ORIGINAL PAPER

IDENTIFICATION OF PIGMENTS, GROUNDS AND BINDING MEDIA IN MURAL PAINTINGS WITHIN ELSHINAWY PALACE, ELMANSOURA GOVERNORATE, EAST OF DELTA, EGYPT

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Abstract. *Micro analysis of pigments, plaster layers and binding media using SEM-EDX, XRD and FTIR within Elshinawy palace proved that blue pigment is cobalt blue, green pigment is malachite yellow pigment is goethite, and binding medium is animal glue. These paintings were carried out on a ground layer of gypsum with animal glue as binding medium, in addition to a portion of calcite added deliberately to increase brightness of gypsum. The protein materials of animal glue gave in alkaline medium and in presence of copper a blue violet or purple color called Birut Molecules.*

Keywords: *Elshinawy Palace, XRD pattern, SEM-EDX analysis, FTIR spectroscopy, Cobalt blue**,** Birut Molecules.*

1. INTRODUCTION

In Egypt, the period from the end of 19*th* century AD to the first half of the 20*th* century characterized with palaces and complexes in similar to European styles; out of these palaces is Elshinawy palace the under investigation palace.

Elshinawy palace is located in El Mansoura City, East Delta-Egypt. The importance of this palace is attributed to its owner Mohamed Bek Elshinawy, a rich merchant and senator in Egyptian parliament, and its unique architectural style that was commonly used in Europe and Italy in this period. The construction of this palace has been started in 1928, on a total area about 4164 m^2; the palace has been built in similar to Italian palaces by an Italian architect, due to the European architectural influences prevailed in Egypt in that time.

Several techniques were used in carrying out mural paintings, the most used techniques were fresco and tempera techniques. In tempera technique paintings were carried out on a prepartoy layer; in the most cases gypsum was mixed with animal glue [1].

In this technique the choice of pigments should depend on their chemical and physical characteristics such as color intensity and resistance to adverse environmental conditions of such as thermal stability [2, 3].

The pallet of the painter contained several pigments, such as blue, red, green to obtain different shadows. Out of the blue pigments is cobalt blue; this blue pigment is a synthesized pigment since 18th dynasty BC from cobalt ores commonly occur in Eastern desert and it use was continued in the modern times due to its thermal stability in the paintings and facades continuously exposed to sun rays in Egypt [4] and its microbial resistance.

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Moreover, the color tone of cobalt blue should depend on the concentration of cobalt oxide, it was well established that concentrations of CoO upto 0.05 per cent gave an intense blue color; this color is changed to violet or indigo when the concentration was increased to 0.2 per cent [5].

Beside blue pigments, green pigments were used. The most ancient green pigment was malachite that was used since prehistory [6], and continued to be used in Egypt till 18*th* (AD) century. The availability of malachite green is attributed to hydration of azuriten that explains the reason of association between both azurite and malachite [7].

With regard to the yellow color, goethite, is an earthy yellow pigment of hydrous iron oxide was one of the first yellow pigments of art history, commonly known yellow ochre, using of goethite beside limonite as yellow pigment could be ascribed to its intense color [8, 9], and its availability whereas goethite occurrences are widely distributed in Egyptian oases, in particular Baharia Oasis [10], and these occurrences are resulted in oxidative decomposition of many iron compounds, that explains why this pigment was not synthesized [11].

The color of goethite is varied, and the variety of color tone should depend on the ratio of hematite to goethite and degree of hydration of the pigment, these are the major factors influencing the resulted color [12].

Tempera technique was use from the beginning of history in Egypt, the main feature of this technique is mixing the pigment with a binding medium such as animal glue to facilitate brushing, to lay these pigments in the pictorial layer, to provide a coherent and homogenous paint layer. These pigments were applied on the stone surface directly or on a ground of gypsum layer or layers to hidden irregularities in the stone surface [13, 14].

Paintings within Elshinawy palace are subjected to different deterioration agents such as geometrical such as micro cracks and settlement, biological symptoms in form of microbiological stains, and humidity in form of forming water drops due to neighborhood to a Nile branch that increased moisture content of mural paintings and enhanced deterioration processes [15, 16].

