

Identification and Conservation State of Painted Wall Plasters at the Funerary House in Necropolis of Tuna El-Gebel, El-Minia-Upper Egypt

Nabil A. Abd El-Tawab Bader*, Abdelkareem E. Ahmed

Conservation Department, Faculty of Archaeology, South Valley University, Qena, Egypt

Email: *nabil.abdeltawab@arch.svu.edu.eg

How to cite this paper: El-Tawab Bader, N.A.A. and Ahmed, A.E. (2017) Identification and Conservation State of Painted Wall Plasters at the Funerary House in Necropolis of Tuna El-Gebel, El-Minia-Upper Egypt. *Open Journal of Geology*, 7, 923-944.

<https://doi.org/10.4236/ojg.2017.77063>

Received: June 4, 2017

Accepted: July 11, 2017

Published: July 14, 2017

Copyright © 2017 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

During this study, the principal aim carried out was to obtain more information about technique and conservation conditions of the Egyptian wall paintings during the Roman period in the funerary house in necropolis of Tuna el-Gabal, El-Minia-Upper Egypt. It's going back to 2nd century AD and involves different sites of Ptolemaic and Roman chapels; some are in the immaculate established style while others are a blend of Pharaonic-Greek style and both are secured with mural painting. Deterioration problems observed on the wall paintings of the funerary house are, loss of plaster layers, disintegration of plaster layers, loss of paint layers (blistering and peeling), discoloration and severely damaged owing to a lot of deterioration factors as weakness of mud brick support, deterioration of surface treatments and to the widespread presence of different salts. The materials used in the painting, preparation layers and the state of conservation of the mural painting at funerary house were investigated by integrated physio-chemical measurements, particularly micro-Raman spectroscopy (μ Raman), light optical microscopy (LOM), scanning electron microscopy (SEM) coupled with an energy dispersive X-ray analysis system (EDX), X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR). In addition, the morphology of multilayer plaster from wall painting was investigated using atomic force microscopy (AFM). A wide color palette utilized as a part of the necropolis has been identified with mineral pigments and pigment mixtures. It is found that, the paints were based on an organic binder and traditional pigments (azurite, hematite, ochre, vegetable black) were used as colorants on plaster. The examination demonstrated that the preparatory layer is verging on made of pure lime while the plaster layer based mainly of lime and gypsum with variable amounts of quartz. The obtained results provided information about the painting technique, chemical

composition, crystal structure in addition to the stratigraphy of the paint layers and the state of preservation and on the causes of the painting deterioration. Furthermore, the obtained results can be used in the conservation and restoration interventions of these sites.

Keywords

Tuna El-Gebel, Roman Mortuary Houses, Pigments, Raman Microscopy, Atomic Force Microscope (AFM)

1. Introduction

The Ancient Egypt site of Tuna el-Gebel is outskirts of Amarna and the capital of the pharaoh Akhenaten is one of several necropolises of ancient Hermopolis (Modern Ashmunein); it situated about 300 km south of Cairo, in Middle Egypt on the western side of the Nile, west of the modern village of Deirut. It is the necropolis of Hermopolis Magna, ancient capital of the 15th Nome and cult centre of Thot, god of writing and sciences [1]. The ruins of Tuna el-Gebel are scattered over an area of about three kilometers. The tombs from the Tuna el-Gebel necropolis are generally dated to the first half of the 2nd century AD and were discovered in 1919 [2]. Most of tombs at necropolis were built of mud brick and only the doorjambs were of limestone. Very important mural paintings decorate the tombs and funerary house and the connected rooms of the tombs. The paintings inside the tombs comprise funeral scenes with ancient Egyptian gods, cartouches with hieroglyphic inscriptions, geometric and floral decorations and imitation of marble revetment (Figure 1(a), Figure 1(b)). The painting is executed in conventional Egyptian way and some of figures are rendered in the tradition and clothing normal for Greco-Roman.

Very few publications are available on materials and techniques used in Tuna El-Gebel necropolis to paint mural decorations and this lack of knowledge may affect the planning and execution of the conservation-restoration very much and

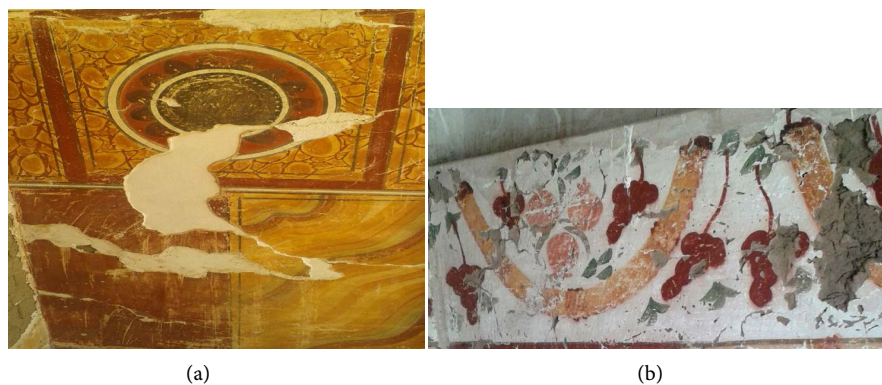


Figure 1. Shows mural paintings decoration at the tombs and funerary house at the necropolis of Tuna el-Gebel (a) geometric decorations and imitation of marble revetment; (b) floral decoration.

this is clear from the restoration work that has been done in the region, which led to a further deterioration of these murals. Although they have been recently restored, the paintings appear severely deteriorated. The murals in all the tombs at Tuna El-Gebel necropolis are in a critical state of conservation. It has been exposed to a wide variety of natural and human threats. These include moisture infiltration/condensation, salt deterioration, devastating fires, bat infestations, detrimental reuse and, in more recent times, the irreversible impact of misguided and piecemeal conservation interventions; these conditions have had a devastating effect. The tombs of the Tuna el-Gebel necropolis were built of mud brick. The predominant clay minerals are high-swelling montmorillonite, which is responsible for the destructive action in tombs affected by moisture. Catastrophic wall collapses have occurred, and the strength and cohesiveness of remaining painted plasters have been weakened (**Figure 2(a)**). Numerous areas demonstrate an extensive network of micro-cracks connected with a spread obscuring of the painted surface and separations were noticed (**Figure 2(b)**). The low part of the paintings was damaged and exacerbated by writings, incisions, the neglect of maintenance work and other vandalism actions, that have caused the total loss of significant parts of them. There is prevalent intra-layer delimitation, as well as significant detachment of these layers from the substrate. In addition, chromatic alteration is generally disseminated; basically, grayish in shading that could be credited to the statement of soot and other atmospheric and fire fine particulates (**Figure 3(a)**, **Figure 3(b)**). The result is a vulnerable, rapidly deteriorating surface that is difficult to read pictorially. The aim of this work was to characterize some of the painting materials used to decorate the walls of the necropolis of Tuna el-Gebel to obtain useful information about the painting technique and to offer scientific view for its conservation state with the final goal



Figure 2. The critical state of conservation of painted surface at the necropolis of Tuna el-Gebel: (a) fallen, losing and separation of painted layer; (b) extensive network of micro-cracks.



(a)



(b)

Figure 3. Vandalism actions at the murals in all the tombs at Tuna El-Gebel necropolis; (a) writings, incisions, the neglect of maintenance work; (b) fire fine particulates, darkening and chromatic alteration of the painted surface.

to set up a scientific conservation and guide for a conscious intervention on these paintings. For this purpose, different optical and analytical techniques were used.

2. Experimental

2.1. Sample and Sample Preparation

Sampling strategy is the first step in the analysis process. A representative sampling from Tuna El-Gebel tombs were performed in close collaboration with mural painting conservator-restorers after careful examination of the painted surfaces. Samples were collected from detached and fallen parts of the paintings, it was cared to collect samples as small as possible in size. Moreover, attention was given to locate and describe the painting techniques (stratigraphy, pigment). Appropriate representative visible different pigments (blue, green, yellow, red, dark red, brown, black and white) were collected and each of the samples was labeled. To identify the stratigraphic characterization of polychrome surfaces, polished cross-sections were carried out. Fragment samples were embedded in Epoxy resin and mounted on glass slides and the cross section is obtained by polishing the embedded sample with abrasive disks using silicon carbide card with successive grid from 120, 400, 800, to 1000.

Different series of laboratory tests were applied to samples to determine their basic characteristics.

2.2. Light Optical Microscopy (LOM)

Paint fragment and polished cross sections were examined using Leica DM 100 stereomicroscope under normal reflected light at 40× to 100× magnification. The photomicrographs recorded with a Leica EC3 12-megapixel digital camera.

