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# CHARACTERIZATION STUDY OF A SILVER TRAY FIXED TO A WOODEN FRAME OF PRINCE MOHAMED ALI MUSEUM, CAIRO, EGYPT

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***Abstract***

*The metallic tray studied here dates back to the prince Mohamed Ali period , consists of three parts, the body of the tray which have multi decorations of flowers , the frame and wooden base connected to the tray without handles , this article describes for the first time in details the examination of the studied tray components. The authors were significantly interested in identification of botanical wooden sort, jointing technique of the wooden base and the chemical composition of the materials which used in this object , in addition, identification of deterioration aspects and {Microbial Decay] fungal decay (biodegradation) included in this study. The optical notice and assessment were done to know the condition of this tray, 3D dimensions software was used to illustrate wood joint technique. The botanical wooden species were identified in thin sections under optical microscope, while scanning electron microscope with EDAX to understand the kind of the metallic part and x-ray diffraction was used in order to identify corrosion products which covered the metallic part in several places.On the other hand The results proved that wooden base was made of Salix Sp., while the body of tray was made of Coin Silver alloy 90% silver.*

***Keywords:*** *Silver; Salix sp; Tughra; Tarnishing; Decay; Fungi; Bacteria.*

## Introduction

Silver and its alloys are deemed as ideal ductile materials and have been excessively employed for the manufacturing of various precious and decorative artefacts [1], such as decorative art, jewellery, coins and silver tableware [2]. The object studied here represents an ottoman tray which backs to 19th century from solid silver connected to the wooden frame without handles, shaped rectangular form, decorated with flowers. The tray is decorated beautifully with engraved leaves and flowers which approximately used for the service of delicate drinks to visitors. The tray composed of two parts as follow: the first part is the metallic (silver alloy) part which separated into two parts, the frame and the base of the tray, the second part is the wooden frame, these parts were fixed together by using iron screws. The dimensions of metallic part are 34cm in length, and 27 cm in width, while the wooden frame dimensions are 20cm in length.

Figures 1 and 2 show the state of the selected tray as this study is focusing on using analytical techniques to conclude a deeper knowledge of the tray components moreover; the authors were especially interested in the object state, the tray damage, and wooden frame.

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**Fig. 1.** illustrates the reverse of the tray

**Fig. 2.** Illustrates the decorated obverse

## Materials and methods

***Documentation of the studied object***

Visible imaging was acquired with Nikon Digital camera D3200, and fitted with a Nikon Nikkor 18-55, which had been used in documentation, detect clear photos of the tray components, and deterioration aspects, while the 3d program was hired to explain the jointing techniques in the wooden frame.

***Sampling***

Certainly the samples taken from the tray were little because the limited distribution of more artifacts-samples. Five representative samples were collected carefully from unseen parts of the metal and wooden frame of the studied tray to identify their chemical composition and deterioration, as shown in table 1.

Table 1. Illustrates the Examination and analysis of samples

| No. | Type of Sample | Examination |
|---|---|---|
| 1 | Swap (Microbial decay) | Optical M |
| 2 | Wood | Optical M |
| 3 | Metallic frame | SEM-EDX |
| 4 | Metallic base | SEM |
| 5 | Powder corrosion | XRD |

***Optical microscope and USB Digital microscope***

Some samples of the studied tray were examined by USB Digital microscope with photo capture resolution ranged from 1000×, while OPTIKA B 9 digital camera illustrated detailed photos in identification of the wooden species, wood samples were examined into the three principal anatomical directions: transverse section (TS), tangential longitudinal section (TLS), radial longitudinal section (RLS), and these sections have been installed on glass slides and observed under transmitted optical microscope [3].

***Isolation and identification of bacteria and fungi***

Swab sampling technique was applied, and nutrient agar media was used to cultivate samples in petri dishes to identify bacterial species, while cellulose agar was used as a media for fungi. After 21 days of incubation at (28-30ºC), identification was carried out based on references [4-6].

***X-ray powder diffraction (XRPD)***

The X-ray diffraction patterns of the powder sample (D) from corrosion were obtained by using a diffractometer PW 1480 Netherland, operated at 35kv, using a Cu and Ka radiation wavelength of 1.54056Å. The measurements were made at room temperature. The reference database used for matching is PDF4, Preparation of each sample consisted of grinding the dry samples on one direction, by using a mortar and pestle to obtain a fine powder. The XRPD analysis was done at XRD Unit in faculty archaeology, Cairo University.

***Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX)***

The microstructure and morphology of the mineral constituents in the studied tray were recorded with a scanning electron microscope: Model Quanta 250 FEG (Field Emission Gun) - FEI Company, Netherlands attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30kV, magnification 14× up to 1000000 and resolutions for Gun.1n). Without coating of the samples with a highly conductive thin film of gold. The SEM.EDX was done at the Egyptian Mineral Resources Authority, central laboratory sector, Giza, Egypt.

## Results and discussion

***Identification of jointing technique***

The 3d program was responsible for illustrating the jointing technique of wooden frame which was made of nine wooden panels connected together by using a half lap joint technique, and fixed together by using iron screws as illustrated in figure 2. The earliest extant example of using this technique was from the Predynastic period was found connecting the corners of a burial box in grave N7454 at Nag el-Deir [7, 8].

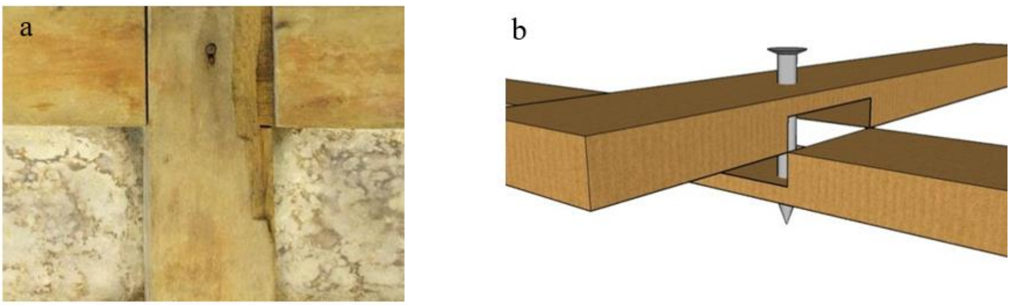


**Fig. 2.** Jointing technique illustrated by 3D program: a – visible, b - half lab

***Examinations by optical microscope***

***Identification of wooden species***

The wooden frame identified as *Salix sp.* based on anatomic features under optical microscope. The beginning of the use of this type of wood was in ancient Egypt for boxes, making camel saddles, funerary garlands and making tent poles [9], shown in figure. 3.

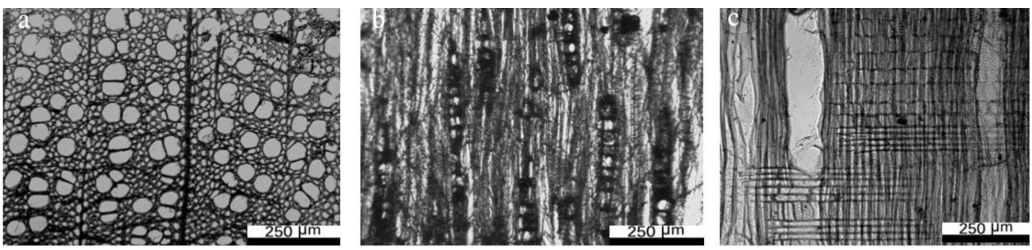


**Fig. 3.** The anatomical characteristics of wood thin section under transmitied optical microscope: a. Transverse section (TS) showing growth ring boundaries distinct by identifying the difference between the late wood, and early wood in vessel size. Vessels are consisted of 2-4 elements in solitary or in radial multiple shape, while axial parenchyma scanty paratracheal; b. Tangential section (TLS) showing rays exclusively uniserate; c. Radial section (RLS), simple perforation plates, inter- vessel pits alternate, fibers with simple to minutely bordered pits (libriform fibers), body ray cells procumbent with one row of square marginal cells [10,11].

***Identification of metallic part***

By using USB microscope some hallmarks appeared which illustrated that this tray was hallmarked with rare "tughra" and " Sah" marks. The tughra mark was the sultan's signature, related to Sultan Abdul Hamid II (1876-1909) and stamped with number 90. So These results revealed that this tray dates back to Ottoman Empire, especially in the period of Sultan Abdul Hamid II and number 90 refers to the caret of the metallic part (silver 900) or coin silver, as illustrated in figure 4).


