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Using Examination Methods and EDX Analysis to Study the Archaeological Vitreous Enamels

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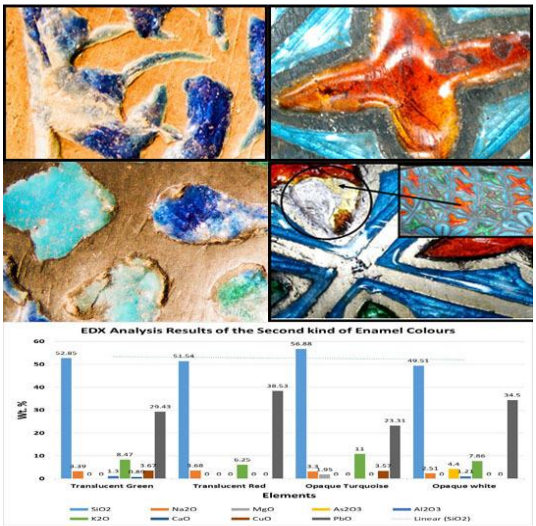
HIGHLIGHTS

- Examine and analyse different samples of vitreous enamel from two objects champlevé and peinture enamel.
- The evaluation process was performed using a stereo, digital microscope and using (SEM−EDX) to identify both types of enamel.
- Vitreous enamel suffers from many different deterioration aspects such as pitting, cracking, separation, and scratches...etc.
- The results proved that the chemical composition of enamel dates back to the 19th century AD.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims to examine and analyse different samples of vitreous enamel from two objects: one in Aljazeera Museum and the other in the Faculty of Applied Arts' Museum in Cairo, Egypt. The applied enamel decoration incorporates two sophisticated methods of enamelling: champlevé and peinture enamel, which are important techniques in enamel decoration, applied onto a metal substrate. Seven samples of different enamel colours were studied, examination was performed using a stereo and digital microscope to document the enamel surface

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and identify the most important deterioration aspects of enamel, which vary between pitting, cracking, separation, micro-cracks, scratches and loss of enamel........etc.

The chemical composition of both types of enamel was identified using (SEM−EDX). The results proved that the enamel contains basically silicon, potassium, sodium, and lead. These enamels are classified as soda-potash glass or mixed alkaline glass. The results also proved that the colouring agents in both types of enamel are copper oxide used to produce translucent green enamel, cobalt oxide for translucent dark blue enamel, copper oxide with more sodium and potassium oxide for opaque turquoise enamel. A thin layer of gold was used under the translucent enamel to obtain the red enamel (this is an ancient technique for obtaining different shades of transparent enamel), and arsenic oxide for opaque white enamel. Moreover, the results proved that the chemical composition of enamels date back to the 19th century.

1. Introduction

The art of enamelling metals is defined as the process of applying small granules of enamel to metal and firing at high temperatures, for the purpose of decoration [1, 2]. These enamels are melted onto the metal, sometimes directly onto the surface, but more often into a depression or cell prepared to receive it [3]. Enamel is a vitreous glaze of finely ground glass which is produced from a mixture of silica, an alkali compound-which lowers the melting temperature-, lead oxides, salts of soda, potassium, boric oxides and various metallic oxides. Enamel can be transparent, opaque or opalescent [4, 5]. The methods of enamel application are different; they are defined as cloisonné, champlevé, painted enamel, grisaille, basse-taille and plique-a-jour etc. [6].

A combination of some of these techniques may appear on the one and the same artefact. The metal is usually gold, silver, copper, bronze, or iron [7]. It is believed that vitreous enamel work had its beginning with early civilizations around the Mediterranean from the sixth century B.C. or even earlier by the Egyptians, Phoenicians, Assyrians, Greeks, Romans, and Etruscans [3-5]. The enamel work has reached a great degree of perfection on Greek sculpture from the fifth century B.C., which shows surfaces with areas of inlaid metal covered with enamel. The ancient Greek goldsmiths inlaid their jewelry with thin coatings of white and blue enamel between gold wires. This is one of the first examples of the cloisonné process. By the third century B.C., the enamel process had spread to England and Ireland. The process continued to move slowly from Europe to Asia Minor and the Middle East, to India and China, and then to Japan by the third century A.D [8].

