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CHEMICAL CHARACTERIZATION AND MANUFACTURING TECHNOLOGY OF SOME LUSTRE CERAMIC DISHES OF THE ABBASID PERIOD, NORTHERN EGYPT

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ABSTRACT

This paper studies some ceramic lustreware dishes with metallic glaze dating back to the Abbasid era (2-3rd century AH/8-9th AD) and preserved in Rashid archaeological stores. The samples were selected based on the diversity of textual and pictoral decorations including written words, plants, animals and geometric elements. The manufacturing process and mineral and chemical composition of the dishes have been subjected to several examination and analytical methods including stereo microscope, scanning electron microscope (SEM-EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (ATR-FTIR) spectroscopy and differential thermal analysis (DTA).

The study revealed a heterogeneous distribution of the color grains on the surface of the dishes and nanoparticles of metallic silver/copper ranging between 50-100nm. The metal oxides of the silver nanoparticles appeared in high percentage compared to nano copper particles on the surface of the lustre metallic layer which fact accounts for the greenish brown color of the dishes. While Arabic gum was used for fixing the decorations, the lustre layer was fired at 500°C and the firing of the ceramic body varied between 700°C and 800°C. A treatment and maintenance plan is suggested to preserve the pieces from further damage owing to their high archaeological value.

KEYWORDS: Abbasid ceramics, metallic lustre, glazing, Rashid, deterioration, examination, preservation, nanoparticles, copper, decoration,

1. INTRODUCTION

During the Abbasid period, ceramics industry flourished in Egypt and lusterware dishes were among the most famous types manufactured in the country. A good testimony of this fact is the collections kept in the archaeological stores and museums. The era of the Tulunides in particular witnessed serious attempts to develop an Islamic decorative style of art in Egypt. It was characterized by attempts to combine various artistic styles, ancient and contemporary decorative themes and to reconcile them in special proportions (Tash 2003; Pérez-Arantegui et al 2001). As for lustre decorations on glazed ceramics, they were first introduced during the Abbasid Caliphate in the ninth century AD (Al-Basha 1990; Caiger-Smith 1991). Decorations were then made of a nanocomposite thin layer of silver and copper metal nanoparticles, encased in an amorphous silica-based matrix (Colomban 2009). Lustre was created by firing the raw paint, which was directly applied to the glaze surface, at temperatures ranging from 500 to 700° C in a reducing atmosphere. Thus, the layer was formed by the reaction of a lustre paint and the glaze (Pradell et al 2005) and the process entailed two stages: a first one in which copper and silver ions enter the glaze surface via ionic exchange of metals from the paint (Cu^+ or Ag^+) with alkali ions from the glaze (Na^+ and K^+). Then follows a second stage in which a reducing atmosphere is introduced in the kiln and silver and copper ions are reduced to their metallic state and form small metal nanoparticles via a nucleation and growth process. Then the remaining paint is water washed away, revealing the lustre layer (Molera et al 2007; Williams 2012). Pertinent earlier analytical ceramic works are numerous for various archaeological periods (Krueger et al., 2021; Pourzarghan et al., 2017; Batmaz and Özkan, 2017; Di Bella et al., 2020; Ashkenazi et al., 2021; Abdallah et al., 2020; Liritzis et al., 2020).

The paper here aims to study some lustre ceramic dishes kept in Rashid archaeological stores. It seeks to analyze their metallic glaze decorations of greenish brown color, the oxides used in their composition, the medium used in installing those decorations and the degree of burning of the dishes. The paper also seeks to determine the level of deterioration in the artefacts and to suggest a method of conservation to preserve them. To achieve these goals the ceramic dishes under study were examined by stereo microscope and scanning electron microscope (SEM) and characterized chemically using EDX, XRF and XRD. Furthermore, IR was used to identify the type of medium used in fixing the decoration and DTA was used to identify the approximate firing temperature of both the lustre layer and the ceramic body.

The examination and analytical methods mentioned above revealed that the Egyptian Abbasid artist used both silver and copper oxides in the metallic lustre layer but the percentage of the silver nanoparticles was high compared to nano copper particles thus accounting for the greenish brown color of the dishes. Both tin and lead oxides were used to achieve the white opaque glaze layer as was the custom in manufacturing ceramics in this era. Arabic gum was used for fixing the decorations while the lustre layer was fired at 500°C and the firing of the ceramic body varied between 700°C and 800°C. Owing to the high archaeological and artistic value of the dishes, a maintenance plan is suggested to preserve them from further damage in the light of the results of this study.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Description of the pieces

The ceramic dishes studied in this paper belong to a group of dishes preserved in Rashid archaeological stores. The three dishes were chosen owing to their importance as a representative sample of the most famous types of Abbasid ceramics in Egypt in the Tulunid era (2nd-3rd century AH/8th-9th AD). Thus, they combine various decorative topics and reconcile them in special proportions distinguishing the art of this period from the styles of preceding and following eras in the art history of the country. Also, they reflect the proportions of the inscriptions and the decorations characterizing the Tulunid period in that they were larger than the natural ones. Moreover, the sample, in addition to being a part of a rich collection dating back to the Abbasid era, highlights the extent of the industrial and artistic diversity signified by special characteristics of each piece. The dishes, therefore, show the artist's ingenuity and his ability to diversify in his decorations and to adapt them in an elaborate and innovative way. This sense was transferred through the use of various botanical decorations, sometimes close to nature, by showing their details, and at other times modified since the 3rd century AH/9th century AD. Fig. 1C includes, for example, decorations characterized by repetition and contrast although they look like a rigid geometric scan, as this was a main theme of decoration. Nevertheless, the artist of this piece succeeded in combining the decorative beauty of the plant and its surroundings through the use of palm fans and their abstract halves as if they resemble in their entirety the shape of a bird with a head, body and tail by using the metallic lustre to highlight those details. The main characteristics of the decorative styles of the dishes can be summarized in the following paragraphs.

Geometric decorations were used in their various forms on the dishes in question, where artists managed to arrange and to organize them into ribbons and geometric compositions. Thus, in our case, the artists excelled in using the triangles in a way that overlapped with other decorative elements to give an integrated geometric composition (Fig. 1B). The shapes of the pajamas and circular areas often combined geometric decorative forms between floral, biblical and living beings (Fig. 1 A, B). The circular decorative elements were also carried out prominently on Abbasid porcelain (Fig. 1B, C) and on the back of Tulunid ceramic dishes, where they appeared in three or four groups of circles which are separated by small, slanted lines (Fig. 1E, F). The ripple decoration was also manifested in the identification of external frames (Fig. 1C), and the shape of the hexagonal star appeared in a clear distinctive way (Fig. 1B). The artist also was willing to use drawings of living beings characterized by their diversity, immobility, distance from nature and creativity in the use of metallic sparkle by decoration, which added some sort of embodiment (Fig. 1C).

The Muslim artists also used textual decorations in the form of Arabic single letters collected in words or phrases, sometimes in complex pattern formations, and as a basic element with other decorative elements (Afifi 1997). Textual decorations also varied between unreadable and readable texts used by the artist for the purpose of documentation (Maher 2005); the point is well illustrated in our first dish (Fig. 1A) for the word 'bless' which was applied with a metallic glaze on the temple of color (Fig. 1B). The leafy Kufic line is repeated twice clockwise.