2.3. Atomic Force Microscopy (AFM)

AFM has been applied to the examination of art and archaeological objects and gave a topographic map of the surface of an altered archaeological surface. The use of an atomic force microscope (AFM) for rapid assessment of the state of ground layer has been investigated and detail of surface topography for this sample was given. The study established an AFM imaging technique that produces data representative of weathering rates of ground layer under a range of weathering regimes of varying severity. The effect of scan size on the average roughness parameter was investigated. The AFM maps of the topography of a substrate by monitoring the interaction force between the sample and a sharp tip attached to the end of a cantilever so that the morphology of the surface of the studied sample can be reproduced at nanometer resolution [3]. The atomic force microscope (AFM) is designed to provide high-resolution (in the ideal case, atomic) topographical analysis, applicable to both conducting and non-conducting surfaces [4]. Atomic Force Microscopy (AFM) was developed by Binnig, G. *et al.* in 1988 [5] to measure forces as small as 10^{-18} N. Surface topography information was obtained by cutting a 12 mm diameter disk from the ground layer, and using Wet-SPM (Scanning Probe microscope) Shimadzu.

2.4. SEM-EDAX

Semi quantitative analyses of elemental composition were obtained using an EDX, X-ray energy dispersive spectrometer analyzer with at an acceleration voltage of 200 v - 30 keV.

2.5. X-Ray Diffraction

Mineralogical structure of support and plaster layers were determined by X-ray diffraction (XRD) analyses performed by PW 1840 diffractometer equipped with a conventional X-ray tube, CuK α radiation, 40 kV, 25 mA, point focus.

2.6. Micro-Raman Spectroscopy (μ Raman)

The collected paint samples have been examined with μ Raman spectroscopy, which is a versatile technique of analyzing both organic and inorganic materials that has experienced noticeable growth in the field of art and art conservation in parallel to the improvement of the instrumentation [6]. Raman spectroscopic studies of wall paintings and frescoes have addressed the composition of pigments and pigment mixtures, their interactions with their substrates [7]. Raman

spectroscopy is a spectral analysis of light scattered from a sample being bombarded by a monochromatic (LASER) light beam [8]. The use of Raman spectroscopy as a technique for the characterization of mineral pigments on historiated manuscripts and wall-paintings has been demonstrated for several scenarios [9]. Components of pigment samples have been probed using Raman microscopy. Micro-Raman spectra were recorded using a laser power at the sample of about 0.3 mW and objective lens of 50× magnification of an Olympus microscope. The Raman analyses have been carried out with a Senterra (Bruker) and a laser at 785 nm, at a power ranging from 5 - 25 mW according with the thermal stability of the compounds to be investigated and Charge Coupled Device (CCD) (−65°C) detector cooled by the Peltier effect at 200°K. A Jasco 2000 spectrometer combined with an Olympus microscope, cooled with liquid nitrogen has been also used with a laser at 1000 nm and a power range lower than 50 mW. The spectra have been generally recorded between 1200 and 150 cm^{-1} . The possible presence of organic substances has been studied at high wavenumbers, whereas the inorganic compounds, oxides and sulphides, have been investigated at lower wavenumbers. For each paint fragment or layer, an average of 30 particles has been analyzed, with a variable collection time according to the magnitude of the scattering signal. It was attached with Olympus U-TV1x-2 camera.

2.7. FTIR Spectroscopy (FTIR)

The binding media of the paint layers was identified by Fourier transform infrared spectroscopy (FTIR) using JASCO FTIR-460 spectrophotometers.

3. Results and Discussions

3.1. Painting Layer Structure

Observation of the prepared cross sections through an optical microscope shows that, there are two or three clearly differentiated layers: an internal layer or mural substrate, fine layer and a pictorial film. **Figures 4(a)-(d)** illustrates the pictorial strata of mural painting sample subjected for the study through an optical microscope following: (1) Mud brick support. (2) Inner (bottom) layer which was applied over the wall structure which is white in color, coarse in texture and was applied in varying thicknesses and in multiple layers to build up and level the mudbrick wall. In some tombs, this layer is reinforced with strips of chopped straw the strip length could be from 300 to 500 μm , according to the LOM investigation, the straw could be from Barley straw (**Figure 4(c)**). (3) A second white plaster (fine layer) was used as a finishing coat and provided the ground for the first mural scheme. It was characterized by surfaces with variable cavities and another sample reveals homogeneous surface composed of fine grains. In some areas, below the main paint layer, over painting technique was observed, the painters put the rough plaster at the mud brick tombs, paint layer with yellow pigment, plaster layer mixed with fine particles of yellow paint and the final is paint layer of the tomb (**Figure 4(d)**). (4) Paint layer.

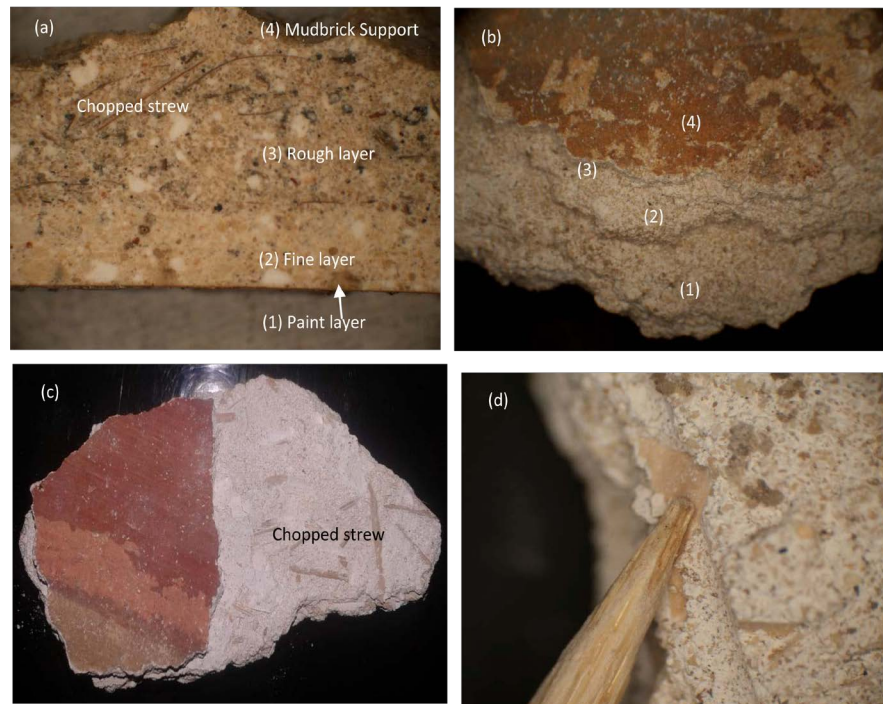


Figure 4. The layer distribution of mural painting at Tuna El-Gabel (a) cross-section images of the stratigraphy of mural painting; (b) the stratigraphy of mural painting under reflected light; (c) chopped straw mixed with rough layer; (d) over painting technique.

3.2. Painting Layer Morphology

The AFM maps the morphology of the surface of the plaster (**Figure 5**) indicated that the surface samples were very rough with the formation of an extensive array of bumpy features. Respectively, progressive pitting and surface damage of the samples suggested that the surface area was subjected to many deterioration aspects. In addition, etching was assumed to remove weak boundary layers from the surface. Because of etching, roughness of the surface increased. Rms roughness data, given as standard deviation over all height values within the surface area of interest, were determined from $1 \mu\text{m}^2$ AFM images. The rms values were given in the (**Figure 6**). The aggregates of rough plasters with particle size between 1033004-184746 NM composed the largest fraction of the total aggregates. Aggregates bigger than 476 nm and the smaller than 189 nm are composed the smallest fraction of the total aggregate). This shows that mostly fine aggregates between coarse (Greater than 1.03 mm.) and very fine (less than 0.18 mm) were used in the preparation of the rough plasters. The aggregates used in the bottom plasters are semi-circular in shape and they are mainly white and semi-opaque.

