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## IDENTIFICATION OF THE BYZANTINE ENCAUSTIC MURAL PAINTING IN EGYPT

Basem Gehad\*<sup>1</sup>, Mona Foad Aly<sup>2</sup> and Hussein Marey<sup>2</sup>

<sup>1</sup>*The Grand Egyptian Museum, Conservation Center, Cairo, Egypt*

<sup>2,3</sup>*Faculty of Archeology, Conservation Center, Cairo University, Egypt*

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Corresponding author: Basem Gehad ([basengehad2013@gmail.com](mailto:basengehad2013@gmail.com))

### ABSTRACT

Encaustic painting uncovered in the hermitage of *Apa Apollo* at *Baouit- Assuit*, was studied by means of spectroscopic, chromatography as well as elemental x- ray fluorescence, the analysis revealed unique information's about the composition of the organic binding medium, as well as its deformation and alteration pattern. The elemental analysis highlights also the types of pigments used in the artistic palette used by the painter in order to execute his paintings.

Beeswax was proved to be used, from bees which feed on sunflower, lead was the major component of the orange pigment indicating the usage of minium, arsenic sulphide mixed with hematite was used for the brownish red color, a copper based blue pigment, probably the Egyptian blue as well as the green earth mixed with Attachmate was also used for green colors.

The results of the study gives a new information's about a unique paintings executed with a rare technique, in Egypt.

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**KEYWORDS:** Encaustic, Monastery, Mural Painting, Byzantine, Assuit, Beeswax, FTIR, GC-MS.

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## 1. INTRODUCTION

It is unknown exactly when and where wax was first used as painting medium, but recent studies highlight a lot of different examples around the Mediterranean basin, and it is assumed that the encaustic paintings started as a pure Greek painting tradition.

The Roman writer Pliny the Elder (1st century AD) states that from the oldest Greek masters –such as Polygnotus– onward, encaustic was a common painting technique in ancient Greece and Rome. This text appears in chapters "on the artists who painted with encaustic by means of palette knife or brush" –as stated in the treatise's index, which is in fact a history of ancient Greek and Roman painting (Rackman, 1952). Unfortunately most of the mural paintings painted in wax in Egypt cannot now be located, only few of them were uncovered in Baouit – Assuit as well as the wadi el Natron. The problem is exacerbated by the lack of published scientific reports for this kind of paintings. On the other hand, another source of encaustic paintings should be considered, as it forms a part of the development of encaustic painting technology in Egypt, which is the mummy portraits or the so-called the fayoum portrait. Studies of these encaustic objects inform us about the technology of encaustic painting in Egypt from the beginning of the 1st century C.E to the end of the 3rd century C.E .

In 1991 the Institut Français d'Archéologie Orientale (IFAO) uncovered a hitherto unknown painting of the annunciation in the western semi dome of the church of the holy virgin in Dier el Surian (Innemeé , 1999). During a continuation of the work in 1995 different painting stratifications were identified; the four layers identified are from different phases of the church.

Another encaustic mural painting was identified in one of the monks' houses at *baouit*. The town of *Bawit* (or *Baouit* in French) is located between *Dayrut* and *Asyut*, 1.25 miles (2km) west of the village of *Bawit* and about 17 miles (28 Km) south of *El Ashmunin*.

The site is famous from the excavations carried out there at the beginning of the twentieth century. The monastery excavated at Baouit was dedicated to saint Apollo and called *Apa Apollo*. Not more than 10 percent of the site

was excavated. The monastery was founded at the end of the fourth century, and the excavation showed that it had become prosperous by the sixth century. The monastery was destroyed by the twelfth century.

In 2005-2006 the IFAO mission uncovered a unique encaustic painting inside the walls of the monks' houses in the northern part of the hermitage of the *Apa Apollo* at *Baouit* (Benazeth, 2010 ) (Fig.1)



Figure 1 Encaustic mural painting on the northern wall, building no.1 , Baouit.

A complete painted room known as sale 7 was uncovered in 4 seasons of excavation and given conservation treatment. Unfortunately the paintings were destroyed in 2010, The detachment and rescue operation was performed by Christophe Guilbaud, Bruno Szkotnicki, Abied Mahmoud and Basem Gehad in April 2010, due to the collapsing of the mud brick walls of the house; now they are detached and kept in trays in the store rooms.