In addition, secondary decorative elements were used together with the main elements as a background of the pictorial subject. Thus, contiguous dots appeared as a cluster on the back of some ceramic pieces, regularly distributed on the areas to be decorated with this decorative element (Fig. 1D, F). Small dots appeared in the shape of folded circles at the bottom of some dishes (Fig. 1B), and the decoration of a pale or modified eye on the back of ceramic dishes (Fig. 1E).

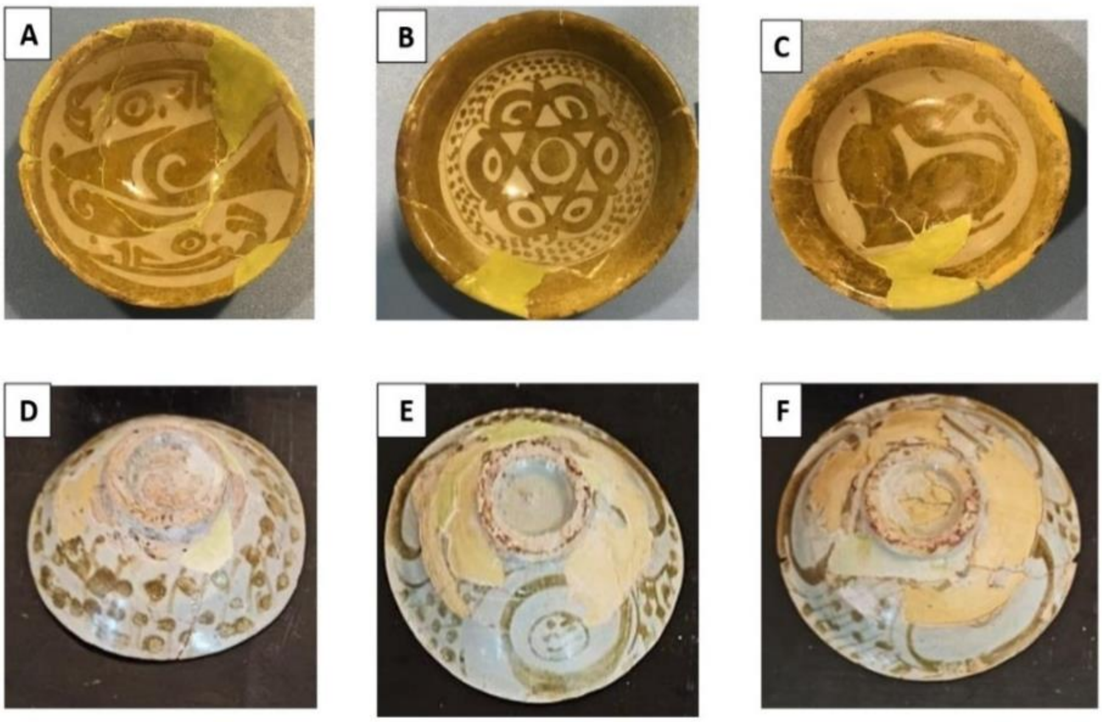

Figure 1. Lustre ceramic dishes. (A, D) modified written and plant elements showing inscriptions and floral decorations, record No. 103. Diameter: 9.6 cm/base: 4.3 cm/height: 3.5 cm; (B, E) geometric motifs as secondary decorative elements, record No.107. Diameter: 12.5cm/base: 4.3 cm/height: 4.3 cm; (C, F) a dish with a bird decoration, record No.110. Diameter: 9.5 cm/base: 3.5 cm/height: 2.6 cm

2.1.2 Deterioration aspects of the lustre

The condition of the sample of our ceramic dishes is not good since they reflect many deterioration aspects including cracks, flaking of glaze layers, fragility of the ceramic body and crystallization of salts. Documentation of their condition was performed using AutoCAD to demonstrate the deterioration aspects and to prepare a damage map (Fig. 2). The investigation showed that the flaking of the glaze layer was due to its weakness and decomposition in some parts of the front and back surface of the pieces. It has resulted from dissolved salts within the substrate body, which were transferred to it during burial in the soil before excavation and which were not treated during the previous conservation of the pieces. Furthermore, the exposure of the pieces to frequent fluctuations in temperature combined with humidity and successive cycles of moisture and drought melting must have also contributed to recrystallization of salts (Buys and Oakley 2011; Ahmed 2015; Stryszewska and Kanka 2017; Eloriby 2021). Considering that the dishes are preserved in Rashid, a coastal city where levels of humidity and salts are considerably high, these factors must have seriously contributed to the bad condition and the deterioration of the artefacts.

The surface also shows some damage resulting from the previous conservation process which was conducted in an improper way and led to a distortion of the aesthetic shape of the sample. The colors and decorations that were applied in completely different colors from the original colors of the artefact resulted in blurring some important details of the original decorations of the artefacts in addition to some irregularity in their surface levels.

