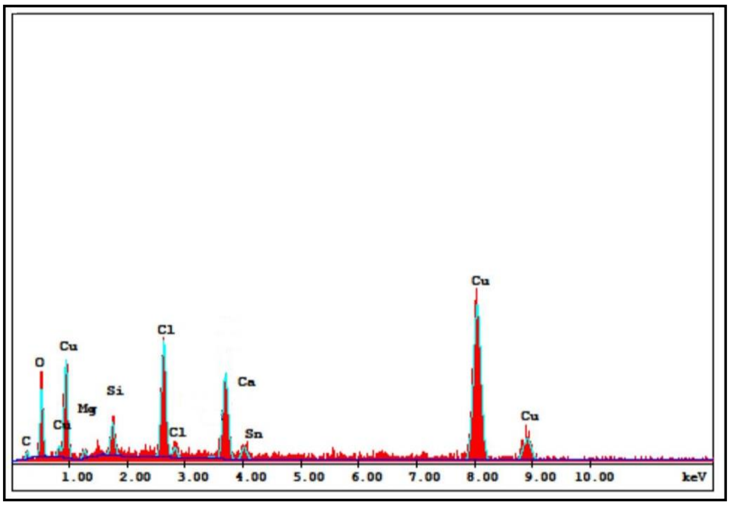


Fig. (4), A, B, C and D. SEM photomicrographs of the copper tray samples Show erosion, corrosion layers, voids, and micro cracks



Element	Wt %	At %
C K	5.24	13.75
O K	19.64	38.67
Mg K	1.85	2.40
Si K	3.93	4.41
Cl K	10.63	9.44
Sn K	0.72	0.19
Ca K	8.30	6.52
Cu	49.69	24.63
Total	100.00	100.00

Fig. (5) Shows EDX pattern of corrosion products sample.

3.5 X-Ray Diffraction analysis (XRD)

More than one sample from different places and in different colors was analyzed from the corrosion formed on the surface of the metal tray, and the results were similar in all the samples that were analyzed. The XRD spectrum of the samples consists of Atacamite $Cu_2Cl(OH)_3$ [2-146] , Paratacamite $Cu_2(OH)_3Cl$ [2-146] and Cuprite (Cu_2O) [05-0667] , Fig. (6) illustrates the XRD Pattern of this sample.

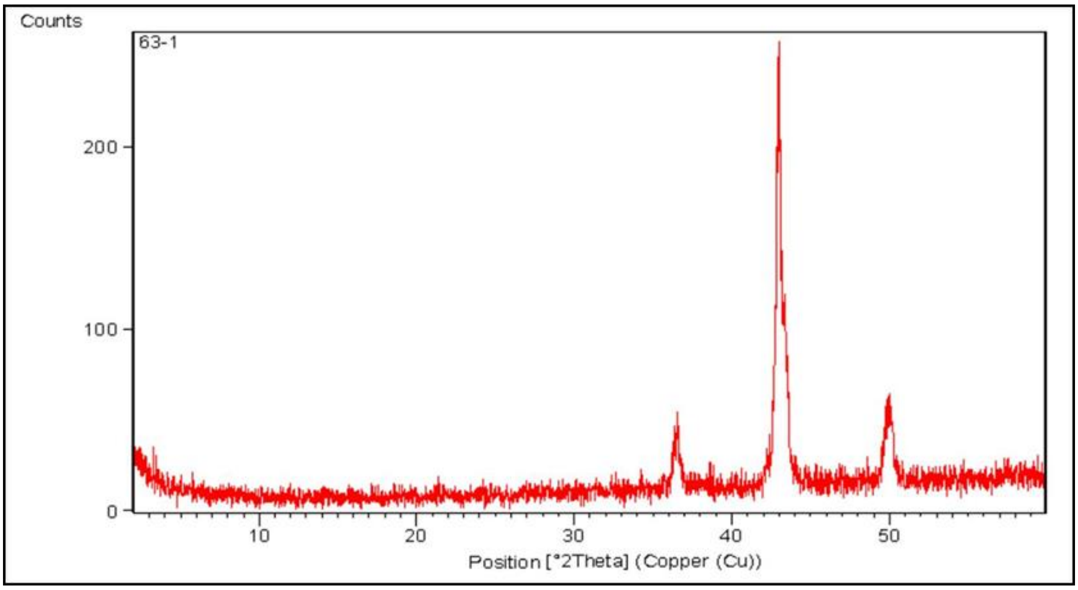


Fig. (6) Shows XRD pattern of corrosion sample.