To put forward a comprehensive strategy for restoration and conservation of these deteriorated mural paintings, identification of pigments (yellow, green and blue), plaster layer and binding media within Elshinawy palace will be described herein. The other aim of this paper is to confirm continuity of artistic materials and methods in the modern Egypt.

2. MATERIALS AND METHODS

2.1. MATERIALS

To identify pigments, layers and binding media, eleven micro samples were collected from Elshinawy palace, El-Mansoura Governorate (East of Delta of Egypt) (Fig. 1) from blue, green, yellow pigments and plaster layers for further investigations (Figs. 2-3). Some samples were collected from flaked and micro cracks in paintings (Fig. 3a, c, d), and some areas were entirely exfoliation (Fig. 3f) and were used for further investigations.

(a) (b)

Figure 1. Location of El-Shenawy palace: (a) Map of El-Mansoura, where the investigated palace is located; (b) facade of El- Shenawy Palace.

(a) (b)

Figure 2. Sampling location: (a) The first mural painting; (b) The second mural painting.

2.2. METHODS

X-Ray Diffraction (XRD)

To identify the elemental composition pigment and plasters within mural paintings of Elshinawy palace XRD Philips (PW1840) diffractometer with Ni-filtered Cu-Kα radiation was carried out where micro samples were scanned over the 0-60° 2θ intervals, at a scanning speed of 1.2° min^{-1}. A quantitative estimate of the abundance of the mineral phases was derived from the XRD data, using the intensity of certain reflections and external standard mixtures of minerals compared to the (JCPDS standards of 1967); the detection limits of the method were ±1 w/w %.

Scanning Electron Microscopy – Energy Dispersive X-ray spectrometry (SEM-EDS)

The same samples were investigated using SEM-EDAX that was performed using a Fei device (version Quanta 200), with following specifications: 24.98 kV, 0.00 tilt, 36.47 take-off, 35.0 ampt, SUTW-sapphire detector type, 129.87 resolution, and a thin gold coat was applied according to the processing instructions.

Fourier Transform InfraRed Spectroscopy (FTIR)

FTIR analysis was conducted on pigment and plaster samples for possible presence of organic media. FTIR Spectroscopy (JASCO FT-IR 61000, National research Centre, Cairo) was used; micro samples were analyzed according to Ciurczak [17] where pigment and plaster samples were mixed with KBr powder (~150 mg). After grinding, the mixed was pressed in an evacuated die to produce a pellet, and resulted spectra were recorded.

Formation of Birut Molecules

After identification of the binding media and observing traces of blue violet color in Fig. 3a, it was important to explain formation of this violet color because of binding media under laboratory conditions. Triple test tubes were used, each one contained 1 ml of animal glue (10 g/L), then 1 m of 1 M $NaHCO_3$ and traces of copper sulphate ($CuSO_4$) were added to each tube, heated in water bath for 15 minutes, and left in the room temperature for one month, and the resulted color was observed.

3. RESULTS AND DISCUSSION

3.1. XRD AND SEM-EDX ANALYSES

3.1.1. Blue pigment

XRD spectrum of the blue pigment obtained from these mural paintings showed presence of zincates (ZnO), carbone (C), cobalt oxide (CoO) and gypsum ($CaSO_4{\cdot}2H_2O$) (Fig. 5a), so the cobalt blue ($CoO{\cdot}Al_2O_{3)}$ is the most probable.

Historically, it was well established that cobalt blue was the third manufactured pigment in ancient Egypt after Egyptian blue and Egyptian green and was used since the King

Tuthmosis III (1479-1425) and used on a large scale within Amarna period (18th dynasty and beginning Ramisside period, 19th dynasty) in the decoration of pottery and lintels houses within Tell Amerna [18], and since 17th centurt, cobalt blue was used in the baroque style painting [19] that may be transferred to Egypt in the 19th century.

This pigment is still used in modern times due to its characteristics qualifying it to be used on a wide scale such as thermal stability, resistant to adverse environmental conditions, unaffected by acids and alkalis [4] resistant to biological degradation due to toxicity of cobalt to a wide range of microorganisms [20].

The identification of this blue pigment was confirmed by data obtained from XRD spectra. XRD pattern revealed that major element in the blue pigment was cobalt oxide (CoO), and its ratio ranged from 0.17 to 0.37 wt %, this cobalt oxide (CoO) gives the metaphor to the blue pigment [21].