Historical background:

First kind of enamel: (Champlevé):

The enamel samples were obtained from an Indian champlevé enameled metal tray that dates back to 19 century AD. The tray originated in the city of Hyderabad in India in the 19th century. It is registered under number 72 and is located at Aljazera Museum, Cairo Egypt, (Fig. 1). Two samples were chosen of translucent (green-dark blue) enamel colour and one sample of an opaque turquoise enamel colour.

Champlevé enamel is the second oldest of the enamelling techniques after cloisonné techniques [9], the word champlevé "means raised field" and when it is applied to enamelling, it means that the enamel is laid into a depression made in the metal [10], the enamel is fused into a sunken surface of the metal in which the design has been carved, stamped, pierced,, or soldered to a background or etched with acid [11]. The enamel colours are mixed with a little spirit of tar.
Enamelling on metals is most successfully practiced in many parts of India [12], In spite of that, there is no mention of enamelling in early Indian texts before the fifteenth century. The only available reference found on this subject is in the Ain-i-Akbari written in the sixteenth century, during the reign of the Mughal Emperor Akbar [13]. Champlevé enamel was mainly used as decoration for jewels, sword-hilts, horse trappings and the handles of daggers [14].

Fig. 1. The first kind of enamel colours.

Second kind of enamel: (Peinture):

The enamel samples were obtained from an Ottoman peinture enameled metal tray in the Museum of the Faculty of Applied Arts, Helwan University, registered under the number 93/5. It dates back to the era of Sultan Abdul Hamid II, 1293-1327 AH / 1876-1909 AD, that is, in the late 13th AH / 19AD century (Fig. 2). Two translucent samples of (green-red) enamel colour and two opaque samples of turquoise and white enamel colours were studied.

The peinture enamel" or wet enamel, is a technique in which a picture can be built up using successive firing [15], painted enamels derive their outlines from the colour scheme only [16] after the enamel colours are mixed with lavender oil [17].

Fig. 2. The second kind of enamel colours.

2. Materials and methods

2.1. Microscopic examination

In this scope, two methods were used to investigate the enamel surface. A stereo microscope and a digital microscope were used to examine the enamel surface and identify the deterioration aspects of the vitreous enamels.

2.1.1. Stereo microscope

The first kind of enamels were examined with Stereo microscope model Zeiss Stemi 2000-C Stereo microscope with visual viewing magnification ranges (6.5x ... 50x). It was used to record the deterioration aspects and examine the enamels at different magnifications.

2.1.2. USB Digital Microscope

The second kind of enamels were examined using USB digital microscope (1.3 Mega Pixels, Manual Focus from 10 to 500mm, and 20 X to 500X), combined with a tiny digital camera (CMOS, CRE Company, China) and connected to a computer. The images seen through the microscope's eyepiece can show the deterioration aspects on the enamels at different magnifications.

2.2. Scanning Electron Microscope coupled with EDX

Samples of enamel were examined and analyzed with SEM-EDX (Quanta 250 FEG attached to EDX Unit, FEI Company, Netherlands) with accelerating voltage 30V. The samples were examined without coating at low vacuum.

3. RESULTS AND DISCUSSION

3.1. Microscopic Examination

The results of the microscopic examination showed many aspects of enamel damage. The enamel has fallen off in several parts leading to the exposure of the metal surface due to the buildup of corrosion products between the enamel layer and metal surface in the contact area. Metal corrosion products are probably the main reason for the occasional lifting of the enamel from the metal surface [18]. And when on composite objects made of glass and metal, metal corrosion occurs in contact with glass, the latter often shows visible signs of corrosion: hazing, wet surfaces or efflorescence, cracking, roughening, pitting [19].

Microscopic examination also demonstrated that the enamel layer itself suffered from cracks, micro-cracks, pits, scratches, (Figs. 3, 4). These aspects weaken the cohesion of the enamel surface to the metal. This could be the result of physical damage due to handling which forces the enamel to fall off or to the breakdown of the vitreous enamel itself [20]. Enamel may be exposed to shatters easily if it is knocked or dropped, once it breaks, it can flake away from the base. Loss of enamel could allow moisture to enter causing corrosion of metal and push more enamel off [21].

3.2. Scanning Electron Microscope coupled with EDX

Analysis of the enamel colours

First kind of enamels: (Champlevé)

Three samples of enamel colours were analyzed by EDX, two translucent enamels (green-dark blue) and one opaque turquoise enamel. The result of EDX analysis of the enamel colours are shown in (Table 1) and (Fig. 5).