4. Treatment and Conservation of the Mamluk Copper Tray

The mamluk copper tray has gone through different stages, until it was treated from all deterioration phenomena, Conservation processes included mechanical, chemical cleaning, Assemble the broken parts, Fill and complete the gaps and missing parts, surface insulation as follows:-

4.1 Cleaning

Choosing the appropriate method for cleaning depends on the results of examinations and analyzes, through which we identify the components of rust products present on the surface of the copper tray, **(Park, J., et al, 2020).**

4.1.1 Mechanical cleaning

Soft brushes were used in different sizes according to the condition and thickness of the Corrosion layer. The frieze was used parallel to the surface to remove excess parts of the weld, which had been done in a previous restoration, to obtain a flat surface, **(Ingo G.M., 2019).** The Frieze was also used to clean the pits that contain corrosion compounds, taking great care to choose the heads that match the corrosion layer and the condition of the copper tray to preserve the patina layer.

4.1.2 Chemical cleaning

Chemical cleaning baths were made in the plastic basins so as not to interact with the effect with the continuous observation of the treated parts. These baths contain rochelle salt then, citric acid at a concentration of 3%, then successive baths containing calcium bicarbonate, to neutralize the alkali with the acid, **(Petiti, C. et al, 2020).** Medical cotton was used to remove layers of corrosion and dirt after the copper tray parts were removed from the plastic basins. Successive baths of distilled water were made to remove any residual chemical cleaning agents. Finally, the dryer was used to ensure the drying of the effect after successive baths of distilled water (at low temperatures so as not to damage the copper tray), fig. (7), A, B and C.

A B C

Fig. (7), A: During Mechanical cleaning of the copper tray, B: during chemical cleaning and C: after mechanical and chemical cleaning.

4.2 Assembly process for copper tray parts

The different parts of the tray were numbered and recorded to determine their locations to return them to their original locations during the assembly process. A mould was made of layers of dental wax to fix the separate parts and to put the filler to fill the spaces between the separate parts that make up the copper tray, **(Park, J., 2020).** The dental wax was isolated with Paralloid-B72 at a concentration of 3%. Silicone and gauze were used to reinforce the separate parts of the tray to be fixed using epoxy pastes (consisting of monomer and hardener). The monomer was mixed with natural oxides and calcium carbonate with the microballoon as filler and placed in a large container. Only the quantity that will be used is mixed with the hardener, **(Petiti, C. et al, 2020).** It was noticed during the assembly process that there was a completed part that was cast in a different color from the rest of the tray parts because of a previous restoration. It is noted that the part completed during the previous restoration on the edge of the tray takes the same inscription text, which indicates that the restorer who completed this part took his fingerprint from the part in the copper tray, and this explains that the text around the edge of the tray is incomplete, but it is repeated, fig. (8), A, B, C, D and E.

A **B** **C**

C **D**

Fig. (8), A, B, C, D, and E, shows steps of the assembly process for the copper tray parts.