Cobalt blue was manufactured from local ores, it has been reported that cobalt occurrences in Egypt are close to Qasr Lebekha near both Kharga and Dakhla oases, 30 km north of the town of Kharga, ratio of cobalt in these occurrences is significant, and the ratio of impurities of zinc, nickel and manganese is varied according to locality of the occurrences of alum [4, 18, 23, 24].

On the other hand, XRD spectra of blue pigment indicated presence of ZnO, and it was well referenced that correlation between the concentrations of CoO and other three transition metal oxides MnO, NiO, and ZnO was used for characterizing the cobalt-blue colorant [23].

The presence of gypsum in the cobalt color (Fig. 5a) may be assigned to traces of plaster layer, and there is no indication that gypsum not added deliberately to cobalt blue. The presence of carbon (C) in the investigated cobalt blue may explain the manufacturing process, these carbon traces may be originated from plant ash or organic fuel resulted in burning cobalt oxide with aluminum hydrate in the range of 900-1200°C [18, 20].

3.1.2. Green pigment

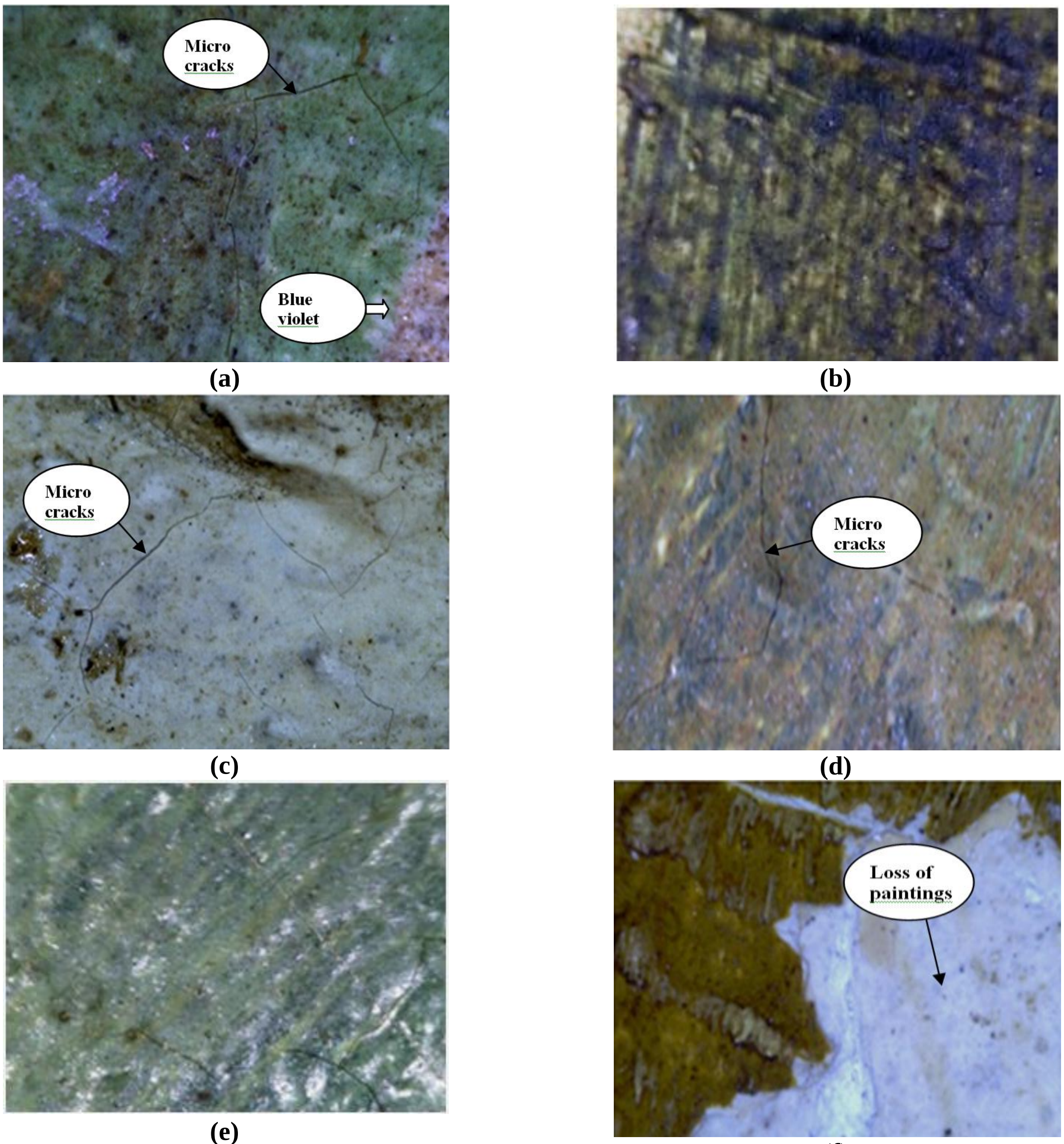
SEM micrograph of the green pigment pointed out the needle form (Fig.4d) whereas the prismatic or needle crystals are standard forms of malachite green [2]. Also, XRD pattern of this green pigment indicated presence of basic copper carbonate [(Cu_2CO_3 $(OH)_2$], gypsum ($CaSO_4 \cdot 2H_2O$), and zincates (ZnO) (Fig. 5b), suggesting that malachite was used as a green pigment.

