Journal of Science and Arts Volume 25, Issue 1, pp. 159-174, 2025

ORIGINAL PAPER

MULTI-ANALYTICAL TECHNIQUES OF A HISTORICAL VALUABLE OTTOMAN ENAMELED OFFICE CREW

NIAZY MOSTAFA MOHAMED [1]

Manuscript received: 02.11.2024; Accepted paper: 22.02.2025;

Abstract. *This study aims to investigate enameled office crew collections from the Faculty of Applied Arts' Museum in Cairo, Egypt. It is a unique collection that is widely distributed in several international museums. Most recent studies have emphasized the importance of studying this type of metal and learning about ancient decoration techniques, causes, and common deterioration manifestations. The collection was embellished with various opaque and transparent enamel colors, as well as champlevé and painting enamel methods. This study explores a rare collection dating back to the Ottoman era, particularly the eras of Sultan Abdul Hamid II (1293-1327 AH/1876-1909 AD) and Khedive Abbas Hilmi II (1320-1333 AH/1892-1914 AD, which is characterized by a unique decorative style. Various analytical techniques were used to determine and investigate the office crew collection. The enamel, metal, and degradation properties were ascertained by analytical methods, such as visual assessment, portable digital microscope, portable X-ray fluorescence, and scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDX). The findings indicated that the metal substrate of each piece in the collection is an alloy of copper and silver, with iron making up a portion of two of the pieces. Also, gold remains were found on the obverse and in a few additional spots, which were not visible due to the black layer covering all parts of the pieces. Furthermore, the examination helped identify the deterioration manifestations of the office crew, including tarnish throughout the metal surface, enamel scratches, pits, fissures, and microcracks. The enamel investigation revealed the presence of silica, potassium, sodium, calcium, and lead; nevertheless, the color tone was attributed to the extremely low quantities of Cu and As and some special cases for each enamel color with the discovery of a unique technique for applying red enamel to the surface of the pieces. The results of the elemental analysis affirmed the authenticity of this collection.*

Keywords: *Silver; enamel; Ottoman; USB microscope; pXRF; SEM-EDX.*

1. INTRODUCTION

Enameled metals are one of the most important antiquities in international museums. They have historical importance and express a type of antique that was widespread in ancient times. Enamel describes all vitreous materials heated and fused on different substrates [1]. Enameling metals for ornamental reasons is the process of pouring small glass particles over metal and heating it to high temperatures [2, 3]. Enamels are composed of various metallic oxides, lead oxides, potassium salts of soda, boric oxides, and silica, an alkali compound that lowers the melting point. Opaque or transparent enamel is possible [4, 5]. Transparent materials enable light to pass through easily; opalescent materials vary in translucency and

---

[1] Aswan University,Faculty of Archaeology, Conservation Department, 81511 Aswan, Egypt.
E-mail: neyazi.mostafa@arc.aswu.edu.eg.

https://doi.org/10.46939/J.Sci.Arts-25.1-b01

opacity, while opaque materials block light from doing so [6]. These enamels are melted into the metal, usually into a cell or depression prepared to accept them, but occasionally right onto the surface [7]. Usually, iron, bronze, copper, gold, or silver are used to make the enamel metals [8]. Cloisonné, champlevé, painted enamel, grisaille, basse-taille, and plaque-a-jour are examples of the methods used to create enamel [9]. Champlevé enamel is the second-oldest enameling technique after the cloisonné processes [10]. Champlevé means "raised field"; the enamel is placed into a depression in the metal [5]. The enamel is applied to a metal surface that has been soldered, pressed, perforated, acid-etched, or carved to create the desired design [11]. The enamel colors are mixed with a small quantity of tar spirit [12].

The history of enameling is extensive [13]. It was used by the Celts, Etruscans, Greeks, Romans, Assyrians, Egyptians, and Phoenicians, among others [9, 14]. Beginning in the 1st century BC, the champlevé on bronze technique, which the Romans and Germans adopted, had never been employed before the Celtic civilization. Celtic art flourished in the enameling industry from the second century AD, when a stunning bronze testament to Celtic-style champlevé was made for the Romans [15]. By the third century BC, the enamel technique had already reached Europe. Then, it gradually spread to Asia, the Middle East, India, China, and, most recently, Japan [16]. Enameling peaked during the Byzantine era, which lasted from the sixth to the eleventh century. Works from the 12th century had a major influence on the production of the West for the rest of that century [17]. Beginning in the fifteenth century, Limoges dominated manufacturing these painted enamel objects. The Renaissance and Baroque art and culture revived in the 19th century, which increased demand for artwork of that type [18].

The Ottoman Empire was established in 1516-1517 after Sultan Selim I assumed the throne in 1512. Selim I overthrew the Mamluks in Egypt because he enjoyed fighting and wished to see the Ottoman Empire grow [19]. Consequently, Egypt joined the Ottoman Empire [20, 21].

Many items from the 19th century that date back to the Ottoman Empire include mirrors, trays, miniature cups known as zarfs, ornate clocks, pocket watches, and dinnerware frequently composed of gold or silver [22].

Although they were more interested in using copper, gold, silver, and iron metals, Ottoman artisans used varying metals and alloys to manufacture and embellish metal objects. Copper was the most common metal in the Ottoman industry, followed by silver. While it was unavailable in Egypt, silver was extensively employed in the metal industries throughout the late Ottoman era [23], as silver was not found in Egypt as a pure metal or silver ores, even if it was found in tiny percentages in both local lead and nickel ore, in addition to being mixed with Egyptian gold [24].