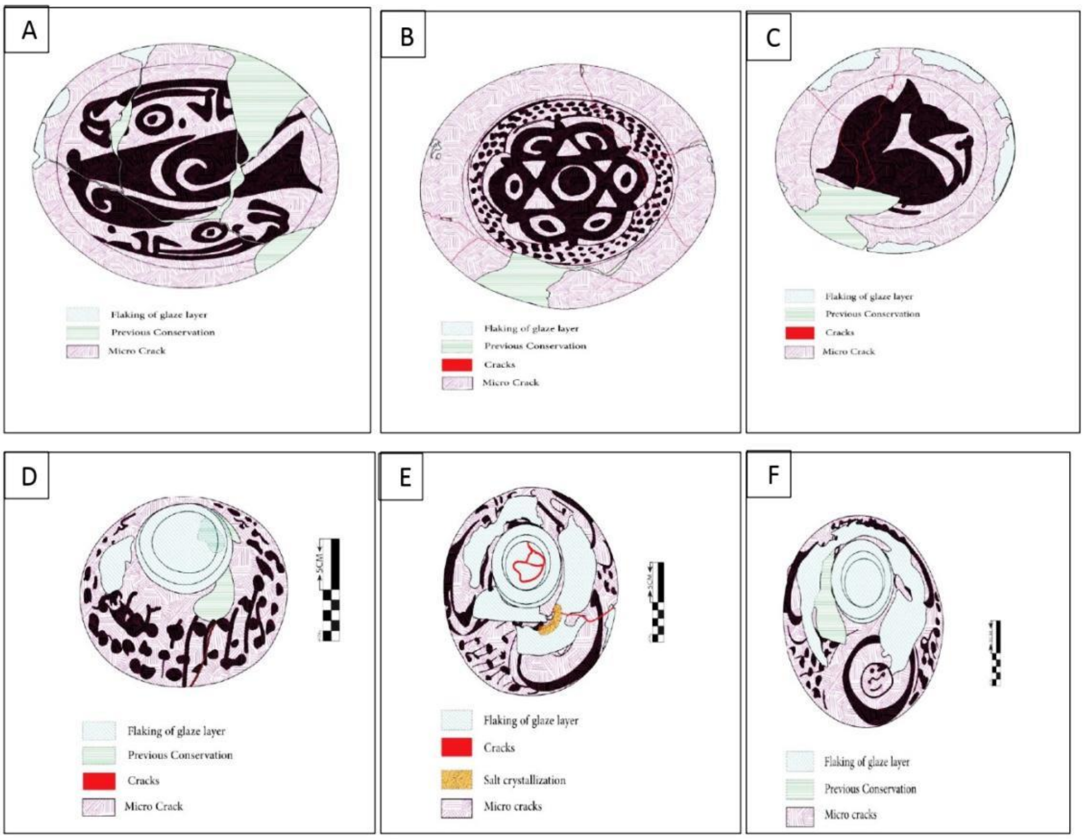

Figure 2. AutoCAD documentation of lustre ceramic dishes

2.2 Samples used in study

Due to the lustreware dishes of study are different from one another in its decorative forms, despite all being in one greenish-brown color, the falling peels from the lustre layer and body have been relied upon in the examination and analytical study, as shown in Table 1.

Table 1. Description of samples used in this study

Sample code	Sample Description
G1	Greenish brown color of lustre layer
G2	White opaque glaze layer
G3	Clay body of ceramic dish
G4	Includes (colored lustre – white opaque glaze)

2.3 Methods

2.3.1 Stereo microscope

The Leica MZ6 stereo zoom microscope is a modular common main objective stereo microscope with a zoom range of 6.3x - 40x with 10x eyepieces, Germany. This procedure was carried out at the General Authority for Metallic Resources in Dokki, Cairo, Egypt.

2.2.2 Scanning electron microscope with EDX

Using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyzes), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolutions for

Gun.1n). FEI Company, Netherlands. This procedure was carried out in SEM lab, Egyptian Center for Nanotechnology at Cairo University, Sheikh Zayed, Egypt.

2.2.3 Analysis of x-ray diffraction

XRD was used for mineral identification by Burker Company model D8, including reflectometry, high-resolution diffraction, in-plane grazing incidence diffraction (IP- GID), and Small-Angle X-Ray Scattering (SAXS).It was used to analyze a sample of lustre layer with body. This procedure was carried out in XRD lab, Egyptian Center for Nanotechnology at Cairo University, Sheikh Zayed, Egypt.

2.2.4 X-ray fluorescence (XRF)

X-Ray Fluorescence by X-MET 7000 series, Oxford Instruments (Benchtop) was used to identify elements of the lustre layer. This procedure was carried out at the General Authority for Metallic Resources in Dokki, Cairo, Egypt

2.2.5 Attenuated total reflectance -Fourier transform infrared (ATR-FTIR) spectroscopy

Fourier transform infrared spectroscopy**:** FTIR 460 plus, Range.400 _ 4000 cm-1, Jascoo, made in japan. This procedure is usually used to identify the chromatic mediator of colored materials and to identify organic and inorganic materials that have varying degrees of absorption in the infrared range by identifying the functional groups of each compound (Chukanov 2014). It was performed in the Micro analytical center, Faculty of Science, Cairo University, Egypt.

2.2.6 Differential thermal analysis (DTA)

Differential Thermal Analyzer: DTA-50-SHIMADZU-Under N2 atmosphere-Japan. This procedure was carried out at the General Authority for Metallic Resources in Dokki, Cairo, Egypt.

3. RESULTS AND DISCUSION

3.1 Stereo microscope

The results of the examination using the stereo microscope revealed that (sample G1) has a greenish brown color with a heterogeneous distribution, which forms agglomerates of smaller particles in some areas (Fig. 3 A) as well as micro-cracks in the lustre surface (Fig. 3B). As shown in (Fig 3.C) the white glaze layer (sample G2) is a thin layer applied to the surface and the stereo also showed salt crystals of a light color precipitated on the surface of the ceramic body (sample G3) (Fig. 3D).

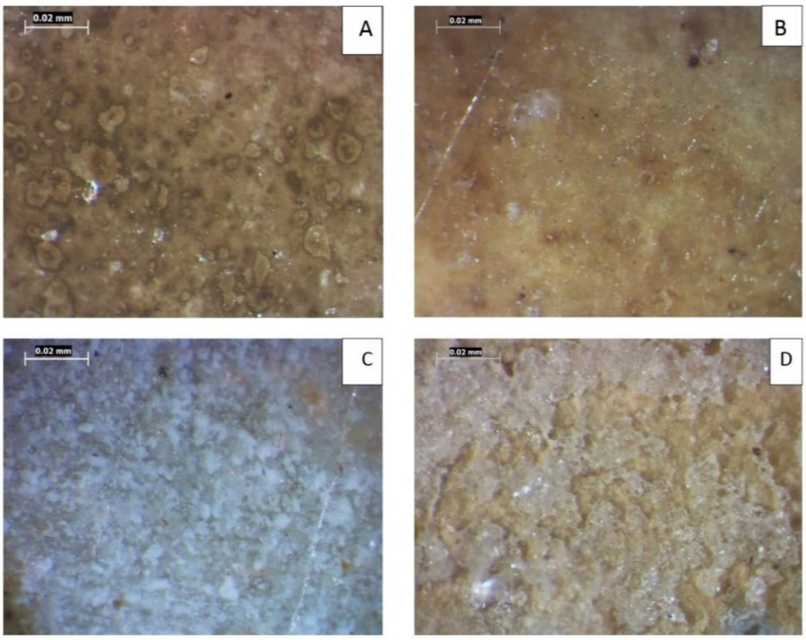

Figure 3. Stereo micrographs of lustre ceramic dish samples; (A, B –represent sample G1) Greenish brown lustre layer; (C –represents sample G2) White glaze layer; (D -represents sample G3) Salt crystallization on the ceramic body.

3.2. Scanning electron microscope with elemental analysis unit (SEM-EDX)

The examination of sample G2 by SEM showed a spread of micro cracks and black points on the surface, indicating the presence of lead oxide. It also showed a heterogeneous distribution of color grains on the surface which appears to be very fragile (Fig. 4A, B). The SEM of sample G1 showed nano particles of metallic silver (marked with a red circle) ranging between 50-100nm (Fig. 4C, D). On the other hand, SEM micrographs of Sample G3 (Fig. 4E, F) showed semi-uniform degrees of homogeneity for the components of the burnt clay, and regular and homogeneous grains, except for the areas of deterioration whose grains appear semi-disintegrated and areas of salt crystallization that are clearly concentrated between the grains of the clay.