**Fig. 4.** Rare tughra Sultan Abdul Hamid ll (a), Mark Sah (b), Caret of the silver alloy stamped with number 90 (c).

***Identification of microbial decay***

Microbial examination revealed to the presence of Stemphylium sp as shown in figure 5. Temperature and humidity are playing an important role to growth the airborne spores, especially on the wooden surface,this kind of fungi can cause reducing in color value, also it can increase the permeability of parenchyma cells to water [12]. The word microbiologically influenced corrosion (MIC) is used to imperfect corrosion due to the existence and effectiveness of microorganism. The presence of G+ve short bacilli spore former bacteria (Fig. 6) may be one of improves which had been occurring as a result of the interactive deterioration between silver and wood. As bacteria have a seriously function in many abrasion procedures in nature and decayed wood could help in increasing microorganism attack. Confirmation for a chemical reduction of sulfur dioxide to hydrogen sulfide in the site of the object was requiring sulfur-reducing. Also, oxidation of the sulfides may form sulfuric acid, which produces further abrasion procedures [13]. So microorganisms do not create singular types of corrosion, instead, they can make pitting [14].

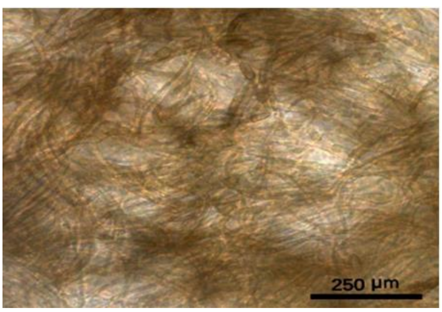


Fig. 5. The presence Stemphylium Sp. [15]

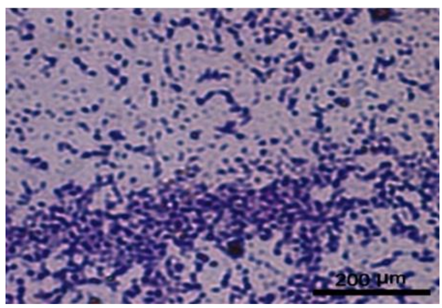


Fig. 6. The presence of G+ve short bacilli spore former bacteria [16]

***Identification of the tray components***

The SEM-EDX for 2 samples in figures 7 and 8. The first sample was taken from the metal frame, while the second was taken from the metallic base. The results revealed that the metallic part of the subjected tray consisted of silver alloy, and confirmed the examination by

USB microscope that it is coin silver 90, as shown in figure 4. As the most common definition of Coin silver means that the item contains 90% silver and 10% copper by mass (table 2) [17].

**Table 2.** refers to the pattern of SEM-EDX analysis of the metallic frame, and base

| Sample | Element | Wt | Total |
|---|---|---|---|
| **6** | **Ag** | 88.69% | **100%** |
| | **Cu** | 11.31% | |
| **7** | **Ag** | 89.73% | **100%** |
| | **Cu** | 10.27% | |