Egypt's lengthy association with the Ottoman Empire is evidenced by the popularity and proliferation of the unique Ottoman arts throughout that time in Egypt. Thus, Egyptian museums have numerous Ottoman-era relics and antiques [22].

1.1. HISTORICAL BACKGROUND OF THE CASE STUDY

In this study, the Ottoman enameled office crew collection was examined and analyzed to identify the metal, enamel, and degradation components using analytical methods, such as a digital microscope, portable X-ray fluorescence (pXRF), and a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDX). This collection dates to the eras of Sultan Abdul Hamid II (1293-1327 AH/1876-1909 AD) and Khedive Abbas Hilmi II (1320-1333 AH/1892-1914 AD) (Fig. 1).

This collection was made of metal using enamel decoration methods (painting enamel and champleve enamel), which were widespread at the time. Additionally, decorative elements were implemented in these artistic artifacts, such as bouquets of local roses and sunflowers [25].

Figure 1. Shows enameled office crew: (A) Pots of inks and sand, (B) Sandbox pot, (C) Inkwell pot, (D) crew ruler, (E) crew knife, (F) crew scissors.

The methods of enamel decoration used by the office crew understudy varied between decoration with the champlevé enamel or painting enamel, as evident in the different parts decorated with rhombus shapes in the champlevé enamel, each with four-pointed star shapes in green or red with half sunflowers in turquoise. Either painting enamel was used to decorate various surfaces, with pink rosettes, blue flower buds, and green rosettes, executed on a white ground (Fig. 2).

Figure 2. Shows enameled office crew: (A) Sandbox pot parts, (B) Inkwell pot parts, (C) Cover of one piece, (D) The ruler's obverse, (E) The ruler's reverse, (F) Knife's obverse, (G) Knife's reverse, (H) Gilded scissor's parts, (I) scissor's hand enamel decoration.

There is not enough information about the old display and storage conditions of this collection because the museum was renovated. Surely, the collection was displayed inside an old-style showcase made of wood and glass and not closed, and the collections were displayed with various collections, some organic. The museum did not have the ideal conditions for storage or display, which may be one of the main causes of damage to this collection. Thus, the study aims to identify the damage causes of this collection.

2. MATERIALS AND METHODS

2.1. MATERIALS

Samples were obtained from the black layer covering the surface of the objects understudy, and four samples of enamel colors were collected from the falling and separated from the enamel pieces. The metal was also analyzed and examined using portable and non-destructive methods to identify the internal components and the important changes that occurred.

2.2. METHODS

2.2.1. Visual examination and assessment

Magnifying glasses and visual examination were part of the initial evaluation. This approach is effective since it simply identifies the mechanisms and causes of degradation.

2.2.2. Optical microscopy

The portable digital microscope (1.3 Mega Pixels, Manual Focus from 10 mm to 500 mm, and 20 X to 500 X) was used to analyze the collections. A digital microscope is preferable for examination for convenient carrying and usage in the workplace; it has been used to record deteriorating manifestations and investigate metal and enamels at various magnifications. The photos of the microscope may be exhibited on computers.

2.2.3. X-Ray Fluorescence spectrometry (pXRF)

The metal substrate of the office crew was inspected using the portable XRF (Thermo Scientific, NITON/XLt 8138, 592 GKV, USA), having a 40 kV X-ray for 1 minute and software version 4.2E (Metal mode). The pXRF spot size was 1 cm (diameter). Since it is challenging to get metal samples, a non-invasive technique was used. The elements' identification was helpful.

2.2.4. Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectrometry (SEM-EDX)

The black layer on the metal surface of the artifacts understudy was analyzed with an EDX (Oxford detector, the JEOL JSM 5400 LV EDX Link ISIS model, at an accelerating voltage of 20 K.V., magnification of x15 to 200000). The samples were inspected without any coating at a high vacuum.

The SEM-EDX (Quanta 250 FEG coupled to EDX Unit, FEI Company, Netherlands) was used to analyze enamel samples at an accelerating voltage of 30 K.V. and a magnification of 14x up to 1000000. The samples were examined without coating at a low vacuum.

3. RESULTS AND DISCUSSION

3.1. VISUAL EXAMINATION AND ASSESSMENT

The visual examination and the magnifying lenses showed that the artifacts understudy were covered by a black layer, which hid the type of metal and the presence of the remnants of the gilding layers; various parts of the metal are warped and irregular. Moreover, corrosion products on the front of the knife and scissors showed loss of parts, cracks in different enamel layers, and scratches in the ivory layer (Fig. 3).

Figure 3. Shows deterioration manifestations: (A, J) Loss and falling in the areas of Limoge enamel, (B) Hole in the metal, (C) Loss and falling in the areas of champlevé enamel, (D) Warped and irregular parts of the metals, (E, K) Gilding residue inside the cap and on the surface of the scissors, (H) Scratches in the ivory layer, (I, L) Corrosion products in some parts.

3.2. OPTICAL MICROSCOPY

Numerous deterioration aspects of enamel and metal were revealed by the microscopic examination results. For example, the enamel fell away from some areas, which caused the metal beneath to corrode and accumulate dust between the enamel layer and the metal surface in the contact area. Additionally, the enamel layer itself had pits, microcracks, cloudy and crumbling areas, and scratches (Fig. 4).