The paintings were uncovered in a construction used as housing, nominated as Building 1, excavated by Marie-Hélène Rutschowskaya and Ramez W. Boutros, consisted of several rooms set around a courtyard. The most southerly of these rooms controlled access to the building, with a door opening to the outside and another opening onto the courtyard. On the north side, two rooms were separated by a corridor that led to a kitchen. On the east side stood an ensemble of five vaulted halls. The walls and the vault of the biggest of these (Hall 7) were decorated with mural paintings (Fig.2).

On the north side of this room, the paintings of the vault depicted episodes from the birth of Christ: the dream of Joseph, the voyage to Bethlehem, the nativity with the miracle of Salome and the shepherds, the presentation in the Temple and the adoration of the Magi. Below, at the base of the vault, is a geometric frieze (Bénazeth et al, 2008).



Figure 2 Room no.7 , building no.1 , during excavation, photo to the north -west ( Courtesy of IFAO).

On the south side of the room, the vault bears the representations of a series of characters in which one can recognise two of the founders of Bawit monastery and nine prophets, each of whom holds a scroll inscribed with a passage from their prophecy. The base of the vault is decorated with a frieze of meanders alternating with birds. The wall itself is decorated with a pattern of diamond shapes each holding a green leaf. Another geometric pattern, covered with large blooming flowers, is painted on the west wall. The east wall, of which only the lower part remains, holds three niches. The decoration of the largest, set in the middle of the wall, was found in the debris. It depicted Christ surrounded by seraphim and the symbols of the four evangelists.

A great effort is being made to reassemble the fragments of the encaustic painting, which is a representation of the saints and the holy family in Egypt in a Coptic and byzantine style.

The precise composition of the medium has proved to be a continual source of disagreement. The etymology of the word encaustic in ancient lexicons and dictionaries is derived from the Greek word *enkaio* or *enkaiein* which means to burn or to be executed by fire (Lieber, 1840). The meaning given by the lexicon indicates the method used in the preparation, which depends mainly on heating the wax before the application. Pliny refers to the impregnation of the pigments with the wax by melting and preparing cylindrical shapes or color cakes. (Doxiadis, 1995).

The hypotheses of painting using molten wax (or the application of hot instruments for painting with the wax) or the use of the Punic wax (saponification wax) mentioned by Pliny has been argued between different scholars. At present the most widely accepted hypothesis states that the ancient technique of encaustic painting consisted of the application of colored beeswax in its molten state, a theory which is based upon ancient literary sources. As the Roman writer *Seneca* wrote that the choosing and applying of the paint was performed rapidly (Doxiadis 1995), this would be possible only with the hot or molten wax. Petrie also mentioned that the environment of Egypt would keep the wax melted or near melting point (Petrie 1911).

But at the same time some scholars have not accepted this idea, disagreeing with the idea of using molten wax for the following reasons: molten wax cannot produce the long thin and diluted brush strokes observed, as molten wax sets and dries very fast, giving only thick and short brush strokes, the faces indicate not brush marks but palette knife marks, which could only be reproduced by saponification of wax, the terminological meaning of the word encaustic could refer to the method and the tools but not the molten wax .

The second hypothesis is the use of water soluble encaustic or *punic* wax. According to ancient recipe given by Pliny, after bleaching the wax using sea water and sun light, the wax was then boiled with an alkaline solution produced from the burning of ash, , as the water filtered from burned ash contains high proportions of potassium hydroxide and minor proportions of sodium hydroxide.

The idea of using saponified wax or *punic* wax has met with great criticism, as there was no direct reference to it, as well as problems concerning the color fading if the saponified wax with its salts was used.

The word *sapo*, Latin for soap, first appears in *Pliny the Elder's Historia Naturalis* (Rackman, 1952), which discusses the manufacture of soap from tallow and ashes, but before this a reference to soap production appears in The *Ebers* papyrus from Egypt, 1550 BC, indicating that the ancient Egyptians bathed regularly and combined animal and vegetable oils with alka-

line salts to create a soap-like substance (Scholl, 2002).

The pigments used by the encaustic painters were, according to the recent analytical results performed in both encaustic mummy portrait and paint saucers from the roman period, red lead (minium) for the orange red color, Egyptian blue for the blue pigment, white lead or gypsum for the white color, ochre mixed with jarosite and in some cases madder lake for the rose and the flesh tones, and ochre mixed.