The results establish that the enamels are composed of Silicon (Si), Lead (Pb), Potassium (K) and Sodium (Na), and relatively high amounts of colouring metals or metal oxides, respectively, as pigments, in addition to traces of Magnesium oxide (MgO) and Iron oxide (Fe_2O_3). Using elemental analysis, it was possible to identify the raw materials, including the type of modifiers that were used as well as the colourants and opacifiers used. Therefore, these enamels can be classified as Soda-potash glass or mixed alkaline glass.

- The EDX results of the translucent green enamel indicated that the green enamel contain traces of iron oxide Fe_2O_3 and also contain large amounts of copper oxide (CuO), This composition refers to using copper oxide as a source of green enamel, Copper oxide is one of the most important oxides that are used with enamel to get the green colour.

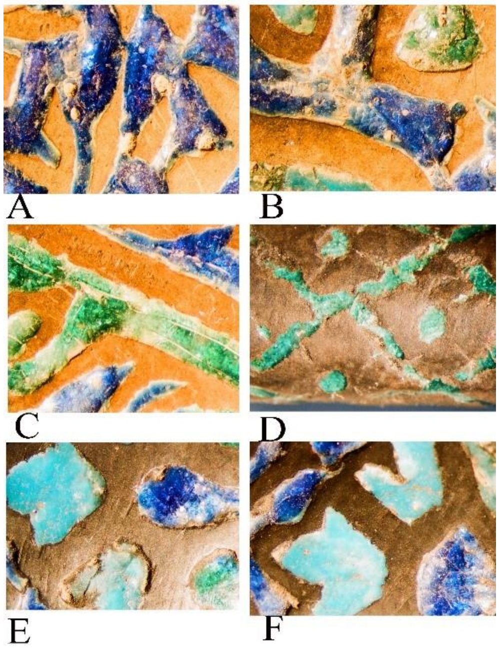

Fig. 3. Stereo microscope photomicrograph of the first kind of enamel colours, A. colour change, B. Husks, C. Scratches, D. Loss of enamel, E. Pits, F. Cracks. (Magnification 40x).

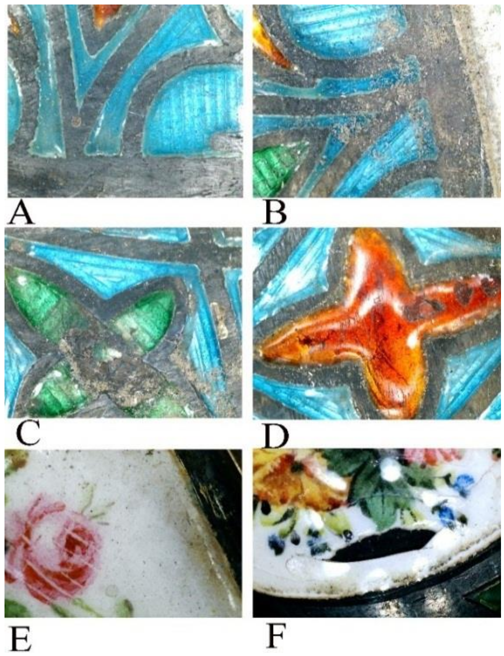

Fig. 4. USB digital microscope photomicrograph of the second kind of enamel colours, A. colour change, B. pits, C., loss of enamel, D. colour change, E., scratches, F. loss of enamel. (Magnification 40x).

- The EDX results of the translucent dark blue enamel indicated that the dark blue enamel contains cobalt (Co) in addition to presence of As_2O_3 with PbO (which is present in a higher amount compared to the rest of the enamel colours) as an opacifier to obtain the dark blue colour.
- The EDX results of the opaque turquoise enamel indicated that the opaque turquoise enamel contains copper oxide in addition to the high percentage of potassium and sodium oxides with the addition of As_2O_3 and PbO as opacifier agents to obtain the opaque turquoise colour.

Second kind of enamels*:* (Peinture)

Two translucent green and red enamel colours and two opaque enamel colours (turquoise and white) were analysed. The results of EDX analysis, are shown in (Table 2) and (Fig. 6). EDX analysis results proved that all enamel colours contain significant amounts of silica and lead oxide with little amounts of the alkalies, sodium and potassium oxides in addition to traces of aluminium oxide, magnesium oxide and calcium oxide. Metal oxides such as copper were usually used for colouring the enamel. It is responsible for the translucent green enamel in this case study. Translucent red enamel contains the essential components of the enamel without colouring oxides. The examination results obtained by digital microscope confirmed the existence of a gold layer beneath the enamel (Fig. 7). Opaque Turquoise enamel also contains copper oxide in addition to high percentages of potassium and sodium oxides if compared with other enamel colours. Opaque white enamel, contains basic components of enamel, described above in addition to another characteristic element, that is arsenic (As) in the form of arsenic trioxide (As_2O_3).