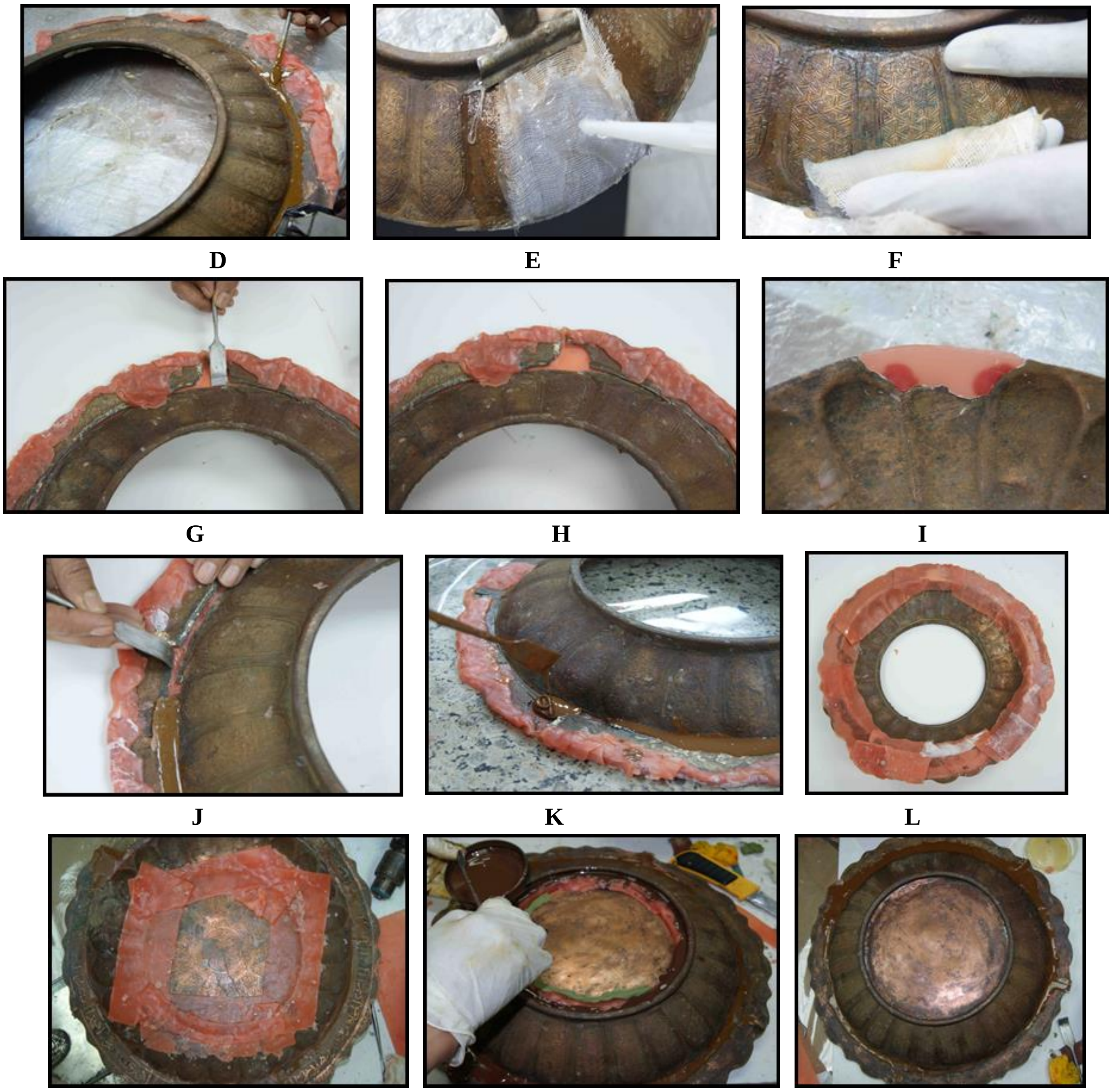
4.3 Completion

Three layers were used to support the completion process for the separated part, where a layer of silicone was used, then after drying another layer of silicone is placed, then a layer of silicone and gauze. Each layer must dry before applying the next layer, **(Park, J., 2020),** and then the gauze layer is fixed with a metal clip until this piece is fixed in place correctly. After the mold that supports the separated part has dried for 24 hours, the existing joints (voids) are completed using (epoxy paste with natural oxides and calcium carbonate with microballoon as filler), **(Ingo G.M., 2019).** The mold was fixed with a sickle and allowed to dry for 42 hours. Dental wax was used by taking an imprint of the missing part of the edge of the copper tray and it was completed with epoxy paste, fig. (9), A – O.