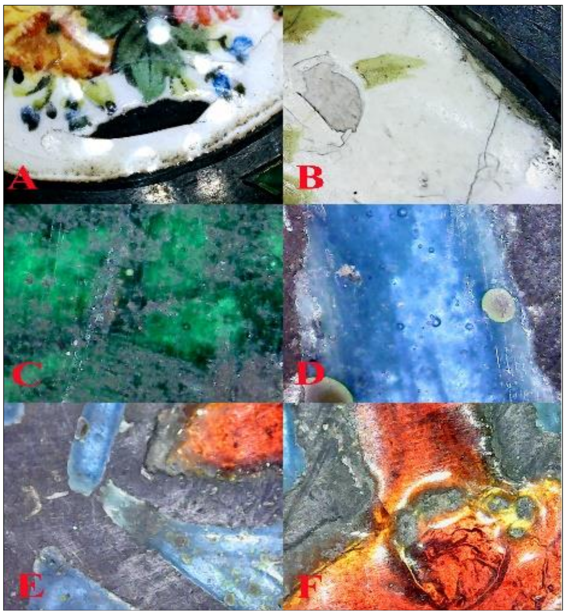


Figure 4. Portable Digital microscope photomicrograph of the enamel with (500X magnification) shows: A. loss of enamel, B. cracks and loss of Limoges enamel, C. scratches, D. pits, E. color change, F. loss of champlevé enamel.

The examination of the metal parts revealed a thick black layer beneath the fallen enamel layer, cuts, corrosion, and scratches on the surface of the metal and ivory (Fig. 5).

Figure 5. Portable digital microscope photomicrograph of the metal with (500X magnification) shows: (A, F) Black tarnish, (B) Cuts in the metal, (C) Corrosion in some parts, (D, F) scratches in ivory and metal.

The visual and portable digital microscope examination showed air bubbles, peeling off, separation, color fading, and cracks in the enamel colors. Additionally, the collection was covered in black tarnish, and a gilding layer covered some areas of the metal surface. The examination illustrated that metal corrosion agents were more likely responsible for the infrequent lifting of enamel from metal surfaces [26]. Furthermore, when metals corrode into glass on objects made of metal and glass, the glass often displays visible signs of corrosion, such as haze, wet surfaces or efflorescence, cracking, roughening, and pitting [27]. These elements weaken the cohesiveness of the metal's enamel surface, which might be the result of physical damage sustained during handling that makes the enamel slide off or the disintegration of vitreous enamel itself [28]. It could also be susceptible to shattering if it is dropped or bumped, and it might flake off the base. Losing enamel can allow moisture to get in, corrode the metal, and scour more enamel away [29].

3.3. X-RAY FLUORESCENCE SPECTROMETRY

pXRF analysis was used to study the multi-layered on the metal surface. Before the analysis, the surface of the analysis point was cleaned. The basic elements of the alloy were identified, including silver and copper, as well as a gold layer covering the surface. Because this technique provides imprecise semi-quantitative data, we should only regard the quantitative findings produced as approximations. Due to the great variety in the object's existing appearance, pXRF examination of the metal surface was conducted to aid in characterizing the complex metal components. An effort was made to determine the surface's original color behind the black tarnish, especially of any corrosive substances on the surface, as some sections seemed silver and others gold.

pXRF illustrated that most metal components of the enameled office crew collection had varying alloying ratios and contents, revealing an enriched or gold-plated silver-copper alloy.

All the artifact's metal sites underwent pXRF analysis, which identified unique compositional differences. Every piece had a distinct component ratio (Table 1). Table 2 and (Figure 6) display the surface elemental chemical composition.

The office crew collection is primarily silver and copper, with a gilded layer. Although exact quantification was not possible, the alloy used can be roughly estimated as follows: silver (85.17% to 96.22%), copper (0.67% to 6.68%), gold (3.08% to 30.97%), and lead (0.50% to 36.75%). The increase in the percentage of lead in the spot (10) was because the analysis included the parts that contained enamel, as confirmed by the elemental analysis of the enamel. Spot 10 caused the Ag percentage to be slighter than other spot analyses. Additionally, a sizable portion of iron was discovered between 68.39% and 99.11%) (68.39%) in the sharp knife tip and (99.11%) in the metal scissors tip, indicating that these components were made of iron. The knife's front section was entirely iron, but the scissors' front half comprised iron together with gilded ornamentation. This was corroborated by the iron rust remnants on both artifacts' surfaces, which were photographed in (Fig.3-I, 3-K, and 3-L) and recorded using a portable digital microscope (Fig. 5-C).

Traces of Sb, Sn, Cd, Bi, Zn, Ni, Mn, Cr, V, and Ti were found. The analysis revealed no mercury, so no amalgam gilding layer was used in this collection. Hence, the primary components of the office crew collection were silver and copper without gold in the internal composition of the alloy (Fig. 7), suggesting that the metal surface under the enamel fell, which shows the surface of the metal known as the shiny silver color and not gilded. All these results indicated the metal alloy was a silver-copper alloy (Ag-Cu), known as sterling silver. Furthermore, no items marked as "nd" were found (Table 2).

Table 1. Spot analysis on the enameled office crew collection.