Malachite and azurite two minerals were used as green and blue pigments respectively in paintings, due to their thermal stability under adverse environmental conditions; with the exception their chromatic alteration if exposed to sulfur based pollutants and acidic rains [24].

Malachite occurrences are widely distributed in Egypt in Sinai and Eastern desert in the upper oxidized zones of copper ores in association with azurite, so the resulted color tone varied according to ratio of azurite and other impurities. To obtain a clear color, malachite is grounded and washed in pure water to get rid of impurities [25].

Moreover, data obtained from XRD pattern indicated presence of Zn in form of ZnO that usually accompanies Cu in carbonates derived from alteration caps of copper ores [26].

On the other hand, it has been observed that streomicroscopic photo indicated forming blue violet color under green malachite (Fig.3a) that may be assigned to Birut Molecules since it has been referenced that copper ions in presence of alkaine media and proteinous traces forming blue violet color called [1].

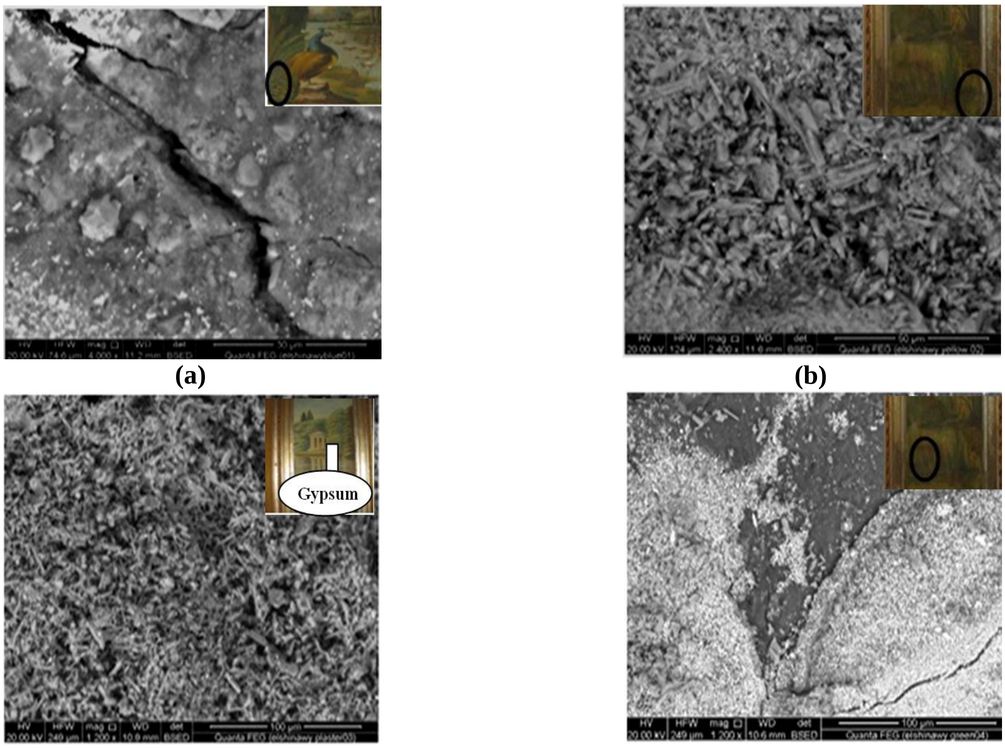


(a) (b) (c) (d) (e) (f)

Figure 3. Sampling locations: (a) Green color with black spots, with traces of violet color, micro cracks, the first mural painting; (b) The blue color interfered with green color, the first mural painting; (c) The second swan; (d) Blue color, with micro cracks, second mural painting; (e) Green color with luster; (f) Yellow color interfered with white color.