4.4 Finishing stage

The freezing machine was used after the completion process to remove any unintended excess parts that formed during the completion process. The levelling of the surfaces of the contact areas between the copper tray parts was also taken into consideration, fig. (10), A, B, C and D.

A **B** **C**

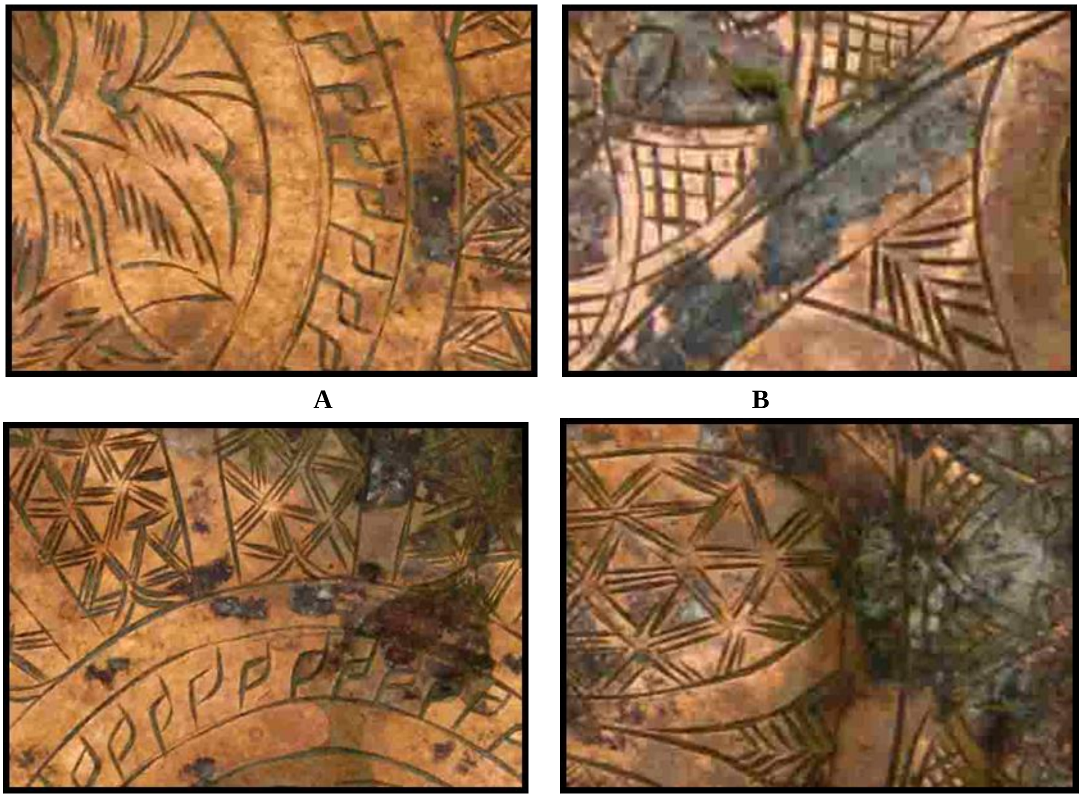


D E F G H I J K L M N O

Fig. (9), A - O, shows steps of completion process for the copper tray parts.

4.5 Protective Coating Process

The surface of the copper tray was protected using benzotriazole at 3% (taking all precautions so as not to affect the health of the restorer), **(Walker, R., 1970)** such as wearing gloves in the hands and a mask on the nose during implementation, fig. (11), A and B, shows the mamluk copper tray after treatment and conservation processes.



A B

C D

Fig. (10), A, B, C and D, shows details of the Mamluk copper tray after treatment process.

A B

Fig. (11), A and B, shows the mamluk copper tray after treatment and conservation processes.