3.3. Composition of Painting Layer

XRD patterns of the rough plasters (**Figure 7**) indicated that, the main constituent is calcium carbonate calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and quartz (SiO_2). Calcite is originated from lime which could be interpreted as a lime based plaster mixed with little Gypsum, quartz from aggregates. Mineralogical compo-

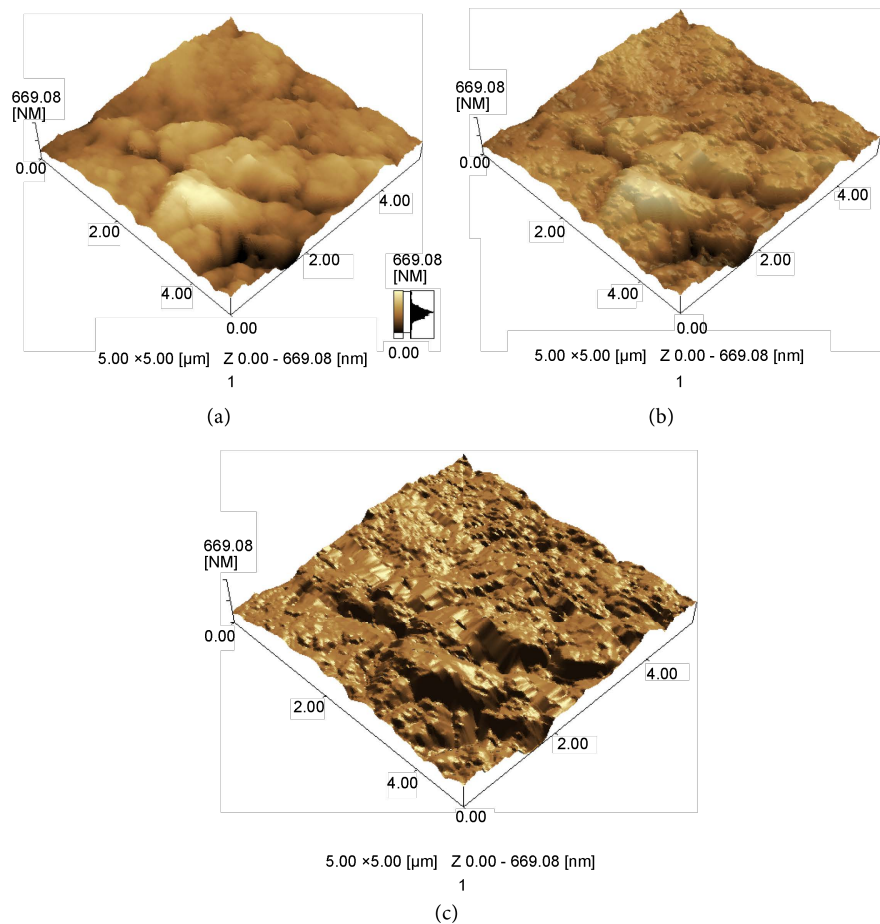


Figure 5. Topographic map of the surface of plaster samples obtained by AFM.

sitions of the fine plasters were mainly composed of calcium carbonate, gypsum and quartz.

SEM-EDS microscopies (**Figure 8**) show that the finishing plaster below the painting layers consisted of high amounts of Ca, S, Si (50.81, 24.92, 16.32) and a small amount of Al, Fe, Ti, Sr (**Figure 8**). Considering these results, it can be claimed that plaster samples were prepared by using lime and gypsum as binder and quartz as aggregates.

3.4. Paint Layer

Inorganic pigments have been identified on different painting layers. **Figure 9** shows optical microscope images of the paint samples under the reflected light. The Identification of the samples was examined using μ Raman spectroscopy and SEM-EDX analysis; **Table 1** provides a summary of the EDX results.

3.4.1. Blue Pigment

The stereomicroscope examination shows variety in color ranging from deep and light crystals spread within a transparent matrix and rich in detachment part, white stains and sand grains (**Figure 9(a)**). μ Raman spectra (**Figure 10**) show the characteristic bands of Egyptian blue (calcium copper (II) silicate

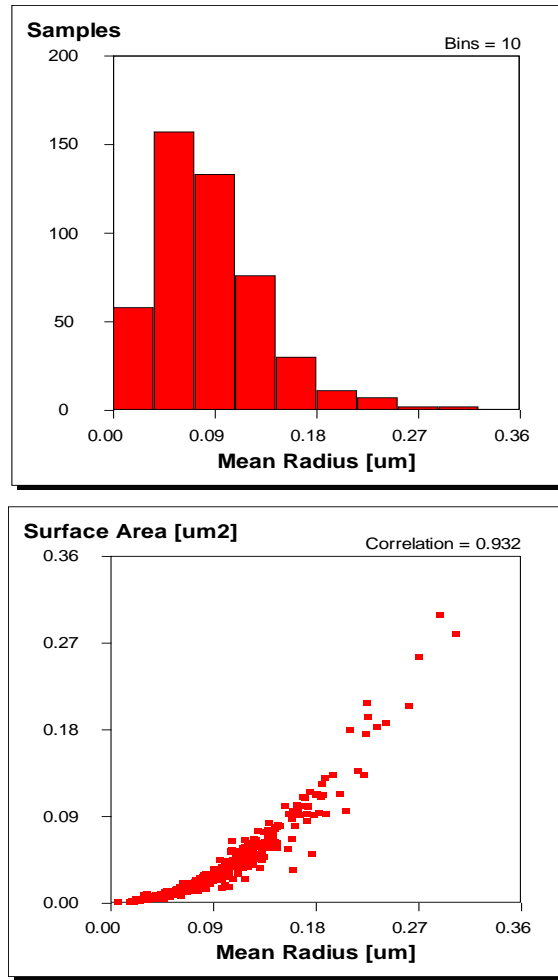


Figure 6. RMS surface roughness of the plaster sample.

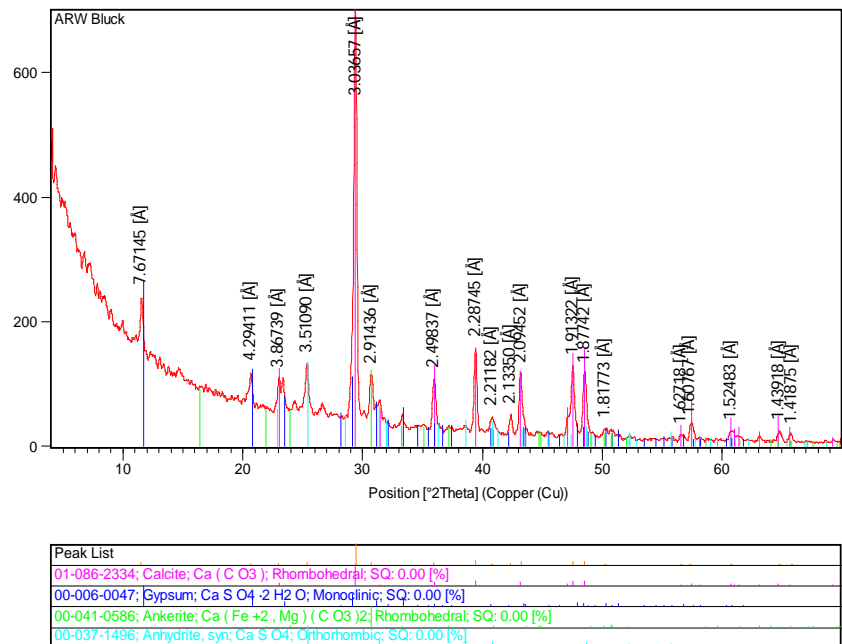


Figure 7. XRD pattern of plaster sample.

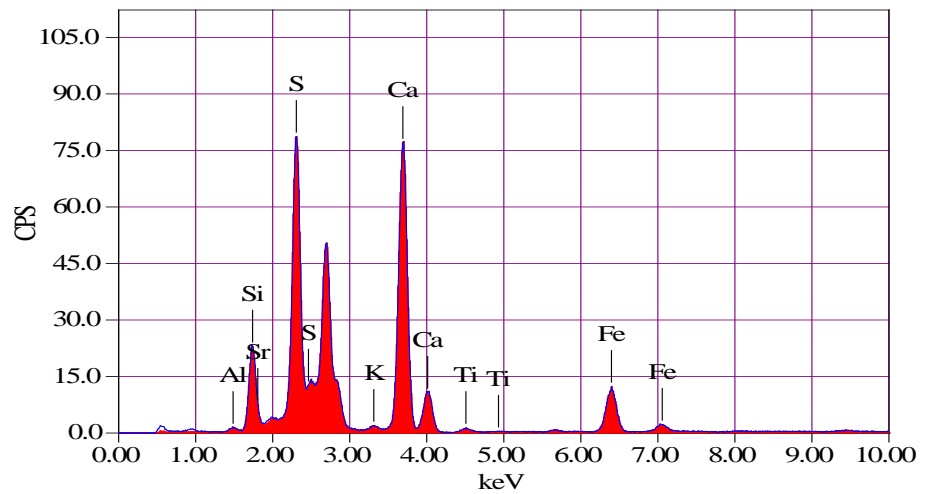


Figure 8. EDX spectrum of plaster sample.