3.1. 3. Yellow pigment

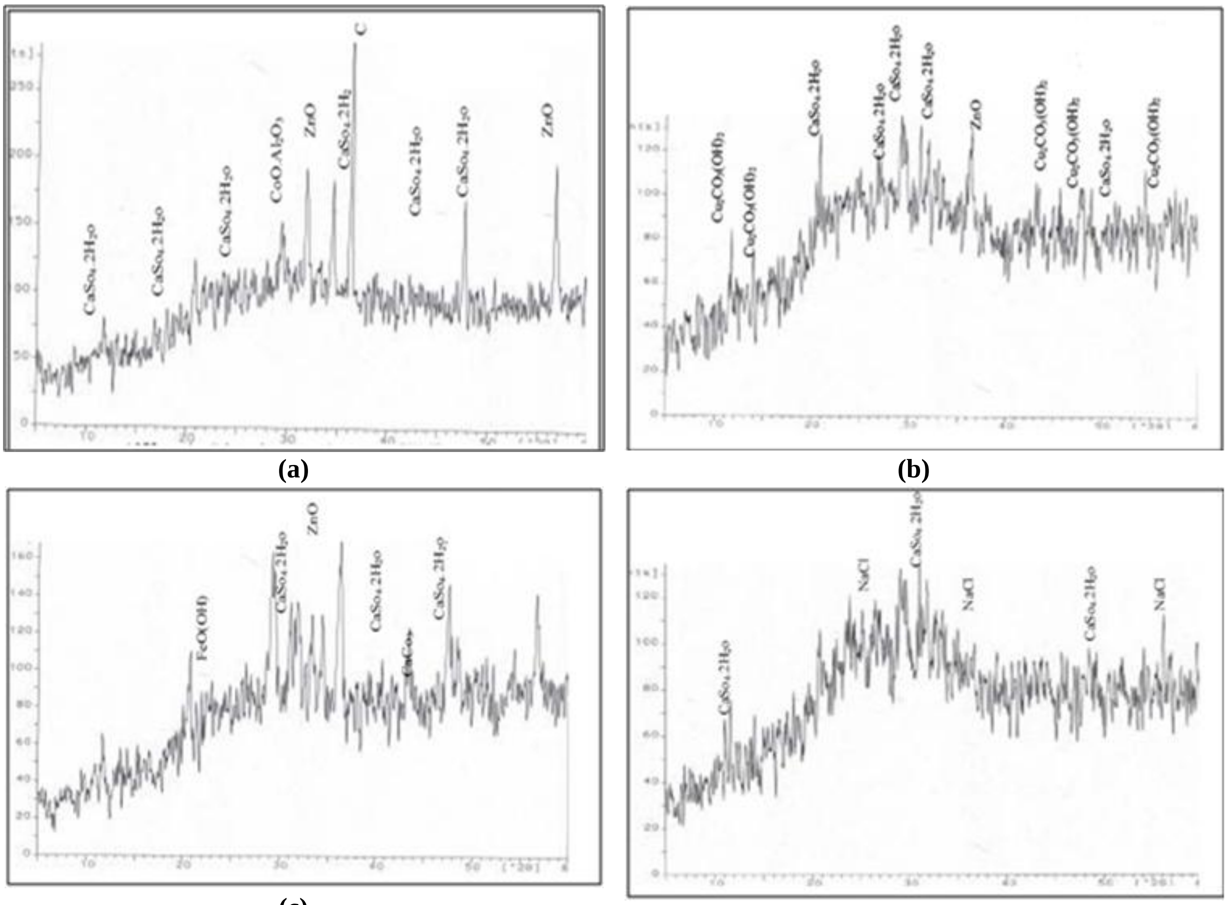
SEM micrograph of the yellow pigment pointed out that yellow pigment is in tabular or fiber form, so goethite (FeO (OH)) is the most probable as a yellow color (Fig. 4b).This in agreement with Ortega *et al*., [27] reported that tabular and fiber forms and fairly regular were characterizing forms of goethite [12]. This result was confirmed by XRD pattern of yellow pigment indicated presence of ferrous oxide [(FeO(OH)], zincates (ZnO), gypsum ($CaSO_4 \cdot 2H_2O$) and carbon (C), (Fig.5c). In addition, it was well established that goethite was used since pre history to present as yellow colorant, and hydrous ferric oxide is the main chromophore [26]. The common use of geothite as a yellow pigment may be assigned to the availability of goethite occurances in El Bahria Oasis.