## 2. MATERIAL AND METHODS

### 2.1 X-Ray Fluorescence (XRF)

Non-destructive chemical- elemental analyses were collected for twelve samples using Niton XLt -793 W portable XRF spectrophotometer device, that produced measurements in parts per million (ppm). The NITON XLt x-ray tube based analyzer is a completely portable instrument with a one hand trigger operation and a touch screen with full navigation, a complete energy spectra view, and an RS232 download port. All samples were exposed for a minimum of 180 seconds. XRF charts were produced using NITON xrf software. The principle components and the cluster analyses were performed using PAST statistical software program, version 2.10.

### 2.2 SEM-EDX

The scanning electron microscope used was a Quanta 3D 200 I (FEI Philips - Holland) coupled with EDX. Column pressure 60 PA, low vacuum, In back scattered mode (BSED).

### 2.3 X- Ray Diffraction (XRD)

For the x-ray diffraction samples were analysis using panlytical X-pert pro with a Cu anode, working at 40 mA / 45 kV. The samples were analysed in a nondestructive mode without any sample preparation. An approximately flat surfaced archeological sample was attached into the sample holder inside the xrd apparatus. The data were interpreted using the embedded software.

### 2.4 Fourier Transform IR spectroscopy (FTIR)

Fourier transform infrared spectroscopy has been widely used in the study of wax and pigments, the method used was in accordance with

(Ramer, 1979; (Meilunas, Bentsen & Steinberg, 1990; Pitthard, Vak, Griesser, Stanek, & Laubenberger, 2007; Kühn, 1960), (Moretto, Orsega, & Mazzocchin, 2011). Infrared spectra were obtained in the mid-range using JASCO-6100 FTIR spectroscopy. About 1 to 3 mg from the archeological samples were ground with 99-97mg of KBr in an agate mortar, Percentage transmittance was collected in the range of 4000–400  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution.

### 2.5 Gas chromatography–mass spectrometry (gc-ms)

Gas chromatography - mass spectrometry is one of the most effective methods widely used for the identification of organic material and the alteration aspect connected to the aging of these materials. GC-MS has been widely used for the identification of wax in general and beeswax specifically, the method followed in this research was described in different research as (White, 1978), (Bonaduce & Colombini, 2004) and (Maia & Nunes, 2013). Type of GC/MS: thermo scientific trace GC ultra-coupled with ISQ single Quadra pole MS, type of column TG5 MS, working protocol followed: initial temperature 50 °C held for 2 min, 50 °C / min ramp to 180 °C, 3 °C / min ramp to 300 °C, 6 °C / min ramp to 320 °C.

For sample preparation, approximately 3 mg of beeswax was dissolved in 4 ml of chloroform; the solution was mechanically shaken for 2 min to complete dissolution of beeswax.

## 3. RESULTS

### 3.1 Plaster and paint substrate

The investigation of the cross sectioned samples, using SEM, indicates six layer in the composition of the mural painting subjected for the study showed that the paint layer could be described according to the SEM-BSED investigations as following:(Fig.3 ):

(a) Silty sand render with a thickness around 2.5mm, this layer is reinforced with strips of chopped straw, the strip length could be from 300 to 500  $\mu\text{m}$ , according to the SEM investigation, the straw could be from Barley straw (*Hordeum vulgare* L.)

(b) A thick lime based render with a thickness about 1.5mm, this layer is also reinforced with chopped straw, and the layer is rich with large

grain sand particles ranging from 100 to 150  $\mu\text{m}$ .

(c) Moderate lime based coat, the thickness of this layer is about 150  $\mu\text{m}$ .

(d) Two fine coats with very fine sand particles, the inner is about 45  $\mu\text{m}$  while the outer is about 120  $\mu\text{m}$ .

(e) The paint layer which ranges from 5 to 20  $\mu\text{m}$ .

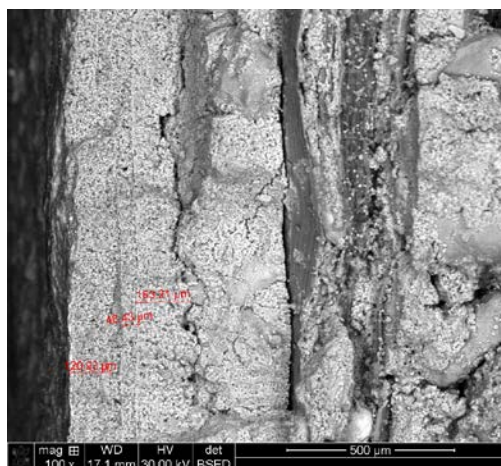


Figure 3 SEM indicating the stratigraphic composition and the thicknesses of the encaustic paint layer and its substrate, Baouit, Building no.1.