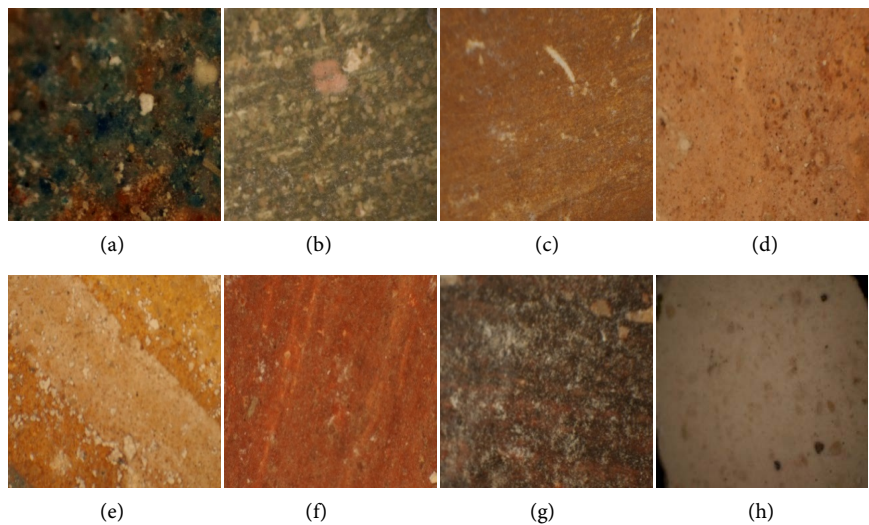


Figure 9. The paint fragments; (a) the blue paint sampled; (b) the green paint sample; (c) the dark yellow paint sample; (d) the light-yellow paint sample; (e) the dark and light-yellow paint sample; (f) the red paint sample; (g) the dark red paint sample; (h) the white paint sample.

Table 1. Elemental analysis of mural painting component from Tuna El-Gabel necropolis.

Sample no/ Element	External Plaster	Blue pigment	Green pigment	Red pigment	Brown pigment	Yellow pigment	White pigment
Al	1.9445	0.8145	2.6415	2.1353	1.0566	0.8682	1.2252
Si	16.3271	10.1555	13.0691	5.2527	3.8304	2.8297	3.6231
S	24.9210	16.1253	12.5365	15.2562	10.826	14.950	3.2200
K	1.3070	0.9283	2.1105	0.9335	0.8068	1.0399	2.3556
Ca	55.6136	66.3276	61.0324	59.5621	73.832	68.804	87.2514
Fe	5.7565	3.8567	11.8389	18.5550	9.6477	11.5073	1.4289
Ti	0.8578	-	0.7935	-	-	-	0.7856
Ce	-	-	-	-	-	-	-
Cu	-	1.7921	0.2004	-	-	-	-

CaO·CuO·4SiO₂). Egyptian blue is identifiable through the characteristic bands at 1022, 965, 563, 538, 510, 497, 412, 328, 361, 241 cm⁻¹. The band at 1086 cm⁻¹ (symmetric stretching, ν₁), is attributed to calcite (CaCO₃). Few spectra at 200 and 400 cm⁻¹ are probably due to the presence of quartz and amorphous silica. The SEM-EDS microscopies of the blue pigment (**Figure 11**), shows that the peaks of Si (54.25%), Ca (22.04%) and Cu (14.54%) are present, and their atomic percentage ratios agree with the formula of cuprorivaite.

EDX pattern of pigment Various analyses suggest that, Egyptian blue was manufactured by heating together silica sand (SiO₂), copper alloy filings or ores (copper compound malachite (Cu₂[(OH)₂, CO₃,]) or azurite (Cu₃[(OH)/CO₃]₂), calcite (CaCO₃) and potash or natron, and was commonly found in artefacts from the 4th Dynasty onwards Lucas A. 1962 [10]. Its earliest recorded use was in the IV Dynasty (2613-2494 BC) and its use lasted throughout the dynastic period and continued into the Roman period [11].

3.4.2. Green Pigment

Under stereomicroscope, the green paint area shows various shades with yellow-orange and blue particles scattered in the matrix. The green particles are pale and some are faded green, combined with the detachment of pigment particles in some areas. The Raman spectrum of the green pigment (**Figure 12**) represent a typical peak of cuprorivaite at 1092, 1040, 501, 433 cm⁻¹, Moreover, the strong band at 632 cm⁻¹ and 240, 550 cm⁻¹ indicates a well-crystallized Goethite.

EDX analysis (**Figure 13**) revealed the presence of iron (Fe), copper (Cu), Silicon (Si) and calcium (Ca), these means, the painter carried out the green pigments by mixed of Egyptian blue and yellow ochre.

Green was obtained from powdered malachite or from an artificial green frit. In some instances, the green color was acquired by mixing Egyptian blue with

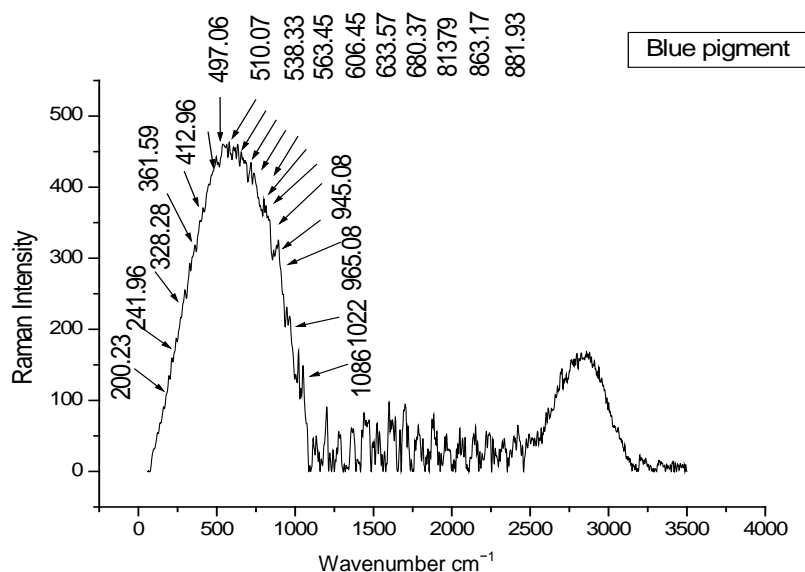


Figure 10. μ Raman spectrum of blue pigment with Raman bands at 1022, 965, 563, 538, 510, 497, 328, 361, 241 cm⁻¹; this confirms that the blue color is due to cuprorivaite.

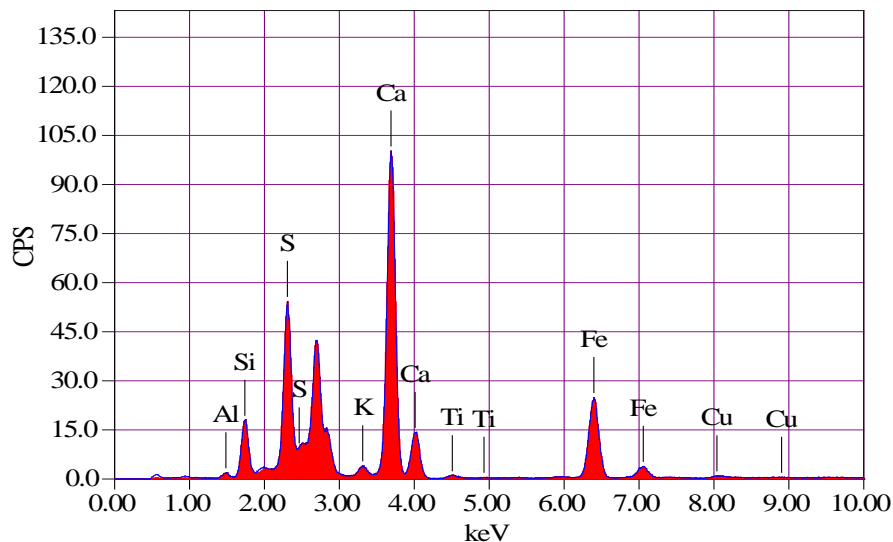


Figure 11. EDX pattern of blue pigment.

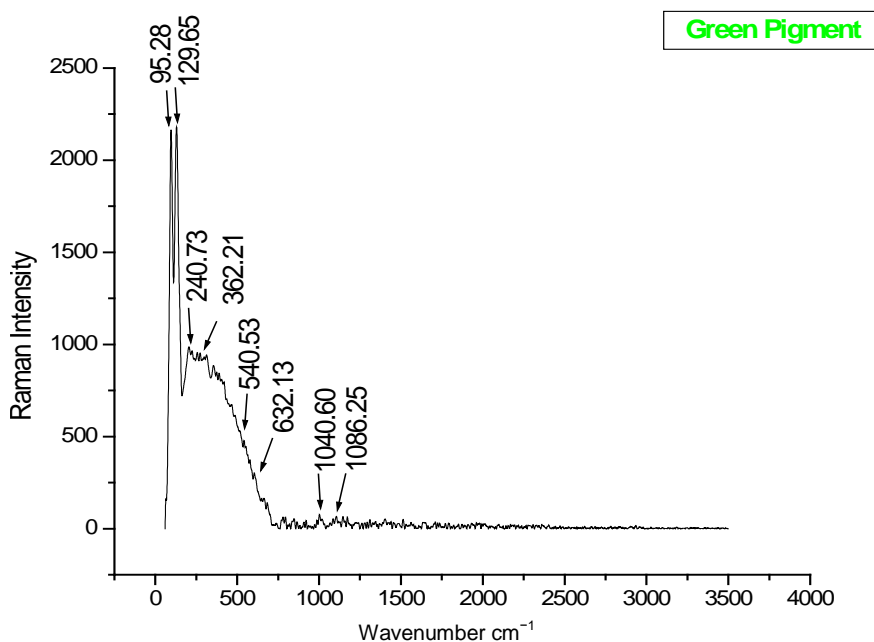


Figure 12. μRaman spectrum of green pigment showing cuprorivaite and goethite in combination.

yellow ochre. Such a technique of obtaining green, which appeared sporadically during the XIIth Dynasty (1991-1786 BC) became much more widespread during the Amarna period (1370-1352 BC) [12]. Howell G. 2004 mentioned that, one of the green pigments specimen from Greco-Roman double coffins formed from an admixture of yellow and blue pigments [13].