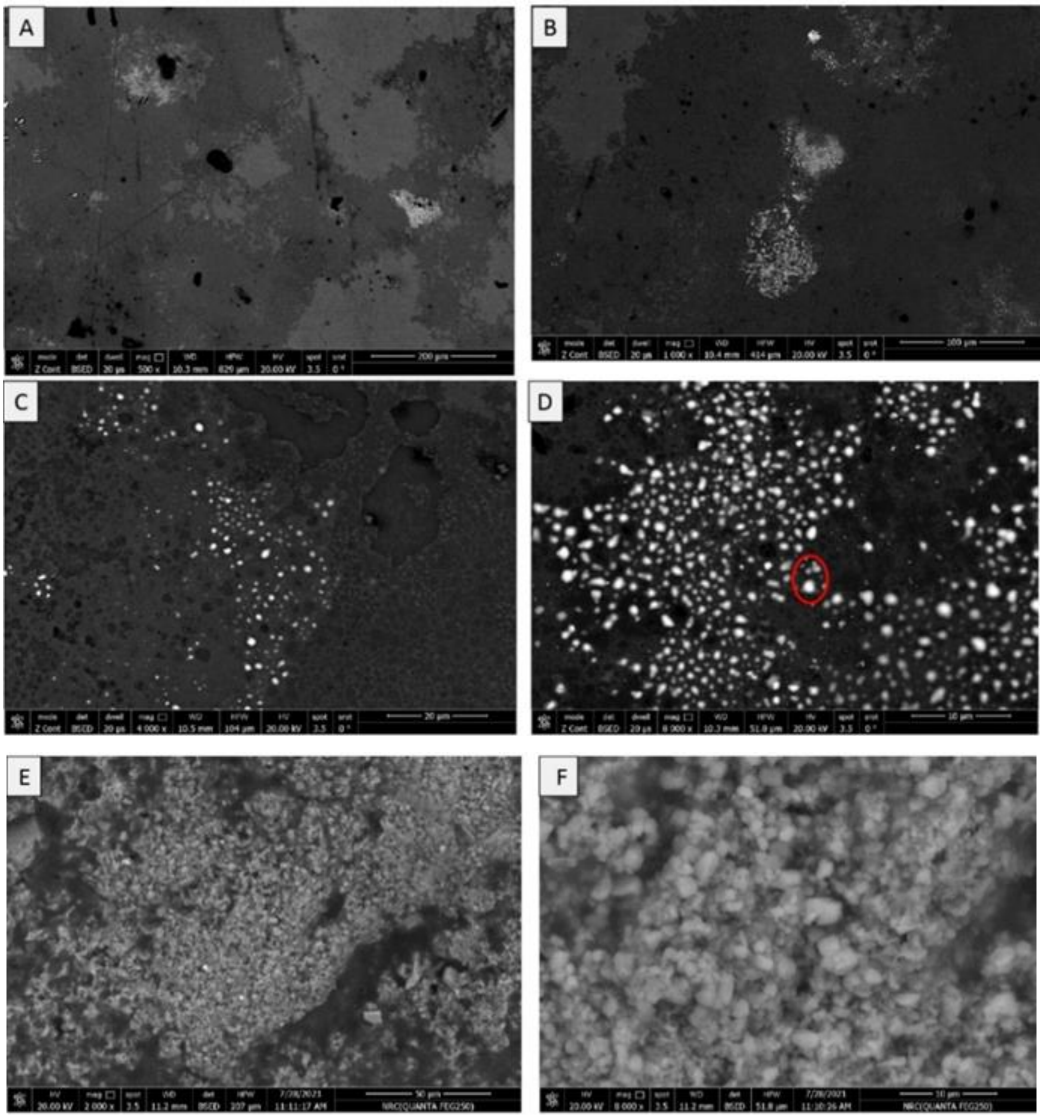

Figure 4. SEM micrographs, (A, B–represent sample G2) white glaze layer with homogeneous distribution of cassiterite particles; (C, D-represent sample G1) greenish brown lustre layer with nanoparticles of silver metallic; the red circle in D surrounds the silver nanoparticles; (E, F–represent sample G3) weakness of body substrate of ceramic dish with semi–homogeneity of particle size

3.2.1 The result of elemental analysis (EDX)

As shown in Table. 2 and Fig. 5, the result of SEM-EDX analysis indicates that sample G2 consists of opacified lead–alkali glaze due to the lead (Pb) percentage (avg. %5.2), sodium (avg. 2.64%), potasium (avg. 2.95%). It also demostrates that the glaze was whitened due to particles of tin (Sn) at percentage of avg. 26.11%, with other elements such as aluminium, calcium (spots A, B, C). The greenish brown lustre layer (sample G1) (spots D, E, F, G, H) shows that the lustre contains a mixture of copper (avg. 1.76%) and silver (avg. 9.90%). Thus, while the rates indicate in this case a rich level of silver and a poor level of copper, in spot (E) the high percentage of silver reached (30.5%) coupled with absence of copper. The high density of silver nanoparticles explains the golden shine being responsible for the brownish color (Reillon and Berthier 2006; Molera et al 2007; Pradell et al 2007; Gutierrez et al 2010). The presence of silver and copper together is observed in all parts of the samples (spots D, F, G, H). The addition of copper in silver rich lustres helps in forming the metal silver nanoparticles (Pradell et al., 2008c).

As for the alkaline ions in the metallic lustre layer, it is noted that their percentage is low, as the proportion average of sodium was 2.26% and potassium 3.34%. This is due to the ion exchange that occurs between alkaline ions and metal ions of copper and silver during the formation of metallic lustre.

During the process of forming this lustre at a low temperature of 550° and in a reducing atmosphere, sodium is replaced by copper and silver replaces potassium which leads to the appearance of nanoparticles of copper and silver and the formation of metallic lustre (Pradell et al., 2005). Lead (Pb) in turn appears in the lustre at a percentage of 5.93% due to its presence in the basic opaque glaze. The influence of lead in the glaze helps promote nanoparticle growth and the formation of thinner and denser nanoparticle layers, resulting in a metallic shining lustre (Molera et al., 2007; Pradell et al., 2007; Panagopoulou et al., 2018).

Furthermore, iron (Fe) appeared in spot C at a percentage of 1.56% because the presence of iron in the glaze enhances the reduction of Cu^{2+} to Cu^{+} through oxidation of Fe^{2+} to Fe^{3+}. This process usually occurs when the temperature is quite high as usually happens while manufacturing molten glass (Schreiber et al 1999; Pradell et al., 2008) and during lustre production at temperatures above 550 (Kido et al., 2006). Sample G3 (Spot I) shows the result analysis of the bodies of the ceramic dishes and indicates a relatively high percentage of calcium concentration of 13.47%, which indicates that the clay was calcareous and that silica (Si) was at the percentage of 32.24%, being the basic component of the clay. The ingredients also contain magnesium, sodium, iron and alumina as components of the clay. Furthermore, the percentage of chloride (Cl) is 4.63% as a result of the crystallization of salts in the granules of the body.