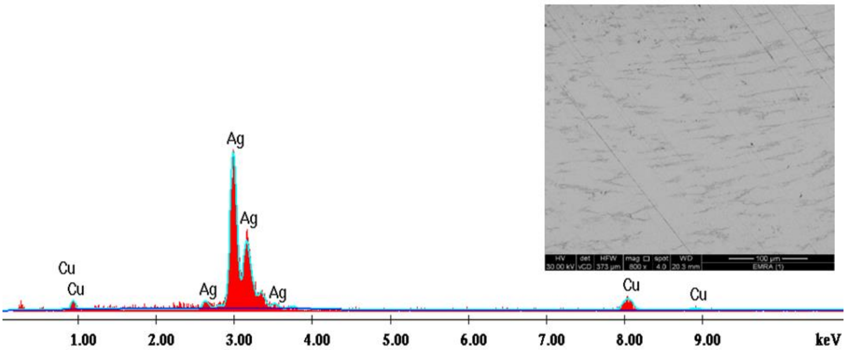


**Fig. 7.** Pattern of SEM-EDX analysis of the metal frame (sample c)

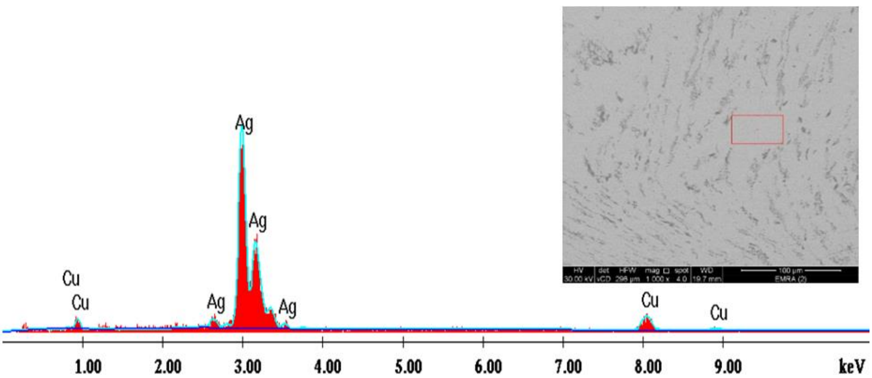


**Fig. 8.** Pattern of SEM-EDX analysis of the metallic base (sample d)

XRD results revealed to the presence of tenorite and atacamite which might be explained that there were small amounts of copper in the alloy. As Silver was usually alloyed with copper to modify its mechanical properties [18,19]. Atacamite and tenorite are corrosion products of copper, tenorite is black, atacamite is dark green and both are non-protective [20]. The copper degradation process is well known as a small amount of Cu play a conclusive role in the corrosion process of silv er alloys due to the preferential oxidation of Cu [21]. Copper-silver alloys contain of a silver-rich phase and a copper-rich phase because of low copper solubility in silver, any alteration of this copper-rich phase and in oxidizing conditions contribute in the precence of green corrosion products on the silver object [22]. As illustrated in figure8 [table.3].

**Table 3.** The approximate XRD analysis results of the studied tray

| Corrosion Product (Component Traces) | |
|---|---|
| Atacamite +++ | Silver oxide ++ |
| Acanthite +++ | Silver ++ |
| Chloragyrite ++ | Silver carbonates ++ |
| Tenorite ++ | |

+ traces (between 1 - 10),
++ minor constituent (between 10 -30)
+++ major constituent (between 30 - 100).

Presence of silver (Ag) referred to the amount of moisture absorbed silver surface lightly covered by its native oxide is a function of relative humidity [23], and the presence of silver oxide because Silver absorbed molecules of oxygen which are slightly transformed into oxygen ions ($O^{2-}$). Silver oxide ($Ag_2O$) is generally produced due to the combination between metal cations and oxygen ion. This layer of oxide is a protective layer. Electrochemical reactions occur when the level of humidity is high [24,25].

The presence of silver carbonates ($Ag_2CO_3$), and acanthite ($Ag_2S$) may be explained to the following reasons: sulphur pollutants represents an important role in the presence of the black corrosion products [26]. Also the presence of gases being in indoor atmosphere can be $O_2$, $O_3$, $H_2O_2$, and $H_2S$, in addition, carbonyl sulphide (COS) were found to be the controlling sulfur–bearing compound, the tarnishing layer was frequently involved silver sulphide ($Ag_2S$) also might be taking place because the atmosphere which surrounded the studied object may contain one or more of the following species: $SO_2$, HCl, $Cl_2$, $NH_3$, $NO_2$, $HNO_3$, $CO_2$, HCHO, HCOOH and $CH_3COOH$.

The presence of acanthine silver sulphide ($Ag_2S$) and chloragryite chlorides (AgCl) may be revealed to the presence of sulphate-reducing bacteria [27]. Reducing sulphur species of microbiological origin can effect on silver and its alloys. In air (e.g., in museum) $H_2S$ can be explained due to the biodegradation of sulphur which contain polymeric materials producing acanthine ($Ag_2S$) [28].

The presence of silver carbonates may be due to the interactive contact between the wooden frame and the silver part. Despite silver is known to be more resistance to organic acids and not active to the most organic molecules or radicals, however, if the amount of organic material on the silver surface is the amounting to a monolayer or more, the mass transport of water and other gases to and from the surface and thus the corrosion rate will be strongly inhibited [23].

Also, silver carbonates being able to occur also as a corrosion product, especially in incorporation with $O_3$, and UV light [26].

## Conclusions

The study proved that this tray suffers from several deterioration aspects caused by microbial, mechanical factors, and environmental degradation, specially this tray made of silver and connected with wooden frame, visual assessment, documentation, and analysis were applied to illustrate and have deepunderstanding of the tray components and degradation rates. The carpenters in this case used salix sp., as hard wood, while microbial examination revealed to the presence of Stemphylium Sp., and G+ve short bacilli spore former, which may cause damage to wooden base, and tray components. Tarnishing of silver can be described as the presence of a blackish silver sulphide layer. The atmospheric pollutants and relative humidity of the air have a serious effect in the presence of electrolyte on the metal surface. $O_2$, $O_3$, $H_2O_2$, $H_2S$, carbonyl sulphide (COS) represent the gases being in the indoor atmospheric corrosion ,which was found to be the prevalent sulphur containing compound, $SO_2$, HCl, $Cl_2$, $NH_3$, $NO_2$, $HNO_3$, $CO_2$, HCHO, HCOOH and $CH_3COOH$. Further more the chemical composition of the alloy and the manufacture process of the object represents an important role in the corrosion mechanism.

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