5. Discussion

The research dealt with a copper artifact belonging to Islamic art. It is a copper tray dating back to the Mamluk era and preserved in the Museum of Islamic Art in Cairo with No. 9315. It is clear from the study of the techniques of copper tray making that it was formed by hammering and manual assembly. Decorative units were made on the surface of the tray by engraving with metal pens. Its parts were assembled by welding. Examination by optical microscope revealed the presence of pits on the surface as well as the presence of layers of corrosion compounds in reddish brown and green colors. It was found from the analysis by X-ray diffraction that the rust products present on the surface of the copper tray are the minerals Cuprite, Atacamite and Paratacamite. **(Scott, D., 2002)** Examination with the EDX unit attached to the scanning electron microscope revealed that the copper tray contains chlorine ions, which explains the formation of the minerals Atacamite and Paratacamite, known as the bronze disease, **(Scott D., 1990).** A layer of copper oxide (Cuprite) is formed in the presence of moisture, **(Pan, C., 2016)** which allows the decomposition of copper into Cu^{+} cations with hydroxyl anions OH^{-}, and this type of corrosion is not completely uniform, but appears in the form of light ripples on the surface, **(Odnevall, W., et al, 2014)** and corrosion continues under the corrosion products through the diffusion of cations or anions. The presence of Cl^{-} anions in the medium surrounding the copper artifacts leads to the activation of local corrosion and corrosion processes, so chlorine anions with a high movement are attracted towards the anodic (negative) areas in the pores. Nozzles, which represent the corrosion positions where the decomposition of the copper object occurs, and the chlorine ions interact with the Cu^{+} ions released as a result of the oxidation of the metal **(Macleod, I. , 1981)** and the CuCl chlorides are formed in the depth of the corrosion positions, **(Park, J., 2020).** It was also found that there is a percentage of the element tin due to the use of tin welding in assembling the copper tray parts together, **(Ingo G.M., 2019).** It was also found that other elements were present in small percentages as impurities that caused internal damage to the copper tray. Examination with a scanning electron microscope revealed the heterogeneity of the corrosion layers formed on the surface of the copper tray and the presence of gaps, cracks, and cavities in them with mixing with different mineral grains. The study and examination with the inverted microscope proved that the presence of clay minerals and quartz grains. The metallographic examination also revealed the presence of corrosion on the surface of the copper tray due to the formation of various corrosion compounds on it, which led to the presence of roughness in the surface and pitting in some places of the surface of the copper tray**, (Park, J., et al, 2020).** Examinations and analyzes also revealed the presence of man – made deterioration in the form of welding the parts of the tray together because of a previous restoration of the tray, which resulted in the presence of extra parts that caused a formal distortion of the tray. These excess parts have been removed by the frieze machine in current treatment and conservation processes. The treatment and maintenance of the tray included the application of benzotriazole because of its protection properties for metallic objects from exposure to deterioration and the formation of corrosion compounds in the future.

6. Conclusion

Examinations for the copper tray showed that, the manufacturing technique was made by cold forming, assembly of its parts was made by welding and the biblical text was formed using engraving technique. Some elements were appeared in analysis by EDX unit as impurities for example, Sn, Cl, Si, Ca and Mg that led to the presence of internal deterioration factors. Besides the external deterioration factors such as polluting gases, with the relative humidity factor, also the human deterioration of bad restoration led to damage of the copper tray. Pollution of the environment with chlorine ion with relative humidity, led to the formation of basic copper chloride, Atacamite $Cu_2(OH)_3Cl$ and Paratacamite $Cu_2 (OH)_3Cl$. The process of assembling the six parts of the copper tray ensures that it is not lost. In addition, completing the missing parts has achieved the goal of being one integrated unit, and this contributes to preserving its artistic and archaeological value. On the other hand, treating the surface with a protective layer ensures that it is protected from damage deterioration. In future, research in the field of using green materials for copper objects protective coatings are suggested.

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