Table 2. EDX data with chemical composition with associated spectra and images. G2-White glaze sample represents spots A, B, C; G1-Greenish brown lustre layer sample represents spots D, E, F, G, H; G3-body substrate sample represents spot I)

sample code	Spot No.	Elements												
		OK	NaK	MgK	AlK	SiK	KK	CaK	FeK	CuK	AgL	SnL	PbM	ClK
G 2	A	34.12	2.66	1.16	1.67	26.57	3.11	---	---	---	---	24.9	5.81	---
	B	28.07	2.69	1.84	1.45	14.71	1.25	---	---	---	---	47.04	2.95	---
	C	38.03	2.59	1.73	1.94	31.22	4.49	3.12	1.56	2.08	---	6.40	6.84	---
G1	D	43.43	2.3	1.88	2.07	30.69	4.16	3.83		1.6	3.31	---	6.73	---
	E	39.21	2.39	1.85	1.6	18.84	--	--	--	---	30.5	2.39	3.22	---
	F	40.23	2.26	1.81	2.17	31.18	4.13	3.29	---	1.79	4.51	1.85	6.78	---
	G	43.68	2.58	1.94	2.15	30.91	4.59	4.6		1.48	1.67	----	6.4	---
	H	40.39	1.78	1.67	1.83	27.78	3.84	4.89	---	1.77	9.53	----	6.52	---
G3	I	34.76	1.39	2.09	7.42	32.24	1.89	13.47	2.11	---	---	----	---	4.63

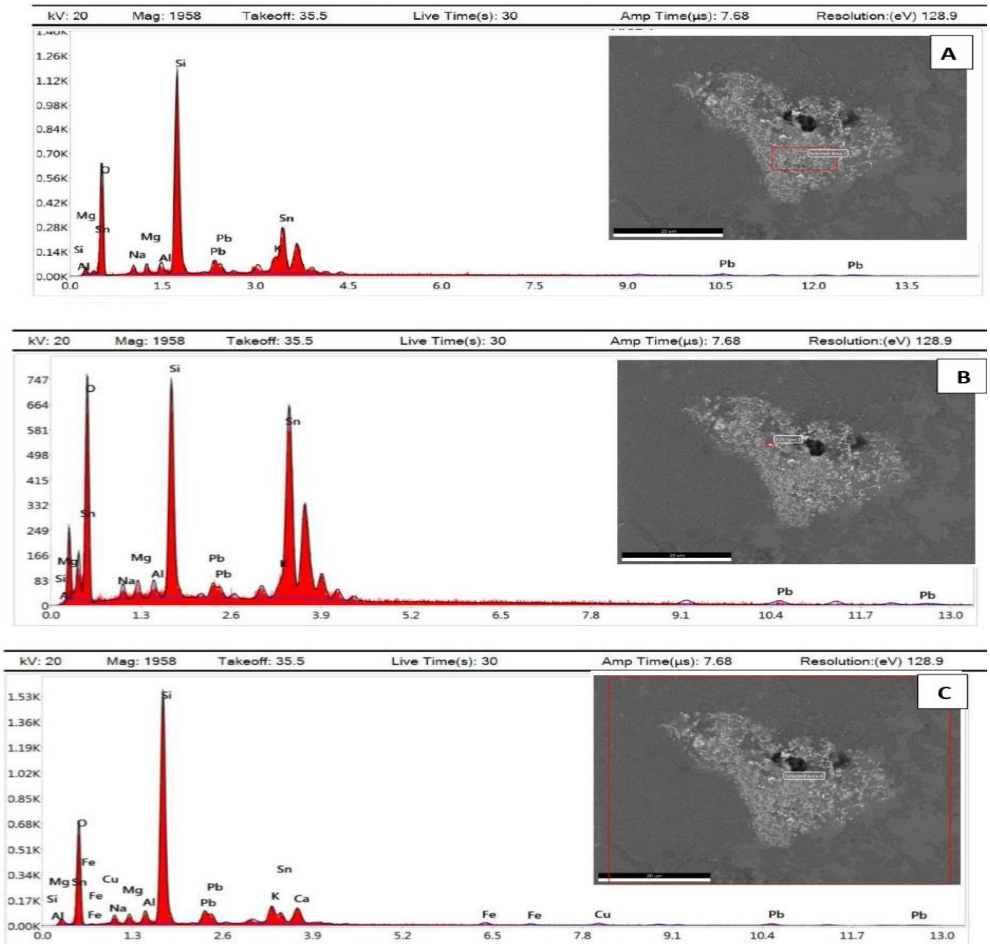
kV: 20 Mag: 1958 Takeoff: 35.5 Live Time(s): 30 Amp Time(µs): 7.68 Resolution:(eV) 128.9
A
B
C
Si
O
Sn
Mg
Na
Al
Pb
K
Ca
Fe
Cu

Figure 5. G2

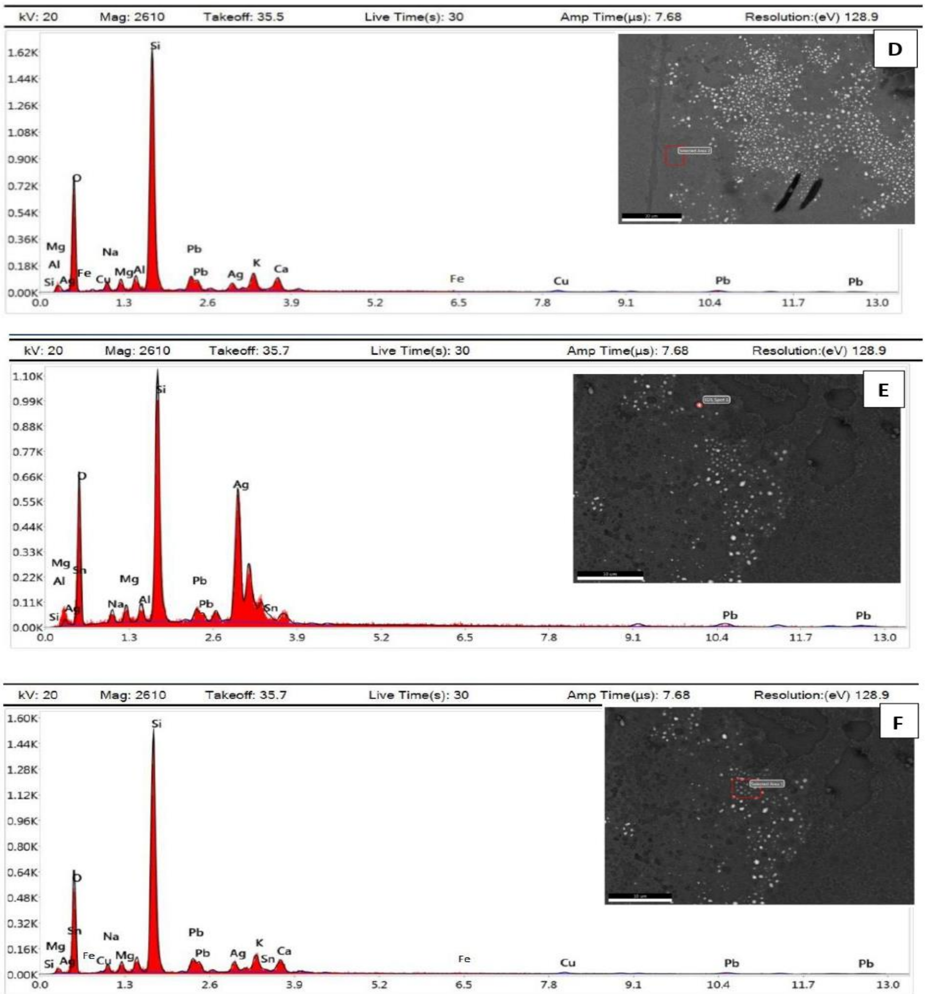
kV: 20 Mag: 2610 Takeoff: 35.5 Live Time(s): 30 Amp Time(µs): 7.68 Resolution:(eV) 128.9
D
kV: 20 Mag: 2610 Takeoff: 35.7 Live Time(s): 30 Amp Time(µs): 7.68 Resolution:(eV) 128.9
E
kV: 20 Mag: 2610 Takeoff: 35.7 Live Time(s): 30 Amp Time(µs): 7.68 Resolution:(eV) 128.9
F