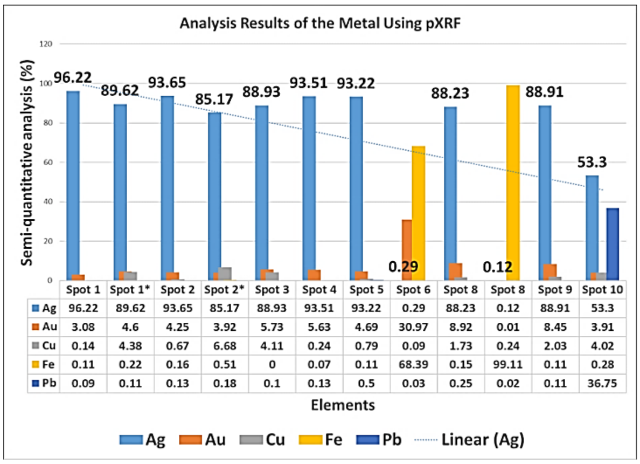
Analysis Spot	Area
Spot 1	Sandbox body in the shape of a teapot
Spot 1*	Hand of the sandbox body in the shape of a teapot
Spot 2	Sandbox cover
Spot 2*	Another area on the sandbox cover
Spot 3	Metal mesh upon the sandbox
Spot 4	Inkwell body

Analysis Spot	Area
Spot 5	Inkwell cover
Spot 6	Metal scissors tip
Spot 7	Metal scissor handle
Spot 8	The sharp tip of the knife
Spot 9	Knife handle
Spot 10	The ruler's obverse

Table 2. Analysis results of the metal parts of the enameled office crew collection using pXRF.

Analysis Area	Semi-quantitative analysis [%]				
	Ag	Au	Cu	Fe	Pb
Spot 1	96.22	3.08	0.14	0.11	0.09
Spot 1*	89.62	4.60	4.38	0.22	0.11
Spot 2	93.65	4.25	0.67	0.16	0.13
Spot 2*	85.17	3.92	6.68	0.51	0.18
Spot 3	88.93	5.73	4.11	nd*	0.10
Spot 4	93.51	5.63	0.24	0.07	0.13
Spot 5	93.22	4.69	0.79	0.11	0.50
Spot 6	0.29	30.97	0.09	68.39	0.03
Spot 7	88.23	8.92	1.73	0.15	0.25
Spot 8	0.12	0.01	0.24	99.11	0.02
Spot 9	88.91	8.45	2.03	0.11	0.11
Spot 10	53.30	3.91	4.02	0.28	36.75

Notes: nd = not detected*



	Spot 1	Spot 1*	Spot 2	Spot 2*	Spot 3	Spot 4	Spot 5	Spot 6	Spot 8	Spot 8	Spot 9	Spot 10
Ag	96.22	89.62	93.65	85.17	88.93	93.51	93.22	0.29	88.23	0.12	88.91	53.3
Au	3.08	4.6	4.25	3.92	5.73	5.63	4.69	30.97	8.92	0.01	8.45	3.91
Cu	0.14	4.38	0.67	6.68	4.11	0.24	0.79	0.09	1.73	0.24	2.03	4.02
Fe	0.11	0.22	0.16	0.51	0	0.07	0.11	68.39	0.15	99.11	0.11	0.28
Pb	0.09	0.11	0.13	0.18	0.1	0.13	0.5	0.03	0.25	0.02	0.11	36.75

Figure 6. Shows pXRF analysis results of the metal parts.

Figure 7. A fallen-off part of the enamel reveals the metal surface beneath the enamel, which is of a distinctive silver color and not covered by a layer of gilding.

The silver and copper alloy used in the collection is a binary alloy (silver-copper alloy). The metal substrate was examined using pXRF to identify this alloy. The gold element indicated gilding, which was not detected by the naked eye because the whole collection was covered in black tarnish. Pure silver is too soft to be used. As a result, adding copper to silver greatly increased its hardness, strength, and wear resistance without negatively affecting its ductility or formability [30]. Some patches of the surface were covered with gold. Coated gems, sculptures, coins, and amulets were produced by applying an Au leaf, foil, or thin film utilizing a range of production procedures to the surface of less expensive substrates, such as metals. These objects were designed to resemble solid gold objects or provide visual appeal by fusing noble metals' ornamental qualities with other materials [31].

3.4. SCANNING ELECTRON MICROSCOPY COUPLED WITH ENERGY DISPERSIVE X-RAY SPECTROMETRY

3.4.1. Examining the black layer

The black layer was separated from the surface as a powder; in some areas, it was separated into very thin flakes. The powder and flakes were taken and analyzed by EDX to identify their components (Table 3). The results showed that in addition to silicon (Si 0.55% wt.%), manganese (Mn 0.07 wt.%), zinc (Zn 1.79 wt.%), and copper (Cu 1.96 wt.%), there were three significant elements: silver (Ag 86.45 wt.%), sulfur (S 7.03 wt.%), and chlorine (Cl 2.15 wt.%). These findings verified that the black layer represented a layer of products from silver corrosion, with sulfur and chlorine serving as its primary constituents.

Table 3. EDX analysis results of the black layer.

Elements	Ag	Cu	S	Cl	Si	Mn	Zn	Total
[wt.%]	86.45	1.96	7.03	2.15	0.55	0.07	1.79	100

The EDX results of the black layer showed elements, including S and Cl, on the collection's surface. The black layer was a corrosion layer that covered the silver's surface, known as the black tarnish.

Metal corrosion rates in the atmosphere largely depend on the kind and concentration of airborne pollutants. The most hazardous gaseous air pollutants are occasionally identified as SO_2, H_2S, HCl, NO_2, O_3, and NH_3 [32] or by carbonyl sulfide (OCS), which is widely present in the atmosphere and is essential to the tarnish process. These elements originate from various places, including rubber, paints, paper treatment centers, and oil refineries [33]. Silver has always been a highly prized precious metal. Silver alloys are susceptible to tarnishing, a thin blackish coating on their surface [34], resulting from the metal's surface reacting with atmospheric pollutants, primarily sulfur dioxide.