The results of the EDX analysis confirmed that the enamels consist mainly of silicon (Si), Lead (Pb), Potassium (K) and sodium (Na), in addition to some other distinctive elements of each colour. Basically, enamel is glass technically called silica to provide special properties such as lustre, fusibility, and elasticity [22]. Silica occurs in nature as quartz (flint, sandstone) and is basically silicon dioxide [23]. Among the components of the enamel, alkali such as K and Na are added in form of oxides which are used in the manufacture of the enamel. The bright, polished, sparkling effect of enamels is partly due to potash in their composition, while the presence of soda renders the enamel more elastic [24].

Lead oxide is the ideal material to lower temperatures since it possesses the highest refractive index and confers the greatest brilliance [23]. Softness and hardness of enamel are determined by the amount of oxide of lead present. High content of oxide of lead produces soft enamel, the harder the enamel the greater the quantity of silica contained in it, and the greater the resistance to atmospheric or chemical action; the softer the enamel the greater its percentage of lead, and the more liable it is to be decomposed by atmospheric influences and chemical agencies [24, 25]. Lead became an almost universal additive to enamels by the 19th century [26]. On the other hand, the harder the enamel the greater the quantity of silica contained in it, and the greater the resistance to atmospheric or chemical action.

It is concluded that in both enamels the green enamel was a copper oxide which can be present in different oxidation states, such as cupric oxide (CuO) which gives green colour [27].

The translucent dark blue enamel is usually obtained by dissolving Co^{+2} ions within the glass silicate network [28]. Small amounts of zinc and arsenic were also found in this enamel. These elements appear to be associated with the origin of the cobalt ore used to make this enamel [29]. The opacity of the dark blue colour obtained by adding lead in the form of lead arsenic. The EDX results confirmed the presence of these elements (As, Pb) may be due to the deliberate addition of lead arsenate opacifier to adjust the hue [30]. Moreover, the sources of cobalt are vein of arsenate secondary deposits (arsenic-rich cobalt ores) [31, 32].

For the red enamel it was found that the enamel was not coloured, but a transparent enamel melted over a layer of gold. The transparent enamel is fused over the foil to give greater brilliancy and protection [17].

Table 1. EDX analysis results of the first kind of enamel colours

Enamel colour	Elements/ Composition (wt.%)											
	SiO_2	Na_2O	K_2O	TiO_2	Cr_2O_3	Fe_2O_3	CuO	PbO	MgO	CaO	As_2O_3	CoO
Translucent Dark Blue	62.61	6.19	9.72	0.24	nd	0.93	4.14	6.14	0.85	6.25	1.05	1.45
Translucent Green	64.16	5.6	7.52	1	0.57	1.63	8.4	4.47	0.86	5.64	nd	nd
Opaque Turquoise	63.39	6.52	7.69	0.09	0.17	0.82	7.62	5.92	0.79	4.32	2.12	0.01