Figure 5. G1

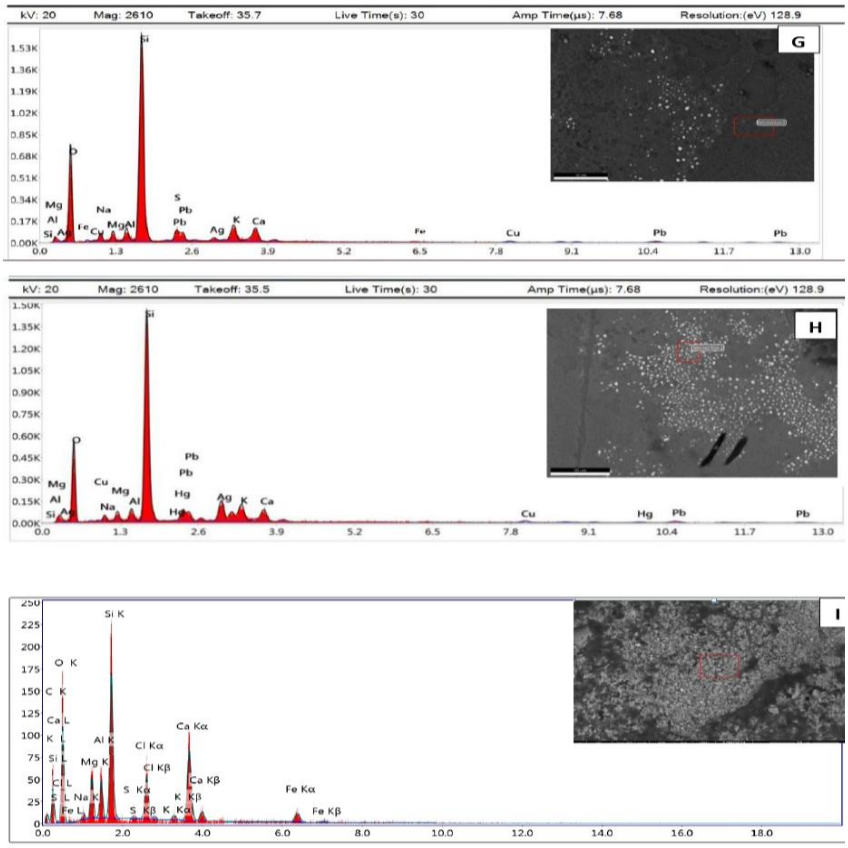

Figure 5. Energy dispersive X-ray (EDX) attached with SEM images of samples at 10 mm, the red square with little white is the analysed spot, microanalysis pattern of white glaze (sample G2 – spot A, B, C). lustre layer (sample G1 – spot D, E, F, G, H) and body substrate (sample G3- Spot I)

3.3 *X-ray diffraction analysis (XRD)*

Metallurgical analysis obtained by X-ray diffraction analysis (XRD) of ancient ceramic bodies provides useful information about raw materials and determines the technological processes related to manufacture (Iordanidis et al., 2009). The XRD data, as shown in Fig. 6 and Table 3 (sample G4), indicate that the lustre pigment contains kaolinite, wollastonite, quartz, cassiterite (SnO2), cuprite (Cu2O), chalcopyrite (FeCuS2), lautite (FeAsS), (Ag2S) and (Ag2So3). The formation of wollastonite is due to the reaction between the calcareous paste and the lustre. This wollastonite reaction layer produces a white background for the lustre decoration (Mason 2004). While kaolinite and quartz are basic components of the metallic clay (Pourzarghan et al., 2017), cassiterite is responsible for the opaque white background layer covering the body. Moreover, tin dissolved in the glaze acts as an incentive factor for the reduction and formation of metal nanoparticles (Pradell et al 2008b).

The formation of cuprite (Cu2O), chalcopyrite (FeCuS2), lautite (FeAsS), (Ag2S) and (Ag2So3) in the lustre are attributed to the reaction between the components of lustre (sulphur, copper and silver) during the firing at a reduced atmosphere. Sulphur causes the formation of a sulphate melt which is responsible for the ionic exchange between the copper and silver from the pigment and for the alkali ions from the glaze (Pradell et al., 2005). Also, some mixed sulphates crystallize during cooling the arsenic sulphide used in the Middle East as the source of the Sulphur (Pradell et al., 2015).

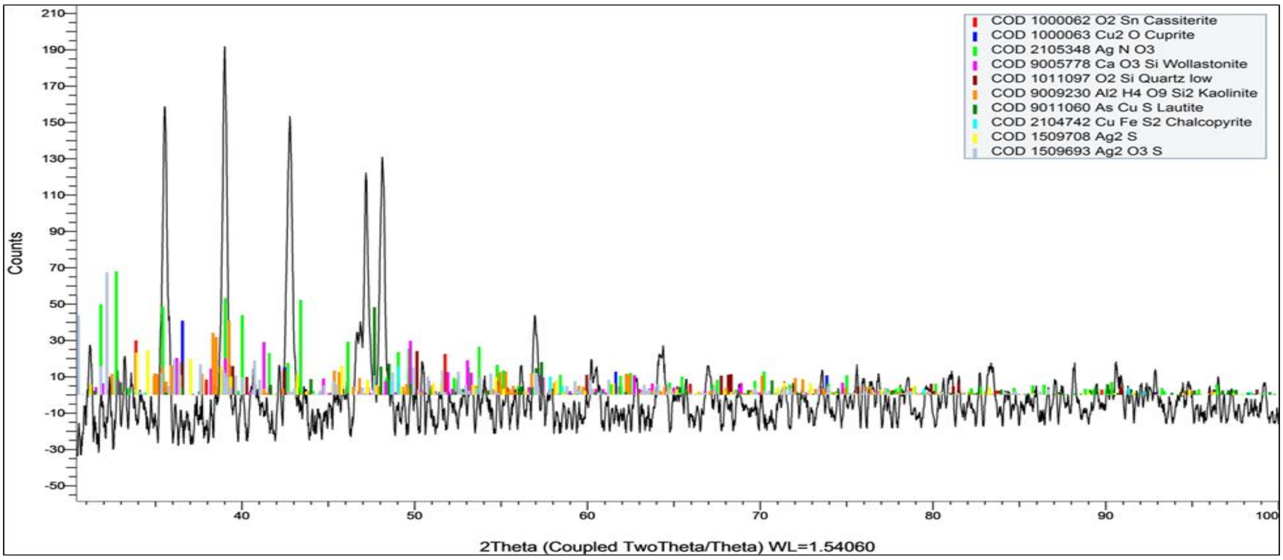

Figure 6. Results of the XRD of the (sample G4) lustre layer with white glaze.