Silver can tarnish brownish-black despite its endurance because of interactions with oxygen, sulfur compounds (H_2S or COS), and air humidity [35]. Most of this tarnish is made of acanthite (Ag_2S), which may eventually turn black. When sulfur compounds and copper combine, black copper sulfides are created [36]. Silver metal artifacts tarnish readily in urban settings. Ag2S forms on the surface of silver when it is exposed to various elements, including sulfur; this process is enhanced by humidity [37]. A thin layer of black silver sulfide (Ag_2S) results from this.

Gray silver chloride (AgCl), which is produced by chlorides, steadily develops and can cause significant distortion to the original item because of the substantial expansion that occurs when a metal turns into a mineral [30]. Tiny, brittle particles of silver chloride accumulate as a coating. Unfavorable conditions, however, result in an object completely turning into silver chloride [38]. The most prominent idea to explain the formation of AgCl from chlorargyrite is the change from Ag_2O to AgCl [39]. The deposition of airborne particles containing chloride from combustion processes or water purification treatment in urban areas could account for the formation of AgCl by the chloride ion Cl, accelerating sulfuration in the presence of H2S and contributing to deterioration [32]. The ratios in the aforementioned data demonstrate that the causes of this specific type of black tarnish are silver sulfide (Ag_2S) and silver chloride (AgCl).

3.4.2. Analysis of the enamel colors

The study's collection includes many opaque and transparent enamel colors, such as Champlevé or enamel paint. An analysis was made on the following enamel colors: opaque white, translucent red, translucent green and translucent turquoise. It was used to determine the percentage concentration of elements in the enamel colors. The samples were taken from the fallen enamel for each color, cleaned well, and analyzed. The sample size was approximately 0.5mm * 0.5mm, and the analysis was carried out on the enamel surface.

Figures 8 and 9 display the outcome of the EDX analysis. The analysis demonstrated that silicon (Si), potassium (K), and sodium (Na), with other distinctive elements of each hue, comprised a substantial portion of the enamel.

Previous studies on the basic enamel elements showed that all enamel colors contain significant amounts of silica oxide (SiO_2), lead oxide (PbO), calcium oxide (CaO), and amounts of alkali oxides (Na_2O and K_2O), along with traces of magnesium oxide (MgO), iron oxide (Fe_2O_3), and relatively large amounts of coloring metal oxides. Elemental analysis helped determine the primary components and the many types of pacifiers and modifiers used. Thus, these enamels could be classified as leaded soda-potash or mixed alkaline glass. High concentrations of silica, low quantities of lime and magnesia, and high concentrations of potash and soda (soda is often relatively lower than potash) are characteristics of this compositional type. The following categories apply to enamel colors:

- The main components of translucent green enamel are SiO_2 (52.85%), K_2O (8.47%), Na_2O (3.39%), CaO (0.89%), PbO (29.43%), and CuO (3.67%); the presence of copper also denotes the use of CuO as a source of translucent green enamel;
- The main components of translucent turquoise enamel are SiO2 (46.51%), K_2O (11%), Na_2O (3.30%), PbO (23.31%), MgO (1.95%), and CuO (3.57%). Translucent turquoise enamel is made from alkali-based glass with a high concentration of copper oxide (CuO), a high percentage of K_2O, and a larger concentration of Na_2O;
- The essential components of opaque white enamel are SiO_2 (49.51%), K_2O (7.86%), Na_2O (2.51%), PbO (34.5%), and trace quantities of As_2O_3 (1.21%). The arsenic (As) in the form of arsenic trioxide (As_2O_3) acts as an opacifying agent to give the opaque white color;
- Translucent red enamel also includes SiO_2 (51.54%), K_2O (6.25%), Na_2O (3.68%), and PbO (38.53%), which are the necessary components of enamel. The analysis findings of red enamel unexpectedly showed that coloring elements were not present. Ultimately, a more in-depth microscopic analysis demonstrated the existence of a gold layer beneath the translucent, colorless vitreous enamel (Fig.10).

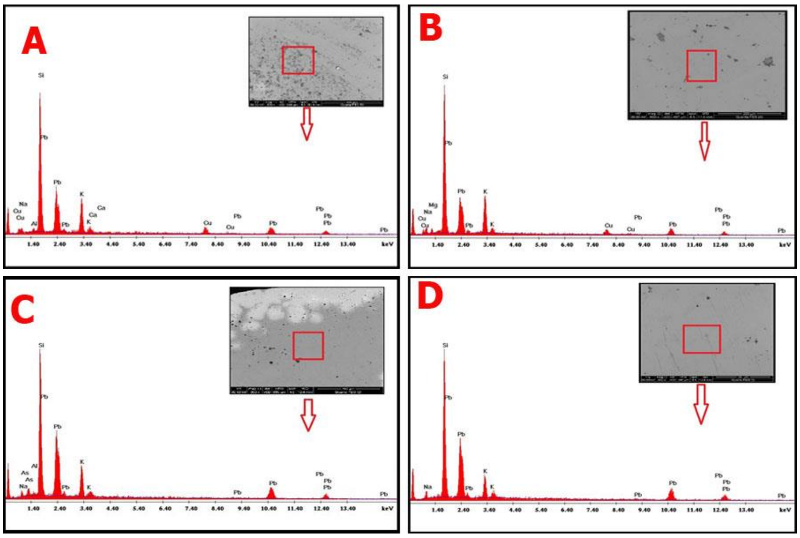
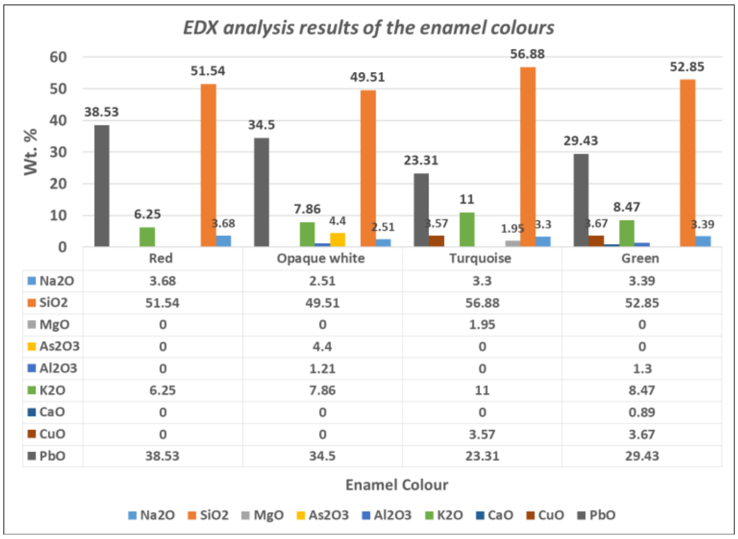