3.4.3. Yellow Pigment

On careful observation under the stereomicroscope, the yellow pictorial layer appeared to have different shades of yellow that can be described qualitatively as bright-yellow, orange-yellow and brownish-yellow and showed small and

rounded grains of the pigment and the hue is affected by impurities found in the layer. EDX analysis of the sample (Figure 14) analyzed from the yellow paint layer indicated that iron (Fe) was abundant element, with some traces of Al, Si and K. Yellow as a token of the Sun and as the color of happiness and prosperity yellow was an important color [12].

The Raman spectra of the yellow pigment indicates that it is like the ancient yellow ocher, yellow ochre is identifiable through the characteristic bands at 1406, 1278, 1200,1086, 1007, 635, 415, 278, 222 (Figure 15).

The only yellow pigment available in ancient and prehistoric art was yellow ochre (hydrated oxide of iron, $Fe_2O_3 \cdot H_2O$) which was not totally satisfactory in view of its pale hue [14].

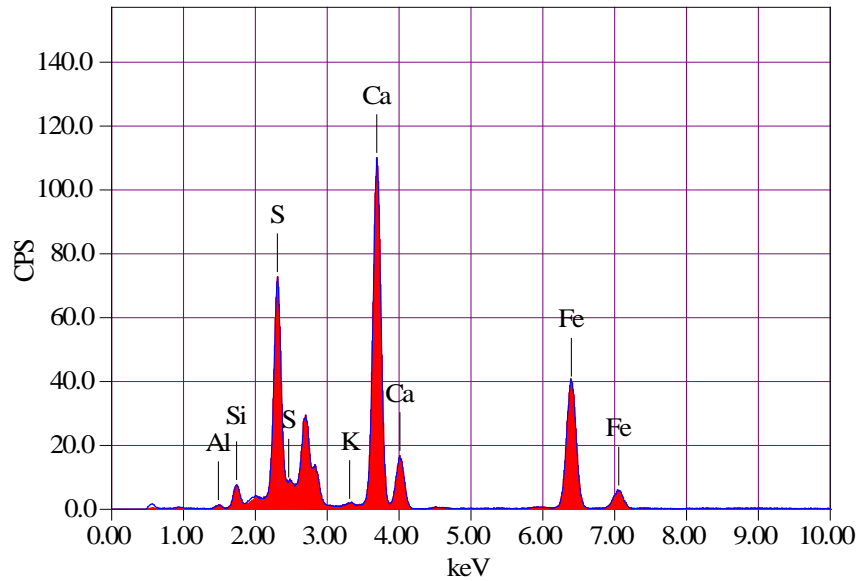


Figure 13. EDX pattern of green pigment.

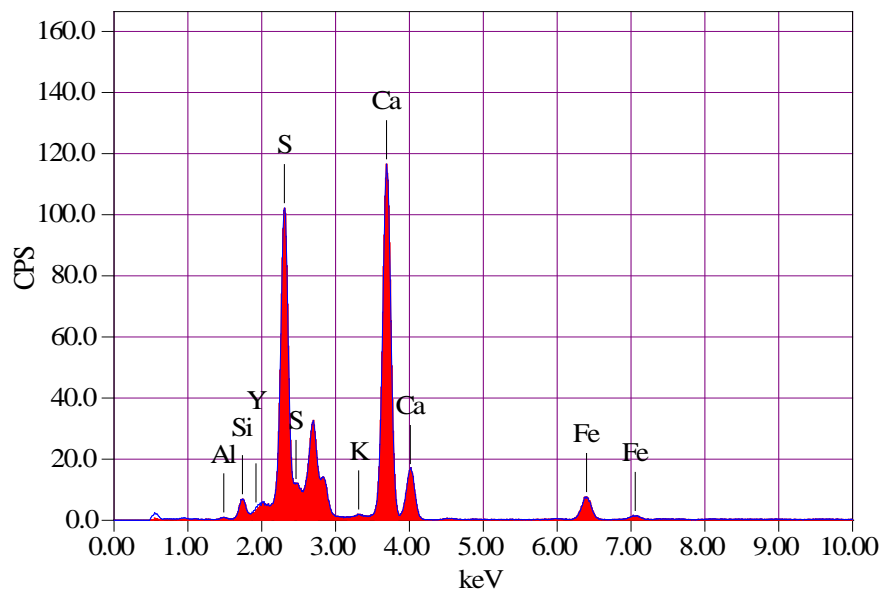


Figure 14. EDX pattern of yellow pigment.

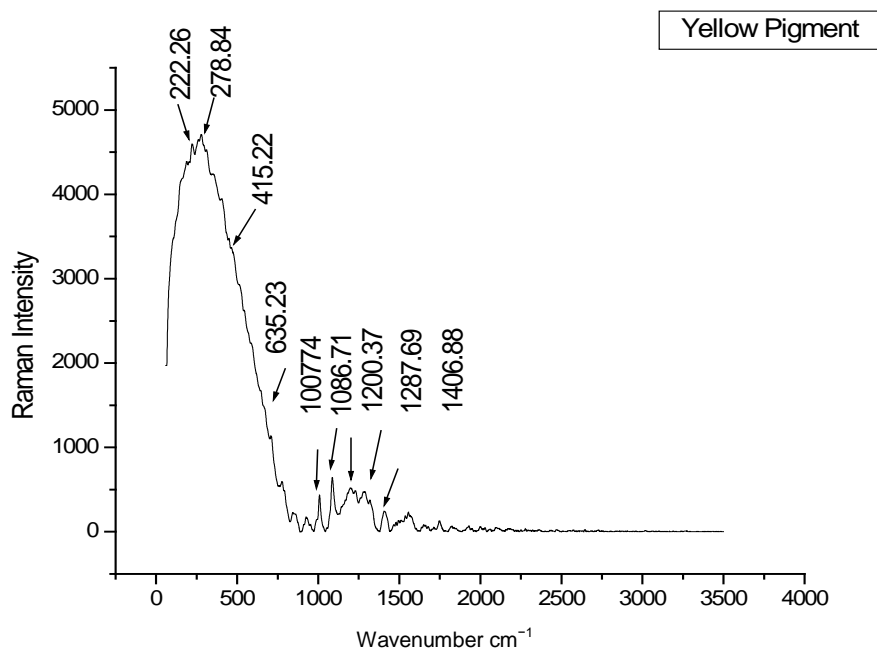


Figure 15. μ Raman spectrum of yellow pigment identifies yellow ochre with Raman band at 635, 220, 286 cm^{-1} .

3.4.4. Red and Brown Pigments

Field observation and stereomicroscope indicated three color grades of red color in Tuna El-Gabel necropolis; red, brown, dark red (Nbiti). XRD analysis indicated that, iron is responsible of all degrees. Iron (III) oxide, hematite, occurs in almost all red pigments studied here, often in admixture with calcite and carbon to give lighter and darker colors. The hematite is not found as a pure mineral pigment in red samples but occurs in admixture with clays and sand to give red ochre. Spectroscopically, it is possible to detect the presence of red ochre through the increased bandwidths of the hematite bands (224.86, 293.24, 411.16, 614.21 cm^{-1}) (Figure 16, Figure 17) caused by the interactions of the mineral with the aluminosilicate clay matrix.

EDX analysis of red pigment (Figure 18) shows that the peaks of (Fe, Si, Al, and K) are present, the presence of quartz from Fine River sand which was sometimes added to assist in the preparation and grinding of the pigment mixture.

3.4.5. Dark Red Pigment

The field observation indicated that the dark red color provides a decorative transition from the dark yellow to the brown-black and then to the light-yellow background. Under the stereomicroscope the sample illustrated very dark particles tend to red and black particles. EDX analysis reveals that, the sample was composed of Fe and C (Figure 19).

The dominant Raman band on this pigment remains at (224, 291 cm^{-1}) typical peaks of hematite. The Raman spectrum recorded on black grains in the brown paint layer shows bands at (1376.22, 1011.52 cm^{-1}) (Figure 20).