(a) (b)

(c) (d)

Figure 4. SEM micrographs (a) Homogenous layer of cobalt blue, (b) Goethite in fiber form (c) Gypsum crystals in needle form within plaster layer, (d) Homogenous layer of green color.



(a) (b)

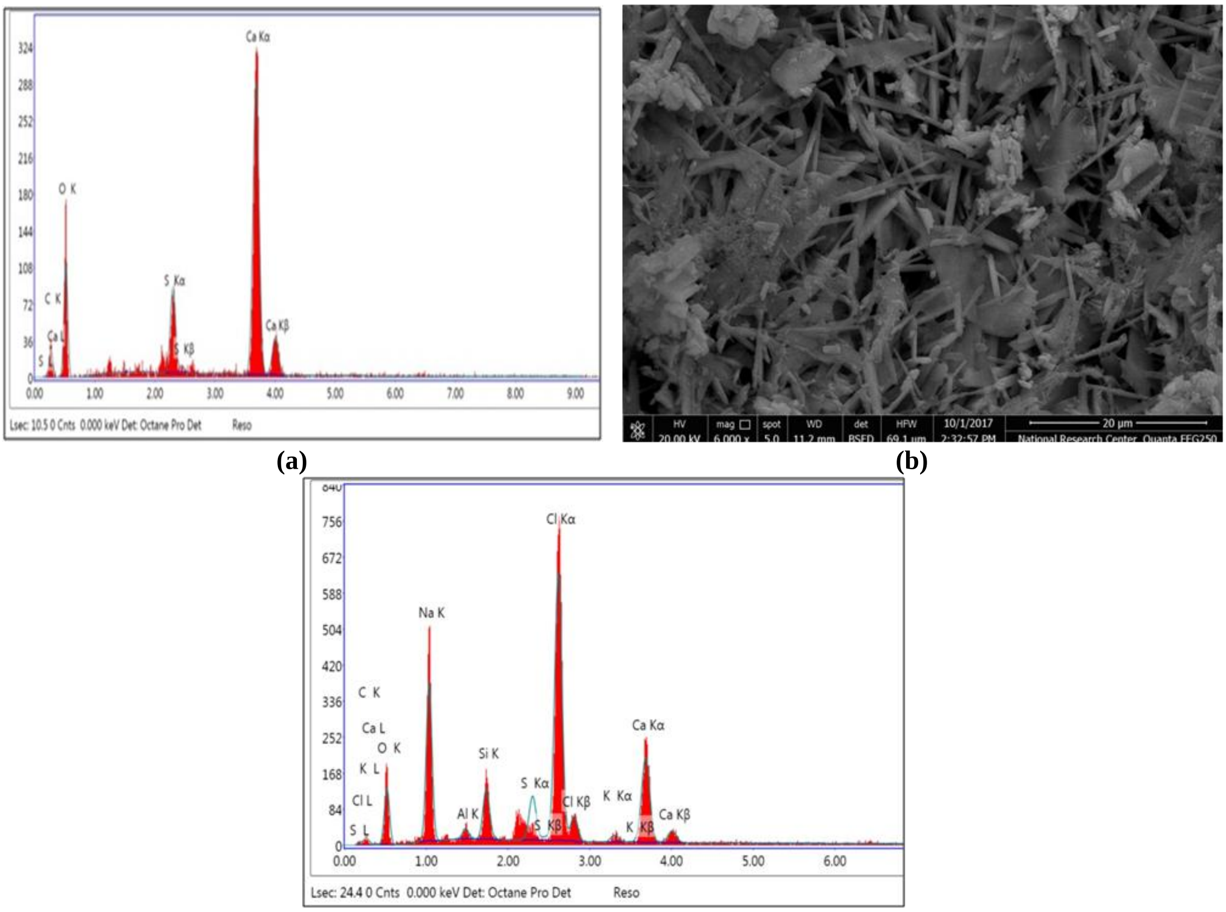
(c) (d)

Figure 5. XRD patterns (a) blue color of cobalt, (b) Green color of copper carbonate, (c) yellow color, (d) plaster layer.