Figure 8. EDX spectrums of the enamel colors with 300X magnification: (A) Translucent green enamel, (B) Translucent turquoise enamel, (C) Opaque white enamel, (D) Translucent red enamel.



	Red	Opaque white	Turquoise	Green
Na2O	3.68	2.51	3.3	3.39
SiO2	51.54	49.51	56.88	52.85
MgO	0	0	1.95	0
As2O3	0	4.4	0	0
Al2O3	0	1.21	0	1.3
K2O	6.25	7.86	11	8.47
CaO	0	0	0	0.89
CuO	0	0	3.57	3.67
PbO	38.53	34.5	23.31	29.43

Figure 9. Shows the EDX analysis results of the enamel colors.

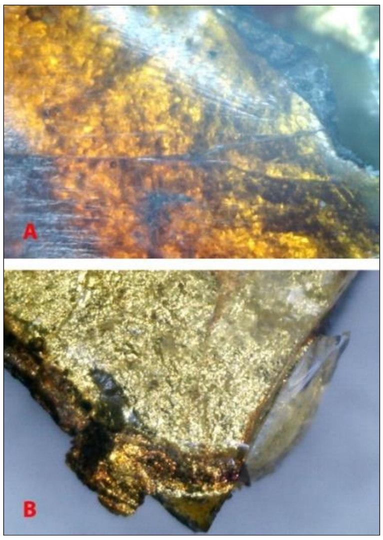


Figure 10. Shows the red enamel: (A) The red enamel obverse, (B) The gold foil reverse of the red enamel.

The EDX analysis results of four enamel colors showed that all enamels contain lead oxide, potassium oxide, sodium oxide, and silicon oxide. To give the enamel its distinctive properties such as shining, fusibility, and flexibility, the enamelist often utilizes silica, which is basically silicon dioxide and occurs in nature as quartz (flint, sandstone) [2, 13]. This result was highlighted by a study that found enamels dating back to the nineteenth century have lead-potash-silicate compositions that include relatively significant amounts of both sodium and potassium oxides and a small amount of lime and magnesium in some kinds of enamels, resulting in a quite unstable composition because of the low concentrations of the stabilizing substances: lime and magnesium [40]. This might be one of the causes of enamel degradation observed in microscopic analysis. Alkali oxides, such as potassium and sodium, which are used to manufacture enamel, are added to the list of ingredients in enamel. Enamels seem bright, polished, and dazzling when potash is included in the mixture [41].

The amount of lead oxide in the enamel determines how soft it is. Lead oxide is ideal for lower temperatures because of its high refractive index and better brightness [13]. Harder enamel is more resistant to atmospheric or chemical action and has a higher silica content, while soft enamel is caused by a high lead oxide content. However, by the 19th century, lead was almost added to enamels, making softer enamel more prone to being broken down by these agents [42, 43]. Furthermore, the enamel's resistance to heat and chemical stress is enhanced by the high amounts of CaO [44].

The translucent green enamels' EDX examination revealed that it contained a considerable amount of copper oxide and was colored by adding copper oxides in rather large amounts to get a more genuine green color from the bluish hue produced by copper oxide alone [40]. Because cupric oxide (CuO) was used to create the green color, copper had several oxidation states [45-47].

The EDX analysis results of translucent turquoise enamel confirmed the addition of copper ion Cu^{2+} to alkali-based glass [48, 49]. This resulted in the production of turquoise enamel, which was made by an opaque glass matrix as a colorant [50] and copper and an alkali base as the main ingredients [51]. Furthermore, the authors argue that turquoise was created by combining copper ions with a high PbO concentration and a high alkali medium (%10–12 K_2O + Na_2O) [52]. In addition to the fundamental elements of enamel, opaque white enamel also included arsenic (As) in the form of arsenic trioxide (As_2O_3), another distinctive ingredient. These elements (As, Pb) were present in the levels indicated by the EDX results. Lead arsenate was added to the opaque white enamel. It is often produced during the firing process when lead-based enamel or glaze reacts with arsenate [53].

To improve opacity, an arsenic compound may also be purposefully added; investigations of Chinese porcelain from the 18th and 19th centuries, as well as the blue embellishments of French enameled glass and metal artifacts from the 17th and 18th centuries, noticed this phase [54]. Glassmakers have been using lead arsenate as an opacifier since the end of the seventeenth century [55].

Until the middle of the seventeenth century, tin oxide crystals in a matrix rich in lead oxide were the only opacifying chemical employed in painted enamels. Around 1750, a novel opacifier known as lead arsenate was first made accessible; by the 19th century, it was extensively used [56]. Therefore, this oxide indicates the use of lead arsenate opacifiers.