Notes: nd= not detected

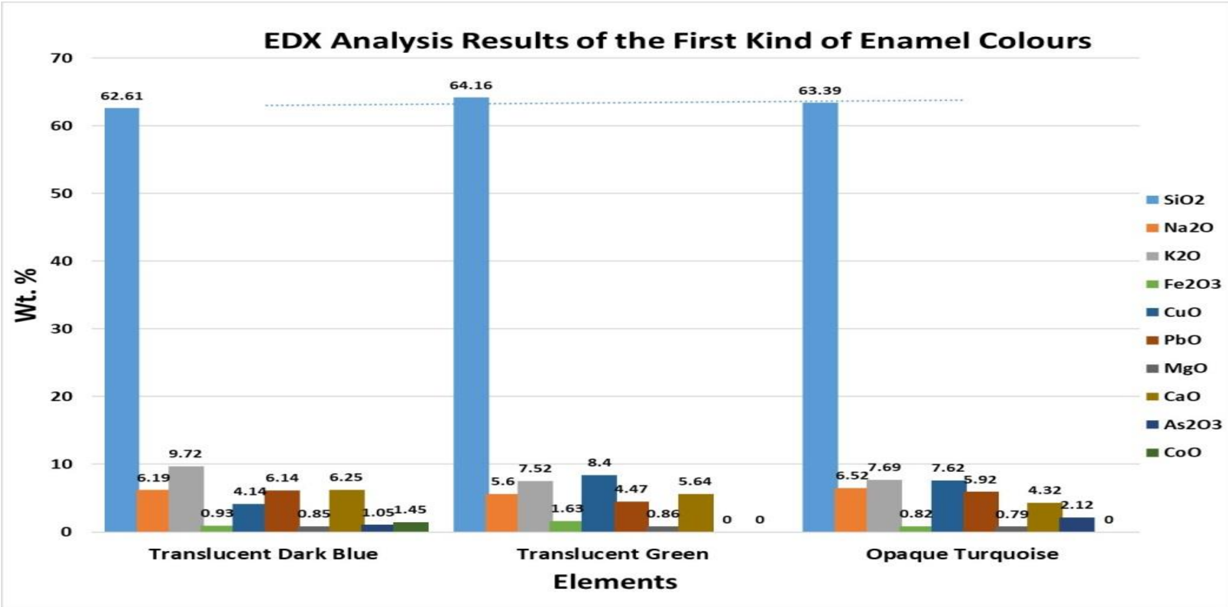

Fig. 5. EDX analysis results of the first kind of enamel colours.

Table 2. EDX analysis results of the second kind of enamel colours.

Enamel colour	Elements/ Composition (wt.%)								
	SiO_2	Na_2O	MgO	As_2O_3	Al_2O_3	K_2O	CaO	CuO	PbO
Translucent Green	52.85	3.39	nd	nd	1.30	8.47	0.89	3.67	29.43
Translucent Red	51.54	3.68	nd	nd	nd	6.25	nd	nd	38.53
Opaque Turquoise	56.88	3.30	1.95	nd	nd	11.00	nd	3.57	23.31
Opaque White	49.51	2.51	nd	4.40	1.21	7.86	nd	nd	34.50