Table 3. Identified minerals % by XRD analysis of (sample G4) lustre layer with white glaze.

Component	Sample G4 (%)
$AgNO_3$	10.2
Wollastonite ($SiCaO_3$)	23.3
Quartz (SiO_2)	10.2
Kaolinite ($Si_2Al_2H_4O_9$)	36.7
Lautite	4.4
Chalcopyrite	1.3
Ag_2S	4.8
Ag_2O_3S	7.1
Cassiterite (SnO_2)	1
Cuprite (Cu_2O)	1

3.4 X-ray Fluorescence (XRF)

One of the most important methods of analysis is the elemental non-destructive analysis (Hahn et al 2006) and X-ray fluorine analysis based on the ejection or the exposure of the sample to the rays or a current of electrons. This process leads to the emission of energy from the sample in the form of secondary fluorinated X-rays, whose wavelengths are characteristic of the components of the material (Pollard 2007). It is widely used in chemical analysis because it is a fast and accurate method (Davison 2003). The components of the sample taken from the metallic lustre and white glaze layer of the ceramic dishes (sample G4) described in table 4 were accordingly identified. The results of the analysis corresponded to those of the analysis using EDX and XRD and the percentage of the tin oxide, which was responsible for the white color of the metal glaze, was 3.7%. Notable also were silver and copper whose presence explains the greenish brown color of the metal glaze. These results are in accordance with other studies concentrating on the manufacture of metal glaze in Egypt in the Tulunid period (Philon 1980; Watson 1985; Caiger-Smith 1991; Farbman et al., 1992; Keblow 2003; Pradell et al., 2008a, b).

The amount of silver in the metal glaze also appears higher than copper where silver is at the percentage of 6.32%, and copper at 3.21%, which is a consistent result with the work of Pradell et al., (2008a). Meanwhile, the level of lead (7.21%) is not high and corresponds with the usual level in our period. The appearance of lead by a small percentage in the metal glaze was not uncommon as well (Mason 2004). At the beginning of the 13th century, the lead rate in the metal glaze industry began to increase to 22% in Spanish ceramics and Hispano Moresque productions (Molera et al., 2001). Na and Cl ions also appeared, which explains the high rate of salts in the dishes. The high rate of salts consequently caused great pressure within the pores of the body (Abuku et al., 2017; Messina et al., 2018) and led to the fall of the metallic glaze layer as evident in the case of the ceramic dishes in question.

Table 4. Chemical composition of the lustre layer and white glaze obtained by XRF

Main constituents	Concentration (wt%)
SiO_2	49.31
Al_2O_3	4.60
K_2O	4.91
Fe_2O_3	0.50
Na_2O	3.03
CaO	4.92
MgO	5.76
SnO_2	3.73
AgO	6.32

CuO	3.21
AS_2O_3	1.60
Cl	3.10
SO_2	1.70
PbO	7.21
L.O.I	2.94

3.5 *Fourier transform infrared (ATR-FTIR) spectroscopy*

As the results of the Fourier transform infrared spectroscopy, shown in Fig.7 and Table 5(sample G4), indicate, the medium of Arabic gum was used in the metal glaze in order to fix the colors on the intended spots on the surface. Markers of silica and kaolin also appeared owing to their presence in the paste used to make the ceramic dishes.

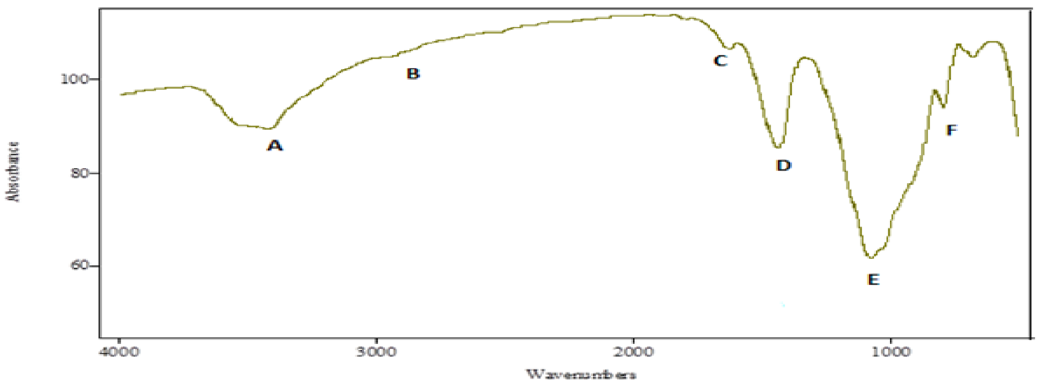

Figure 7. IR pattern for the lustre layer and white glaze (sample G4)

Table 5. FTIR for the lustre layer and white glaze (sample G4)

symbol	Function Group	Wave numbers	Standard Wave numbers
A	O-H Stretching band	3410	3600 -3200
B	C-H Stretching	2820	2800-3000
C	O-H bending band	1626	1650
D	C-H bending band	1436	1300 -1480
E	C-O Stretching band	1024 Overlapping with Si-O-Si	1300-900 1100-1000
F	SI-O Stretching bands	828	910 -830

(A, B, C, D) Gum Arabic – (A, E, F) Kaolin, (E) Silica

3.6 *Differential thermal analysis (DTA)*

The following observations were obtained from the thermal curve of the lustre layer and the substrate body (Figs. 8A, B). In the lustre layer curve (sample G1) (Fig. 8A), it was shown that an endothermic reaction occurred at 80.50°C upon the dehydration of compound water. Also, an exothermic reaction occurred at 450°C upon the burning of organic carbonates from the exothermic and endothermic reactions. It was also found that the firing temperature of the lustre layer was 500°C; this result agrees with the previous studies of Molera et al., (2007) and Pradell (2008b).

From Figure 8B, showing the thermal curve of the substrate body (sample G3), it was observed that an endothermic reaction occurred at 269.79°C, upon the dehydration of the compound water. An exothermic reaction occurred at 588.51°C. Between 550 °C and 650 °C, the clay displayed a dehydroxylation process involving transformation of kaolinite to metakaolin (Chin et al., 2017; Kılıç et al., 2017). Quartz was transformed from the alpha phase to beta phase at 573°C (Ibrahim and Mohamed 2019). Furthermore, an endothermic reaction occurred at 895.71°C, indication the decomposition of carbonates during this and the exothermic reactions. Finally, it was also observed that the firing temperature of the ceramic dish ranged between 700°C-800°C.