XRD pattern of goethite indicated presence of ZnO and $CaSO_2\cdot 2H_2O$ (Fig.5c), that may be attributed to the matter of fact that goethite is not in pure form but contains a percentage of impurities such as quartz, feldspars, calcite, dolomite and other carbonate minerals [28]; various clay minerals and possibly gypsum, so the hue of goethite varies according to the ratio of these impurities whereas higher ratio of manganese oxide resulted in brownish color. Furthermore, the resulted hue should depend on its crystallinity and elemental purity. In general, characteristics of pigments enhanced the painter to use specific pigments, so goethite was used due to its resistance to alkaline and acidic solutions [2, 12, 29].

3.1.4. Plaster layers

XRD pattern of the ground layer pointed out presence gypsum ($CaSO_4\cdot 2H_2O$) and halite (NaCl) (Fig. 5d). In addition, SEM-EDX of plaster layer sample revealed 39% calcium (Ca), 29% oxygen, 17% carbon, 11% sulfur (Fig.6a). On the other hand, SEM micrograph pointed out presence of fibroid form or tabular form of gypsum, the ideal form of gypsum (Fig.6b).



(a) **(b)**

(c)

Figure 6. SEM –EDX micrograph of plaster layers, sample.

Furthermore, it was well referenced that gypsum was used in Egypt since prehistory and still used in modern Egypt as a preparatory layer with a binding medium such as animal glue due to the availability of gypsum occurrences in Egypt. EDX pattern pointed out presence of Ca and C, so calcite may be present. Calcite was added deliberately to enhance brightness of gypsum especially if these gypsum occurances contained traces of clay and humic substances [30].

Both XRD (Fig.5d) and SEM-EDX (Fig.6c) of gypsum plaster revealed presence of halite, that may be originated from impurities in gypsum occurrences widely occurred in Egypt; and it was well referenced that halite is a common mineral in marine sediments such as gypsum occurrences [31, 32].

3.2. *BINDING MEDIUM*

3.2.1. FTIR spectra of preparatory layer

FTIR spectra of preparatory layer indicated presence of stretching band at 3543cm^{-1} characterizing NH group, stretching band of C=O group appeared at 1140 cm^{-1} and stretching band of SO_4 appeared at 3406 cm^{-1} (Fig.7) [33], using animal glue as a binding medium is the most probable. From review literature it was found that gypsum with diluted animal glue was used as a preparatory layer to hidden the defaults and roughness of the stone support and other inner layers [34, 35] providing a smooth surface that facilitates brushing [13].

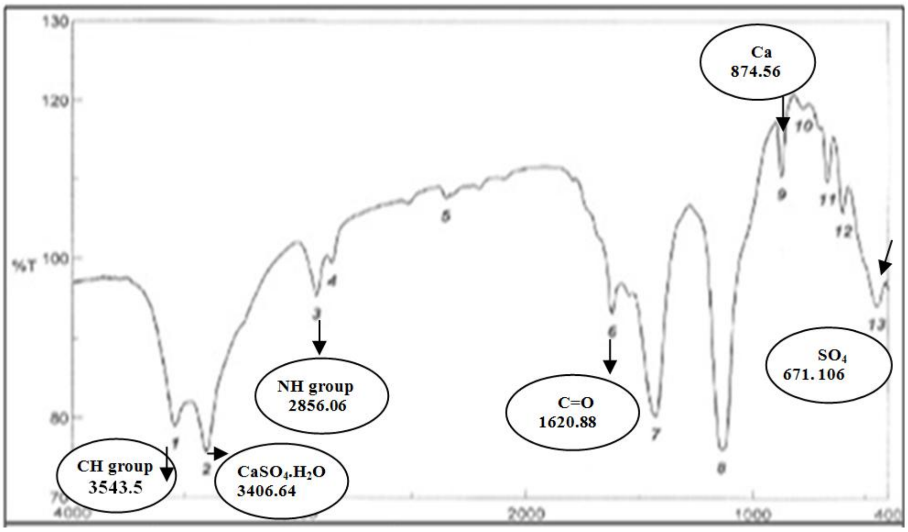


Figure 7. FTIR spectra of the preparatory layer.