While EDX results indicated that the red enamel had all the essential elements of enamel components without colored oxides, the portable digital microscope confirmed that the red enamel was applied gold foil underneath the enamel. This is a traditional enamel decorating technique where a layer of foil, either gold or silver, is applied underneath the enamel [57]. Translucent enamel provides more brilliance and protection when fused over gold foil [4,11].

4. CONCLUSIONS

The paper provides several investigation and analysis techniques for analyzing enameled office crew. The visual examination and the magnifying lenses showed that a black layer covered the items of the collection, various parts of the metal were warped and irregular; corrosion products on the front of the knife and scissors showed loss, cracks in the enamel layers, and scratches in the ivory layer. Additionally, a portable microscope examination of the enamel revealed several deterioration-related features, including fall of the enamel, dust, cracks, pits, scratches, and hazy and less transparent surfaces, as well as several deterioration-related features, including scratches, black tarnish covering metal, cuts, and corrosion, on the metal surface.

pXRF results illustrated that the main component of the collection was an Ag-Cu alloy, along with gold in the form of gilding layers. The EDX analysis of the black tarnish on the enameled office crew confirmed that this layer consisted of silver, chlorine, and sulfur, which indicated the corrosion layer, such as silver sulfide (Ag_2S) and silver chloride ($AgCl$); among the most common corrosion products on silver when exposed to air pollution gases loaded with sulfur and chlorides in museums.

The EDX analysis results of the different kinds of enamel colors in the collection illustrated that each enamel included silica, potassium, sodium, lead, and calcium, in addition to some distinctive elements of each color. The EDX analysis illustrated that the translucent green enamel had copper ions, and the translucent turquoise enamel had relatively significant volumes of iron and copper oxides for coloring. Furthermore, the opaque white enamel contained lead in the form of lead arsenate, while the red enamel comprised the basic elements of enamel without coloring oxides. The portable digital microscope examination results verified the presence of a gold layer underneath the red enamel. The red color effect was caused by the interaction between the gold color and the transparent enamel. The results of this investigation provide an overview of the critical steps involved in determining the constituents and degradation manifestations of this composite metal material.

The examinations and analyses showed that the collection under study had various manifestations of degradation, whether in storage or exhibition. These results are useful in identifying the stages of different restoration activities, depending on the damage and the state of the object and its components.

The data indicated that most of this collection dates to the late 13th AH/19th AD century or early 14th AH/ 20th AD century.

Acknowledgment: *I would like to thank professor Wafaa Anwar Mohammad, Professor of Restoration and Conservation of Metals at the Faculty of Archaeology, Cairo University, for her constant support for this article in all its various stages.*

REFERENCES

[1] Davidson, P. W., *Educational Metal Craft, Longman*, Green and Co, New York, 193, 1913.

[2] Matthews, G. L., *Enamels, Enameling, Enamellists*, Chilton Book Company, Pennsylvania, 5, 1984.

[3] Wiener, L., *Hand made jewelry*, A manual of techniques, D. Van Nostrand Company, Inc., New York, 173, 1948.

[4] Chamberlain, M., *Metal Jewelry Techniques*, Watson-Guptill Publications, New York, 173, 1976.

[5] Grath, J. M., *First Steps in Enamelling*, Singapore, The Apple Press, 16, 1994.

[6] Untracht, O., *Enameling on metal*, Chilton Company, New York, 17, 1962.

[7] Arthur, F., Payne, B.S., *Art Metal Work with Inexpensive Equipment*, Illinois, The Manual Arts Press Peoria, 169, 1914.

[8] Maryon, H., *Metalwork and Enameling*, Dover Publications, Inc., New York, 169, 1971.

[9] Rose, A. F., Cirino, A., *Jewelry Making and Design*, Dover Publications Inc., New York, 109, 1967.

[10] Dipasqualex, D., *Jewelry Making, Prentice* – Hall, Inc., Englewood cliffs, New Jersey, 55, 1975.

[11] Pack, G., *Jewelry and Enameling*, 2nd ed. D. Van Nostrand Co., Inc., New York, 146, 1953.

[12] Wigley, T. B., *The Art of the Goldsmith and Jeweller: A Treatise on the Manipulation of Gold in the Various Processes of Goldsmith's Work, and the Manufacture of Personal Ornaments, &c. for the Use of Students and Practical Men*, Charles, Griffin and Company, Ltd, London, 174, 1911.

[13] Winter, E., *Enamel Painting Techniques*, Elsevier Publishing Company, Barking, Essex, England, 41, 1970.

[14] Hawkins, L. V., *Art Metal and Enameling*, Chos. A. Bennett CO., Inc., USA, 200, 1973.

[15] Stapleton, C. P., Freestone, I. C., Bowman, S. G. E., *Journal of Archaeological Science*, 26(**8**), 913, 1999.

[16] Kuemmerlein, K., *Metal Enameling*, University of Wisconsin System, Madison, 1, 2004.

[17] Davran, A., *Enameling Application on Metals from Past to Future*, M.Sc. Thesis, Department of Design Studies, İzmir University of Economics, Turkey, 11, 2011.

[18] Linden, V., Schalm, O., Houbraken, J., Thomas, M., Meesdom, E., Devos, A., Dooren, R., Nieuwdorp, H., Janssenf, E., Janssens, K., *X-Ray Spectrom*, **39**, 112, 2010.

[19] Quataert, D., *The Ottoman Empire, 1700–1922*, Second Edition, Cambridge University Press, New York, 21, 2005.