The X-ray diffraction analysis of the paint layer proved that the white preparation layers are mainly calcium carbonate (Fig. 4), which could be interpreted as a lime based plaster, executed on a silty sand render. The main components of the plaster were quartz and calcite, while the silty sand render represented by albite as one of its main components. From the XRD results, no alumino-silicate materials were found (ex: Pozzolan) and that confirms that air lime and not hydraulic lime was used.

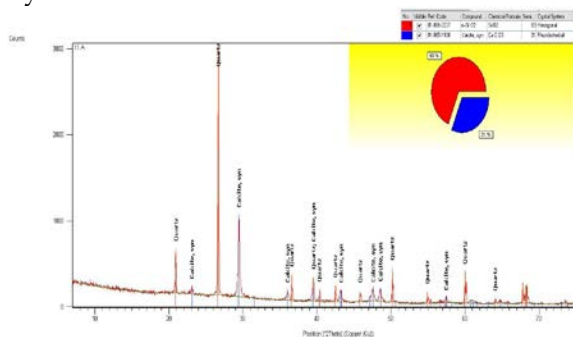


Figure 4 XRD pattern for the encaustic mural painting substrate indicating the presence calcite and quartz, indicating the presence of lime based plaster, with no alumino-silicate materials.

### 3.2.1 Orange paint layer

Two samples from the orange paint layer were investigated and analysed by means of SEM coupled with EDX, indicating the presence of highly back scattered elements in the paint layer, while elemental analysis using XRF and EDX proved the presence of Lead (Pb) as a major element as well as Iron (Fe) and Mn, Cu, As. (Fig. 5,6)

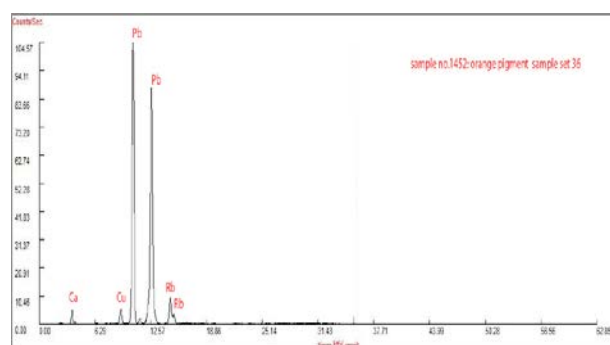


Figure 5 XRF pattern for the orange pigment, lead was the major element indicated in the sample.

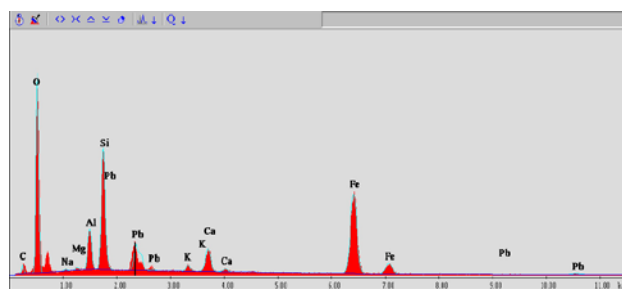


Figure 6 EDX analysis for the orange paint layer indicating the presence of Pb, Fe, Al, Ca and traces from Mn and K.

The presence of red lead was confirmed by means of XRD analysis, where both minium and calcite were identified (Fig.7).

### 3.2.2 Yellow paint layer

XRF analysis of three samples analysed from the yellow paint layer indicated that iron (Fe) was the most abundant element, with some traces of Ca, Cu.

Two samples (bulk and powder) were analysed using XRD. The analysis revealed the presence of natrojarosite, hydrated sodium iron sulphate,  $[\text{NaFe}_3(\text{SO}_4)_2(\text{OH})]$  for the lemon yellow pigment used (Fig.8), a mineral previously reported as a yellow pigment in ancient Egypt by Le fur (Le fur, 1994) and Colinart (Colinart, 2001).