On the other hand, FTIR spectra gave a strong band at 874 cm^{-1} is a bending band of calcite (CO_3), it was well refrenced that the fingerprint region of calcite is 900-650 cm^{-1} [36] confirming adding a portion of calcium carbonate deliberately to increase brightness of gypsum containing a portion of clay minerals and humic substances as impurities [30]. FTIR spectra of groud layer pointed out presence of carboxylic group at 1620 cm^{-1}, that may be resulted in the degradation reactions.

3.2.2. FTIR spectra of of pigment medium

Figure 8 shows FTIR spectra of the binding medium that gave an intense band at 3552 cm^{-1}, the fingerprint region of amide group (NH) and 2858.3 cm^{-1} (CH stretching bands), 1620.1 cm^{-1} (C=O stretching), bonding band appeared at 1427.2 cm^{-1} characterizing amide III (NH) group, but spectra at 1130.2 cm^{-1} is a stretching band of carbonyl group (C=O) [36-41], suggesting that animal glue is the most probable binding medium that was commonly used in mural painting [34]. Animal glue was extracted since the Pharaonic period from local and available sources such as hides, bones, muscles, or from fish, and the resulted glue was used in traditional woodworking, grounds and painting [42-44].

3.2.3. Blue violet color formation

Finally, after one month of formation molecules experiment, the color of test tube was changed into blue violet or purple shades, that may be attributed to formation of Biuret molecules ($(H_2N\text{-}CO\text{-})_2NH$) reported by Rose in 1833. It has been well established that the protein materials gave in alkaline medium in the presence of copper traces a blue violet color that may explain the blue violet shades under the green color of malachite and animal glue as a binding medium previously pointed out in Fig. 3a. This phenomenon was well documented in some mural painting dated back to the 13th/14th century from St. Stephens Cathedral in Vienna [45].

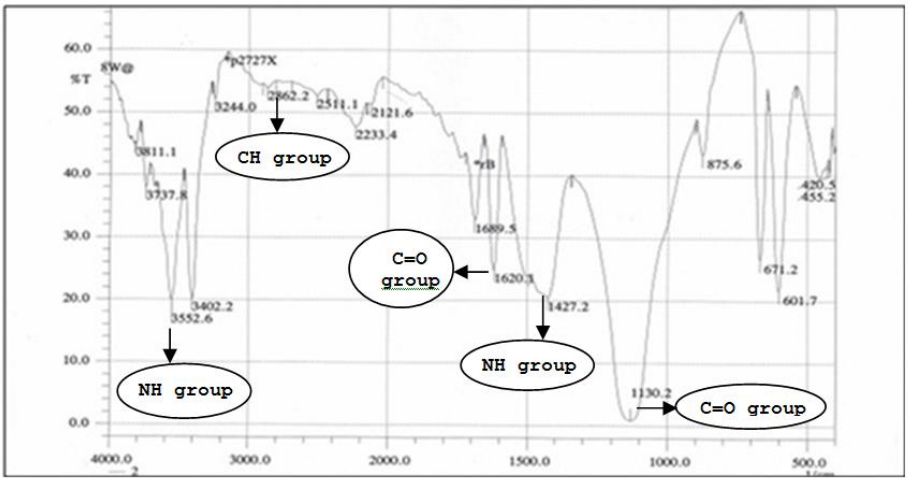


Figure 8. FTIR spectra of the binding medium from mural paintings.

4. CONCLUSIONS

Elshinawy palace was exposed to different deterioration aspects such as micro cracks, and water drop forming. The mural paintings within this palace were carried out on a preparatory gypsum layer.

Current investigations pointed out that blue color is cobalt blue, yellow color is goethite, green color is malachite and plaster layer is gypsum, the binding medium is animal glue. Finally, green malachite in alkaline medium with proteinous medium formed Biuret molecule with blue violet color.

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