Notes: nd= not detected

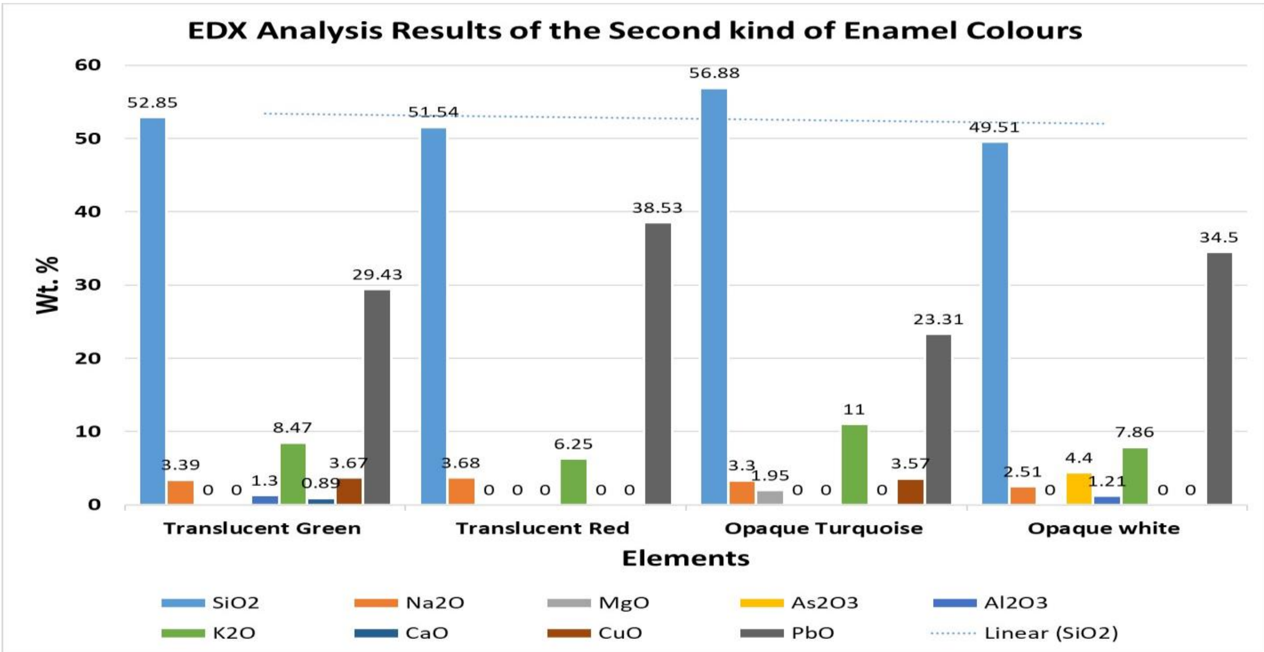

Fig. 6. EDX analysis results of the second kind of enamel colours.

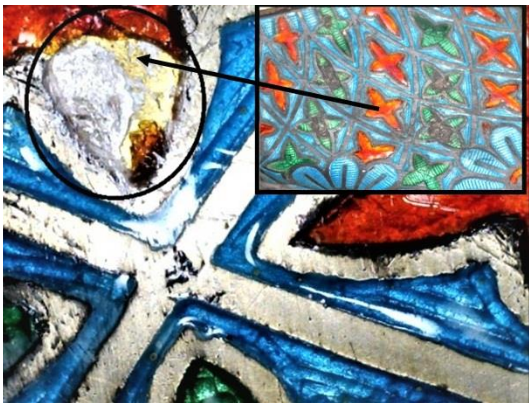

Fig. 7. Digital microscope photomicrograph of the gilding layer beneath the enamel layer.

This is an old practice of decoration with enamel in which, a layer of silver or gold foil is applied beneath the enamel layer. These results are consistent with the results of a painted enamel Qajar pendant [26] where the enamel was applied on a 20 carats gold foil.

The results confirmed that the opaque turquoise enamels in the two kinds of enamel were achieved by the presence of copper ions together with a high alkaline medium (K_2O + Na_2O) in addition to a high content of lead oxide PbO [33, 34].

The opaque white enamel contains white crystalline lead arsenate in the glassy matrix as a colourant and opacifier. It was introduced around 1750 and became the most used opacifying agent in the 19th century [35]. Therefore, the presence of this oxide refers to the use of lead arsenate as a colourant and opacifier [36].

A relatively high concentration of lead was found in the transparent enamel. This result is in agreement with the assumption that lead potash glass was used for painted enamel [26]. This can indisputably be assigned to the 19th century production [35]. The use of arsenic in the form of oxide with opaque turquoise and white enamel as a opacifying agent. Lead arsenate is the opacifier which glassmakers used from the end of the seventeenth century [37]. Moreover, the only opacifying agent used in painted enamels until the middle of the 18th century was tin oxide crystals in a lead oxide rich matrix. Lead arsenate was introduced around 1750 and became a commonly used opacifying agent in the 19th century [14]. There is similar compositions in only a few of the enamels from Indian objects, probably examples of European imports, which have lead-alkali compositions and contain lead arsenate as the opacifier [38].

4. Conclusions

This paper presents the results of the examination and analysis of two enameled objects in Aljazeera Museum and Faculty of Applied Arts' Museum in Cairo, Egypt. The examination was performed using a stereomicroscope and a digital microscope which revealed several aspects of deterioration (e.g., fall of the enamel, dust, cracks, pits, scratches and colour change) on the investigated samples.

The results of EDX analysis of the enamels confirmed that all of enamels consist of silicon, potassium, sodium, and lead in addition to some of the distinctive elements of each colour, and that the presence of high lead in the enamel colours and arsenic in white enamel are as colourants and opacifier agents. The EDX results proved that the colouring agents in both types of enamel are copper oxide to obtain green enamel, cobalt oxide for dark blue enamel, copper oxide with more sodium and potassium oxides for opaque turquoise enamel. The opacity of the dark blue and opaque turquoise enamels is obtained by adding lead in the form of lead arsenic, while a layer of gold was used under the translucent enamel to obtain the red enamel, this is an old practice of enamel decoration in which a layer of silver or gold foil is applied beneath the enamel layer and using arsenic oxide with opaque white enamel to obtain white colour enamel. Furthermore, the results proved that the chemical composition of enamel dates back to the 19th century AD, this was confirmed by the fact that lead arsenate, a new opacifier, was introduced around 1750 and became a commonly used opacifying agent in the 19th century, it is one of the important results which confirm the history of this enamel.

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