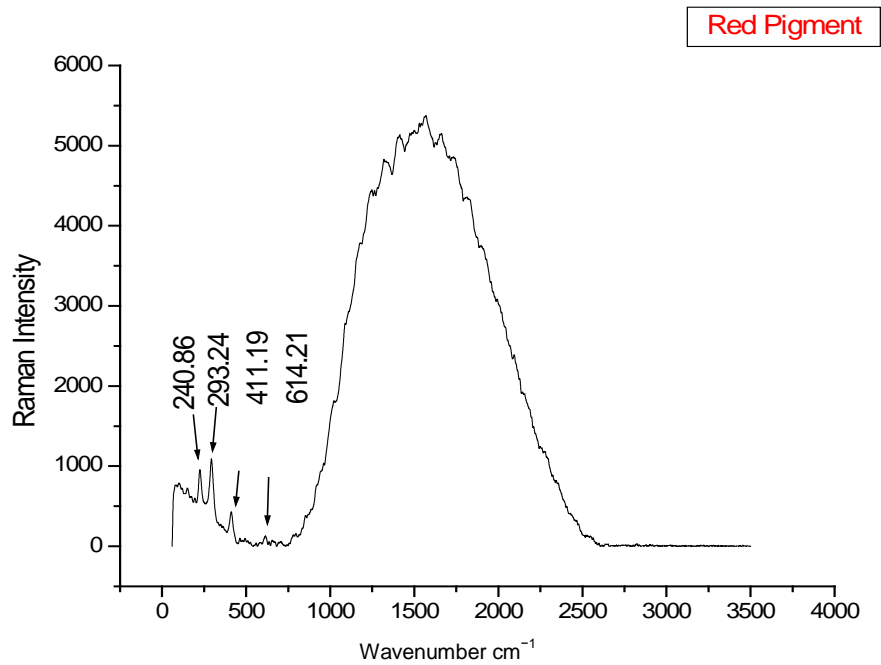


Figure 16. μ Raman spectrum of red ochre pigment diluted with calcite to produce a light red showing signatures of red ochre with Raman band at 645, 411, 220 cm^{-1} .

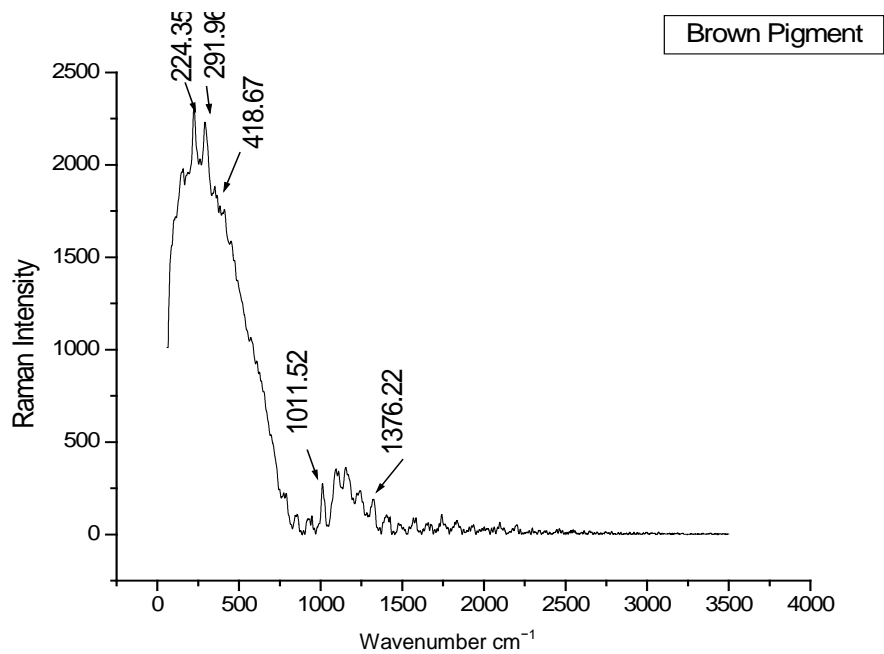


Figure 17. μ Raman spectrum of brown pigment identifies red ochre. Calcite (weak), μ Raman spectrum of carbon particles in admixture with red ochre to produce a dark red (nbiti) pigment.

3.4.6. White Pigment

Optical microscopic investigation shows the white paint layer is slightly thick with different chromatic hues range from red to yellow, rich in voids and covered with dust. EDX analysis (**Figure 21**) confirmed the presence of elemental

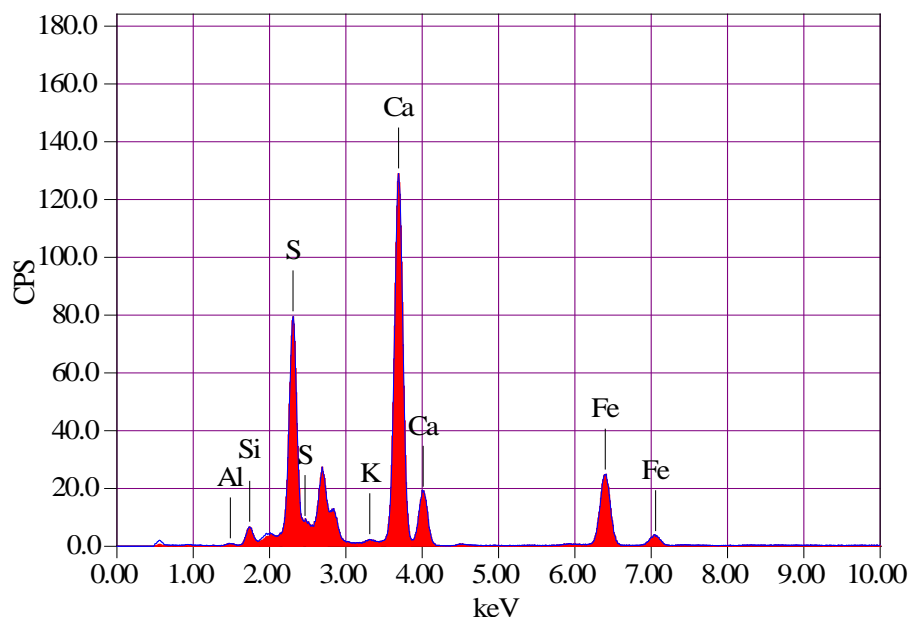


Figure 18. EDX pattern of red pigment.

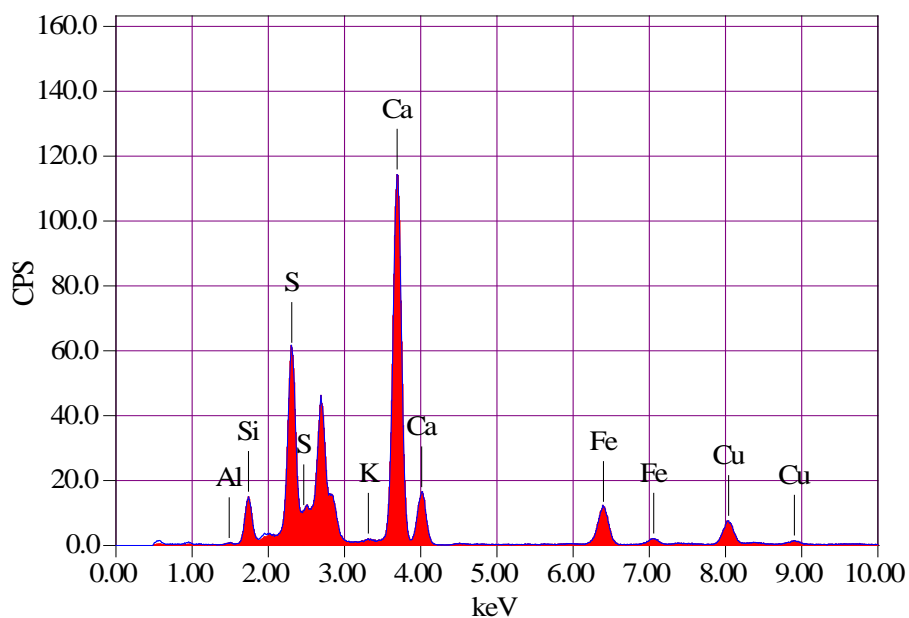


Figure 19. EDX pattern of dark red pigment (nibiti).

calcium (Ca, S), this indicate that the material used to create the white pigment was lime which like the painting layer. μ Raman spectra (**Figure 22**) indicate the presence of calcite bands at (1085.19, 515.07, 279.86, 153, 89 cm^{-1}).

All outcomes acquired from analyzed of mural painting specimens from Tuna El-Gabel are listed in **Table 2**.