[20] Ágoston, G., Masters, B., *Encyclopedia of the Ottoman Empire*, Facts on File, Inc., New York, 3, 2005.

[21] Hoving, T. P. F., *The Metropolitan Museum of Art Bulletin*, **26**(5)**,** 1, 1968.

[22] Mason, L. E., *Asian art*, London, Woodbridge, Suffolk: Antique Collectors' Club, 31, 2002.

[23] Khalifa, R. H., *Islamic Arts In The Ottoman Era*, fourth edition, Zahraa Al-Sharq Publications, Cairo, 200, 2007.

[24] Lucas, A., *Ancient Egyptian materials & industries*, second edition, E. Arnold & Co., London, 450, 1934.

[25] Shadia, E. A., *Journal of the Faculty of Archaeology*, **16**, 261, 2012.

[26] Stambolov, T., *The Corrosion and Conservation of Metallic Antiquities and Works of Arts, Amsterdam*, Central Research Laboratory for Objects of Art and Science, 207, 1985.

[27] Eggert, G., *Science and Technology*, **45**(5), 414, 2010.

[28] Davidson, S., *Conservation and Restoration of Glass*, Bath press, Butterworts, New York, 217, 2003.

[29] Simpson, M. T., Huntley, M., *Sotheby's Caring for Antiques: A Guide to Handling, Cleaning, Display, and Restoration*, Conran Octopus, London, 110, 1992.
[30] Al-Saad, Z., Bani Hani, M., *International Conference on Strategies for Saving Indoor Metallic Collections with a Satellite Meeting on Legal Issues in the Conservation of Cultural Heritage*, TEI of Athens, 177, 2007.
[31] Ingo, G. M., Padeletti, G., Tilde de Caro, C. Riccucci, G. Guida, E. Angelini, C. Grassini, *International Conference on Strategies for Saving Indoor Metallic Collections with a Satellite Meeting on Legal Issues in the Conservation of Cultural Heritage*, TEI of Athens, 9, 2007.
[32] Volpe, L., Peterson, P. J., *Corrosion Science*, **29**(10), 1179, 1989.
[33] Costa, V., *Studies in Conservation*, **46**, 18, 2001.
[34] Gouda, V., Abdel Ghany, N., Awad, A., *Egyptian Journal of Chemistry*, **52**(SI), 29, 2009.
[35] Gharib, A., *International Journal of Archaeology***,** **8**(1), 1, 2020
[36] De Figueiredo, J. C. D., Asevedo, S. S., Barbosa, J. H., *Applied Surface Science*, **317,** 67, 2014.
[37] Vassiliou, P., Novakovic, J., Samara, K. L., *Conference on Strategies for Saving Indoor Metallic Collections with a Satellite Meeting on Legal Issues in the Conservation of Cultural Heritage*, TEI of Athens, 132, 2007.
[38] Marchand, G., Guilminot, E., Lemoine, S., Rossetti, L., Vieau, M., Stephant, N., *Heritage Science*, **2**, Article Number: **5**, 1, 2014.
[39] Wan, Y., Wang, X., Li, Y., Sun, H., Zhang, K., *International Journal of Electrochemical Science*, 10(**3**), 2336, 2015.
[40] Wypyski, M. T., *ICOM Committee for Conservation, ICOM-CC*, 15th Triennial Conference New Delhi**,** Vol. **I**, 246, 2008.
[41] Taylor, L. S., *Copper Enameling*, A.S. Barnes and company, south Brunswick and New York, 28, 1977.
[42] Bates, K. F., *Enameling Principles and Practice*, The World Publishing Company, New York, 41, 1951.
[43] Fisher, A., *The Art of Enamelling Upon Metal with a Short Appendix Concerning Miniature Painting on Enamel*, Offices of "The Studio", London, 9, 1906.
[44] Firas, A., Atef, S., Wassef, S., *Mediterranean Archaeology and Archaeometry*, 17(**3**), 201, 2017.
[45] Heck, M., Hoffmann, P., *Archaeometry*, 42(**2**), 341, 2000.
[46] Mohamed, W. A., Mostafa, N. M., *International Journal of Conservation Science*, 8(**1**), 15, 2017.
[47] Mohamed, W. A., Mostafa, N. M., *International Journal of Conservation Science*, 9(**2**), 265, 2018.
[48] Wypyski, M. T., *Metropolitan Museum Journal*, **35**, 150, 2000.
[49] Colomban, P., *The Royal Society of Chemistry*, **2**, 1, 2019.
[50] Biron, I., Verità, M., *Journal of Archaeological Science*, **39**, 2706, 2012.
[51] Day, L.F., *Enameling*, B.T. Batsford, London, 1907.
[52] Kirmizi, B., Colomban, P., Quetteb, B., *Journal of Raman Spectroscopy*, **41**, 780, 2010.
[53] Van Der Linden, V., Olivier, S., Jos, H., Mienke, T., Eva, M., Annemie, D., Van Dooren, R., Hans, N., Elsje, J., Koen, J., *X-Ray Spectrum*, **39(2)**, 112, 2010.
[54] Colomban, P., Kirmizi, B., Zhao, B., Clais, J., Yang, Y., Droguet, V., *Heritage*, **3**, 915, 2020.
[55] Gratuze, B., *Provenance Analysis of Glass Artefacts, Modern Methods for Analysing Archaeological and Historical Glass*, 5.1, First Edition, John Wiley & Sons, Ltd., Belgium, 309, 2012.

[56] Wypyski, M. T., *Materials Research Society*, 223, 2002.
[57] Mohamed, W. A., *eConservation*, **19**, 70, 2011.