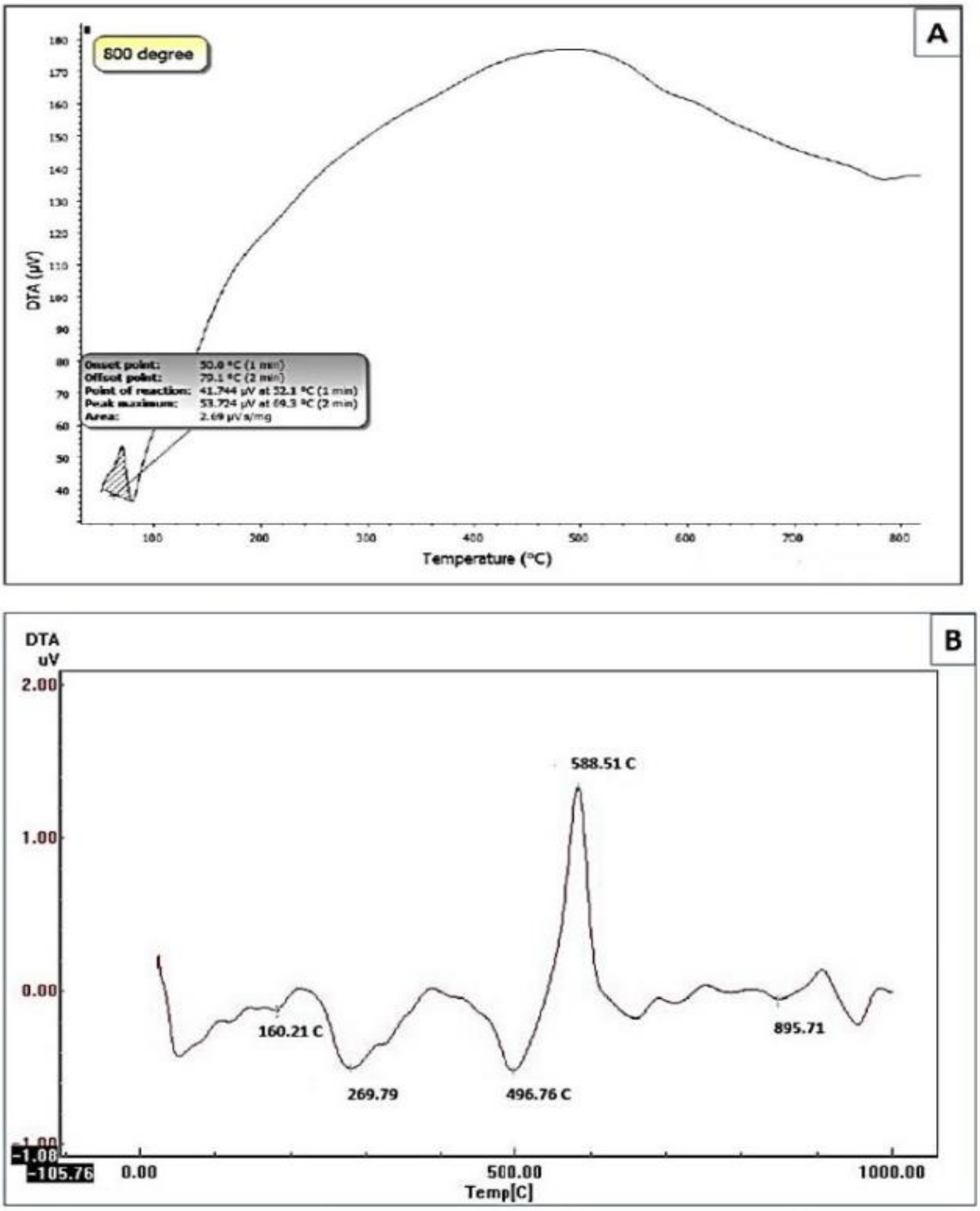

Figure 8. DTA curve of a ceramic sample. A) sample G 1- from lustre layer shows a firing degree around 500°C; B) sample G3- from body clay shows a firing degree ranging between 700-800°C.

4. METHODOLOGY PLAN TO TREAT THE DETERIORATION ASPECTS

Due to the weakness of the metallic glaze layer, there are some crusts that are about to fall from the surface of the dishes. It is therefore suggested to strengthen the artefacts using paraloid B-82 dissolved in acetone at the percentage of 5% (Abdel-Rahim 2016) and to remove dust and dirt carefully by mechanical cleaning. Considering the poor condition of the ceramic dishes, chemical cleaning may also be applied using warm water, acetone and diluted ethyl alcohol if necessary (Abd-Allah 2013). Since the previous restoration caused some distortion to the shape of the pieces, it is also advisable to remove the newly restored and added parts, which caused this distortion both in color and level of the surface. In particular, the use of polyfilla can be taken into consideration in completing the missing parts (Newton and Davison 2003; Ibrahim and Mohamed 2021) since its color is suitable to light color of the body of the dishes. Then the decorations are to be completed using similar decorative elements (Madkour 2014). After the coloring process, the restored decorations are to be covered with a layer of polyurthan polish to simulate the appearance of the surface metallic lustre layer. After that, it is possible to strengthen and isolate the fragile pieces of lustre layer using Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% (Eloriby et al., 2022).

5. CONCLUSION

Through the study of our sample of ceramic dishes with metallic lustre layer kept in Rashid archaeological stores, it was shown through various examinations and analyses that the lustre layer of those dishes consists of a mixture of silver oxide and copper on a white glazing layer containing a mixture of alkaline glazing and lead. In addition, a high percentage of silver in the metallic lustre layer, compared to copper, was observed through examination by the scanning electron microscope where particles of silver nanoparticles were significantly spotted on the surface as also observed through analysis by EDX and confirmed by analysis by XRF. This phenomenon was common in the manufacture of ceramic dishes with metallic lustre layer in the early Abbasid period as well as during the Tulunid period, which is the case in our study.

The percentage of lead used in the manufacture of the white glazing layer was notably low, as confirmed by previous studies on the artefacts of the Abbasid era. Meanwhile, cassiterite was used to obtain white glazing covering of the hull of the ceramic dishes to give a clear background to the drawings and colors with metallic sparkle. Also, analysis has shown a percentage of sulphur, which was used to help reduce silver and copper during burning in a reduced atmosphere to enhance the appearance of the lustre layer.

As it was found by infrared analysis (FTIR), the medium used to help stabilize the color on the surface of the body was Arabic gum and it became clear through DTA that the firing degree of the lustre layer was 500 °C and that firing of the body varied between 700°C and 800°C. As shown by examinations and analyses, the state of weakness and damage of our sample of ceramic dishes is considerable. Peeling and fall of the lustre layer were observed as well as a significant crystallization of salts between the pores of the ceramic body, which lead to great pressures causing the fall of the metallic glaze layer. Bad preservation and environmental conditions ought also to be considered in this context since they helped greatly in the crystallization of salts and the weakness and fragmentation of the metallic lustre layer. It is therefore recommended that a new restoration and maintenance of the dishes be performed following the previous steps to prevent further deterioration.

AUTHOR CONTRIBUTION

This paper is the outcome of a joint effort undertaken by its three authors who collaborated throughout the stages of the study. RAE and AHS conceived the idea, chose the sample dishes under investigation, AHS obtained the permissions to publish them. RAE determined the methodology, the tools and the software, and conducted the formal study of the results of examinations and the analytical methods. Both authors prepared the original draft of the paper. ASA contributed to the formal analysis, reviewed and edited the final version. All authors have read and agreed to the content of the final manuscript; they collectively share mutual responsibility for this joint endeavor and its results.

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