3.5. Composition of the Binder

In the FTIR spectrum (**Figure 23**) of the organic binder, a typical stretching of alcohols bands is present in the OH stretching bands at 3403 cm^{-1} , the alcohols

Table 2. Summary of the outcomes acquired from mural painting specimens from Tuna El-Gabel

Sample	Colour	Optical observation	SEM-EDX	μ -Raman	FTIR
Inner Painting layer	White	- Course in texture, varying thicknesses and in multiple layers.	Ca, S, Si, Al, Fe, Ti, Sr.	Calcite Gypsum	Calcite Gypsum
		- particle size between 1,033,004 - 184,746 nm			
Preparation layer	White	- reinforced with strips of chopped straw	Ca, S, Si, Fe, Al	Calcite Gypsum	Calcite Gypsum
		Characterized by surfaces with variable cavities, homogeneous surface and composed of fine grains.			
Pigment	Blue	Light blue crystals spread within a transparent matrix and rich in detachment part.	Ca, Si, Cu, S, Al, K, Fe	Cuprorivaite	
Pigment	Green	- Various shades with yellow-orange particles scattered in the matrix.	Ca, Si, Cu, Fe, Al, K	Cuprorivaite Yellow ochre	
		- The green particles are pale, rounded and translucent with some exhibiting of grainy texture			
Pigment	Yellow	- The surface is bright-yellow to orange-yellow and brownish-yellow	Ca, S, Si, Fe, Al, K	Yellow ochre Calcite	Red ochre Calcite Gypsum
		- Small and rounded grains of the pigment and the hue is affected by impurities found in the layer.			
Pigment	Red	Reddish color tends to yellow and fall of voids	Ca, S, Si, Fe, Al, K	Red ochre Calcite	Red ochre Quartz
Pigment	Brown	Deep brown to reddish with black particles in the layer.	Ca, S, Si, Fe, Al, C	Red ochre carbon	Red ochre Calcite
Pigment	Dark red	Deep brown to reddish with black particles in the layer.	Ca, S, Si, Fe, Al, C	Red ochre carbon	Red ochre Calcite
Pigment	White	Slightly thick with different chromatic hues range from red to yellow, rich in voids and covered with dust.	Ca, S, Si, Fe, Ti, Sr, K	Calcite Gypsum	Calcite Gypsum

OH bending at 1142 cm^{-1} , C-H stretching bands at 2873 cm^{-1} , the double bond (C=C) and carbonyl (C=O) group at 1620 cm^{-1} and 1034 cm^{-1} respectively. The infrared spectra of the six samples are very similar. The comparison of the FTIR charts proved that the archeological samples were like Arabic Gum as a coloring medium used in the pigment samples in Tuna El-Gabel mural painting. In all analyzed samples.

Inorganic materials were indicated by the presence of a secondary absorption

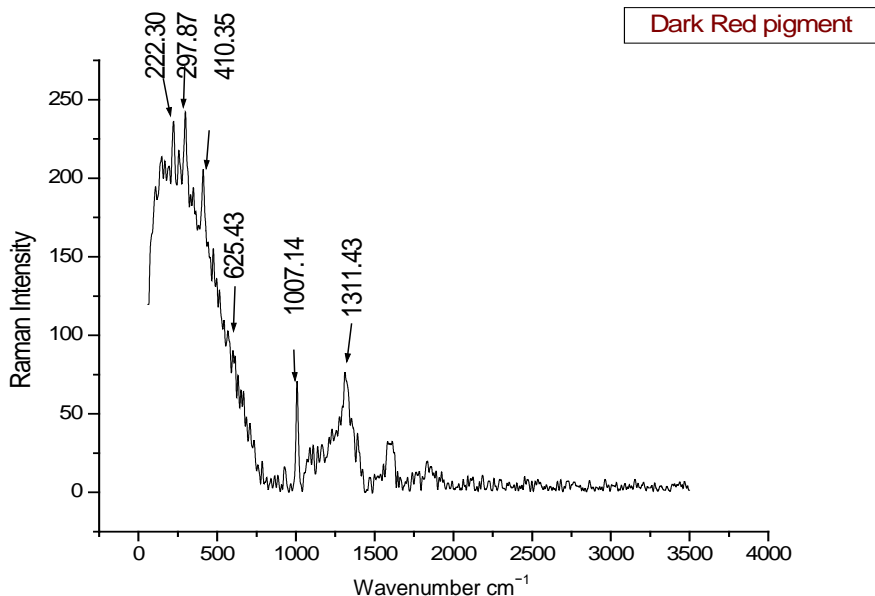


Figure 20. μ Raman spectrum of black grain in red pigment identifies carbon at wave-number range, 1311, 1007 cm^{-1} .

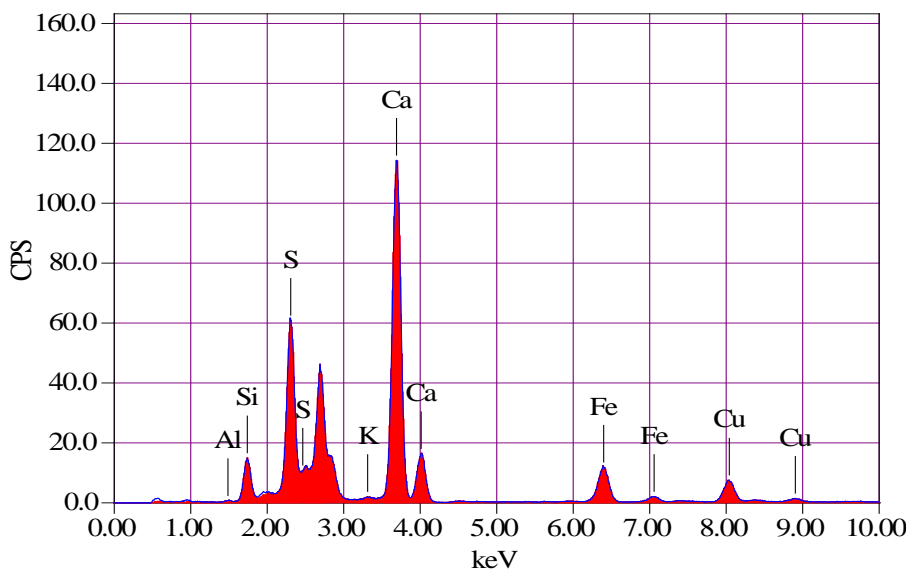


Figure 21. EDX pattern of white pigment.

band of the CO_3^{2-} group of calcium carbonate in the region 1430, 873, 694 cm^{-1} assignable to CO_3^{2-} and sulphate (SO_4^{2-}) at 1143 cm^{-1} was indicated (Table 3).

4. Conclusions

This study was carried out the end goal to frame a database of the application technique and material properties of the mural painting of Tuna El-Gabel necropolis with the motivation behind preservation.

The field observation and lab analysis indicated that, the mural painting in Tuna El-Gabel necropolis was consented in Roman Period and executed by

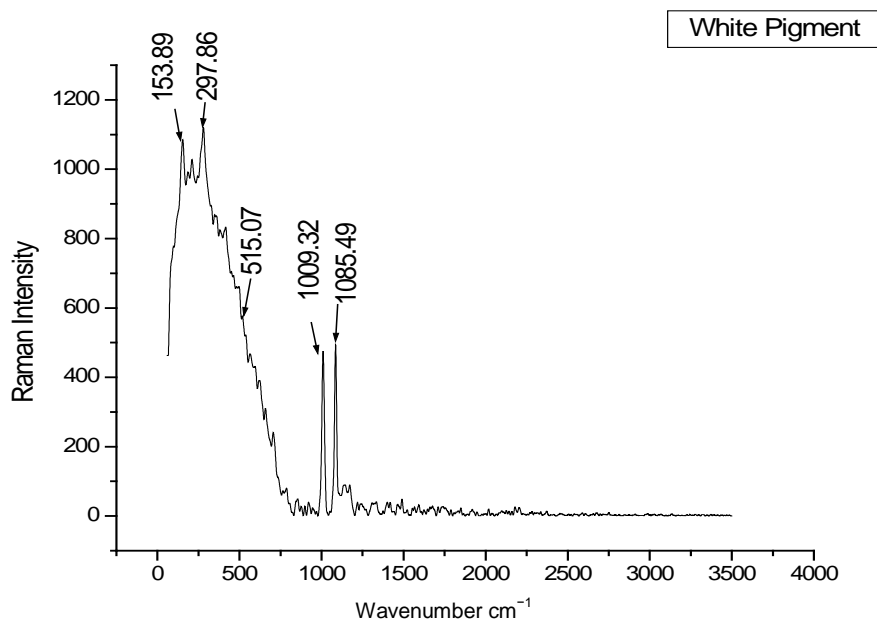


Figure 22. μ Raman spectrum of white pigment identifies calcite with Raman band at 1085, 515, 279, 153 cm^{-1} .

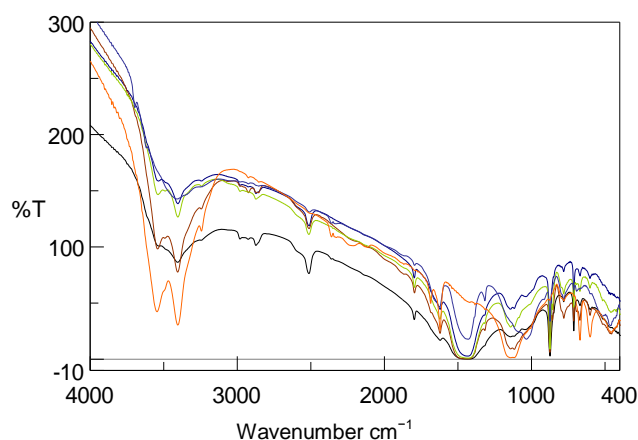


Figure 23. FTIR patterns shows comparison between the paint layer from Tuna El-Gabel with the control samples of Arabic gum.

tempera technique over lime plaster.

Most of tombs at necropolis were built of mud brick and only the doorjambs were built of limestone and the walls were plastered with mud mortar tempered with chaff, and given a coat of lime-and-sand plaster which acted as ground for the painted decoration.

The different techniques of examination and analysis provided us with information about the identification of the mural painting layers at Tuna El-Gabel necropolis as follows:

There are two or three clearly differentiated layers of the mural painting at the necropolis.

Coarse plaster layers have a denser coat than fine layer and applied in varying thicknesses in multiple layers to build up and level the brick wall. It composed of

Table 3. FTIR results of binding medium paint layer in Isis temple.

							Characteristic IR Absorption Bands
Blue P.	Green p.	Red P.	Brown P.	Dark red P.	Yellow P.	White P.	
3403.74	3413.39	3545.49	3403.74	3541.64	3402.78	3545.49	O-H Stretching band 3600 - 3200 cm
2512.79	-	-	2873.42	2854.13	2873.43	-	C-H Stretching bands 3000 - 2800 cm
1622.8	1624.73	1620.88	-	1621.84	1620.88	1620.88	O-H Bending band 1650 cm
1432.85	1430.92	-	1432.85	1445.39	1431.89	-	C-H Bending band 1 480 - 1300 cm
1142.39	1301.17	1142.62	1143.52	1116.58	1144.55	1142.62	C-O Stretching band 1300 - 900
874.56	873.59	779.10	873.59	874.56	874.56	779.10	O-C-O bending band of carbonate group of calcite. 900 - 650 cm
670.14	694.24	670.14	670.14	671.10	670.14	670.14	SO ₄ ²⁻ bending band of gypsum. 700 - 600 cm

lime, Gypsum, aggregate and straw for reinforcement.

Fine plaster layer contains high amount of lime and more little sand and doesn't contain strew.

Arabic Gum was used as a binder in the preparation paint layer in mural painting.

Many pigments were used and executed in tempera technique on dry surface rendering. For the pigments components, μ Raman spectrum and EDX data showed that different pigments had been employed:

- White pigment sample consists of a mixture of calcite CaCO_3 and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
- Black pigment contains carbon C.
- Blue pigment consists of Egyptian blue $\text{CaCuSi}_4\text{O}_{10}$.
- Green pigment is mixing of cuprorivaite and Goethite FeOOH .
- Red and brown pigments contain hematite Fe_2O_3 .
- Dark red pigment consists of hematite and traces of carbon.
- Yellow pigment is yellow ochre.
- All pigments were mixed with Arabic gum as binder.

The field and lab investigation indicated that, the mural paintings in Tuna El-Gabel necropolis is suffering from a lot of deterioration aspects. The serious deterioration phenomenon of the tomb is a clear detachment between the rough layer and the mudbrick wall and a lot of wall paintings were completely losing due to the loss of adhesion between the mudbrick support and the plaster. The problem is more complicated by the existence of salts. Deterioration observed on the mural painting were formed by the thermal alteration in the building.

Detaching layers of the paintings must be consolidated with appropriate materials and methods after carrying out experimental studies (modified lime base

mortar is recommended).

Restoration of the paintings must be performed after the consolidation of the building. Paintings must be covered with suitable methods in order to avoid any damage that can occur during the restoration of the building.

The restoration should be followed by a long-term conservation plan according to scientific and analytical study.

Acknowledgements

The authors would like to thank Prof. Hussien M. Aly, Minia University for his helping in preparing samples.

References

- [1] Fassbindera, J. W.E., Kühneb L. and Flossmann-Schützec M. (2015) The Helenistic Settlement of Tuna el-Gebel, Egypt. Institute of Archaeology and Ethnology Polish Academy of Sciences, *Archaeologia Polona*, Vol. 53, 276-280.
- [2] Lefebvre, G. (1923) *Le tombeau de Petosiris*. 3 vols, Le Caire.
- [3] Domenech, A., Teresa, C.M. and Costa, T. (2009) Electrochemical Methods in Archaeometry, Conservation and Restoration. In: XIV, Springer-Verlag Berlin Heidelberg, 1-32. <http://www.springer.com/in/book/9783540928676>
- [4] Ralston, J., Larson, I., Mark, W. and Feiler, A. (2005) Atomic Force Microscopy and Direct Surface Force Measurements. *Pure and Applied Chemistry*, **77**, 2149-2170. <https://pdfs.semanticscholar.org/7696/6398c77d59a98e8e7d02c253462754820a6b.pdf>
- [5] Binning, G., Quate, C.F. and Gerber, C. (1988) Atomic Force Microscope. *Physical Review Letters*, **56**, 930-933. <https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.56.930>
- [6] Edwards, H.G.M., Beale, E., Garrington, N.C. and Alia, J.M. (2006) FT-Raman Spectroscopy of Pigments on a Hindu Statue, Kali Walking on Siva. *Journal of Raman Spectroscopy*, **38**, 316-322. <http://onlinelibrary.wiley.com/doi/10.1002/jrs.1645/epdf>
- [7] Howell, G., Edwards, M., Wolstenholme, R., David, S., Brooke, C. and Pepper, M. (2007) Raman Spectroscopic Analysis of the Enigmatic Comper Pigments. *Analytical and Bioanalytical Chemistry*, **387**, 2255-2262. <https://link.springer.com/content/pdf/10.1007%2Fs00216-006-1113-y.pdf>
- [8] Hayez, V. (2002) Study of the Composition of the Pigments Used in the Christ "Maestas Domini" Painting of the Ename Church by Means of Micro Raman Spectroscopy. *The Art 2002: 7th International Conference on Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, Antwerp, 2-6 June 2002.
- [9] Edwards, H.G.M., Farwell, D.W., Newton, E.M., Rull Perez, F. and Jorge Villar, S. (2000) Raman Spectroscopic Studies of a 13th Century Polychrome Statue: Identification of a "Forgotten" Pigment. *Journal of Raman Spectroscopy*, **31**, 407-413. [http://onlinelibrary.wiley.com/doi/10.1002/1097-4555\(200005\)31:5%3C407::AID-JR5530%3E3.0.CO;2-Y/pdf](http://onlinelibrary.wiley.com/doi/10.1002/1097-4555(200005)31:5%3C407::AID-JR5530%3E3.0.CO;2-Y/pdf)
- [10] Lucas, A. (1962) *Ancient Egyptian Materials and Industries*. 4th Edition, rev. Harris JR. Arnold, London, p. 150.
- [11] Wledemann, H.G. (1982) Bayer. *Analytical Chemistry*, **54**, p. 619.
- [12] Ragai, J. (1986) Colour: Its Significance and Production in Ancient Egypt. *Endeavor, New Series*, **10**, 74-79.

<http://www.sciencedirect.com/science/article/pii/S016932786901341>

- [13] Edwards, H.G.M., Jorge Villar, S.E. and Eremin, K.A. (2004) Raman Spectroscopic Analysis of Pigments from Dynastic Egyptian Funerary Artefacts. *Journal of Raman Spectroscopy*, **35**, 786-795. <http://onlinelibrary.wiley.com/doi/10.1002/jrs.1193/epdf>
- [14] Lee, L. (2000) Quirke. In: Nicholson, P.T. and Shaw, I., Eds., *Ancient Egyptian Materials and Technology*, Cambridge University Press, Cambridge, 104-110. <http://assets.cambridge.org/052145/2570/sample/0521452570WSC00.pdf>



Scientific Research Publishing

Submit or recommend next manuscript to SCIRP and we will provide best service for you:

Accepting pre-submission inquiries through Email, Facebook, LinkedIn, Twitter, etc.

A wide selection of journals (inclusive of 9 subjects, more than 200 journals)

Providing 24-hour high-quality service

User-friendly online submission system

Fair and swift peer-review system

Efficient typesetting and proofreading procedure

Display of the result of downloads and visits, as well as the number of cited articles

Maximum dissemination of your research work

Submit your manuscript at: <http://papersubmission.scirp.org/>

Or contact ojg@scirp.org