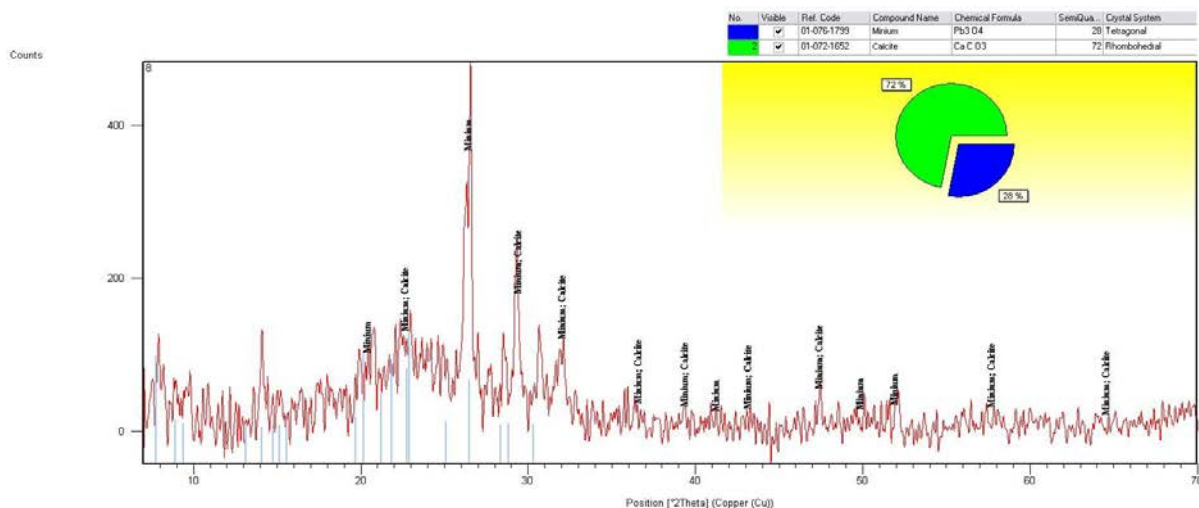


Figure 7 XRD pattern of the orange pigment indicating the presence of minium  $Pb_3O_4$  and calcite  $CaCO_3$ .

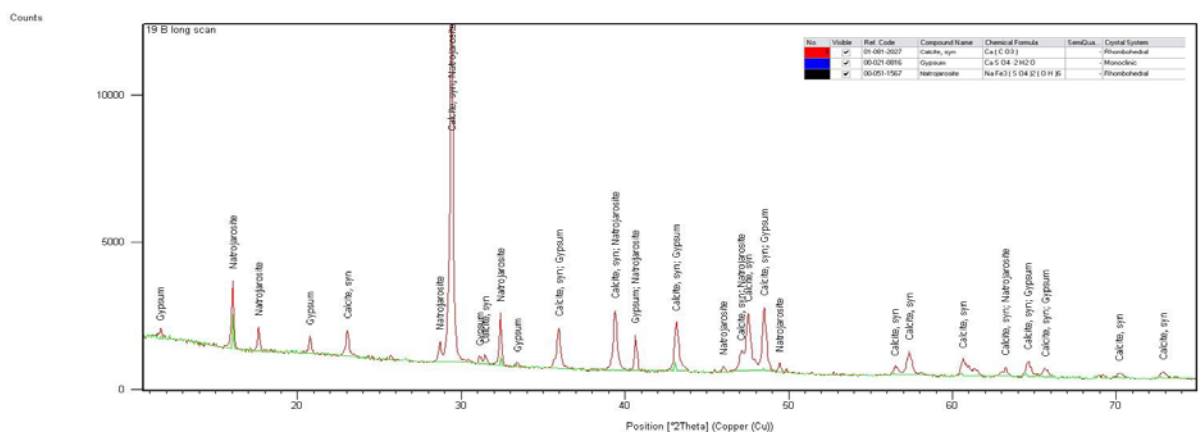


Figure 8 XRD pattern for the yellow paint layer revealed the presence of natrojarosite, hydrated sodium iron sulphate,  $[NaFe_3(SO_4)_2(OH)]$  for the lemon yellow pigment

The pigment was also identified in different painting examples from the old kingdom (Akhetotp mastaba 6th 6 dyn. Saqqara) towards the middle kingdom period, (ex.Karanak, Luxor), as well as some other examples from the Ptolemaic period.

### 3.2.3 Green paint layer

The olive green pigment used in the monastery of Baouit was prepared in thin sections, which allowed a clear observation of large and well crystallized grains, embedded in a deep green matrix.

Analysis of the green pigment using XRF indicated the presence of copper and iron as major components (Fig.9), with some traces of magnesium and Arsenic. The XRF elemental analysis

cannot be relied on as a solo analysis technique, whether the green pigment was iron based or copper based was not clear.

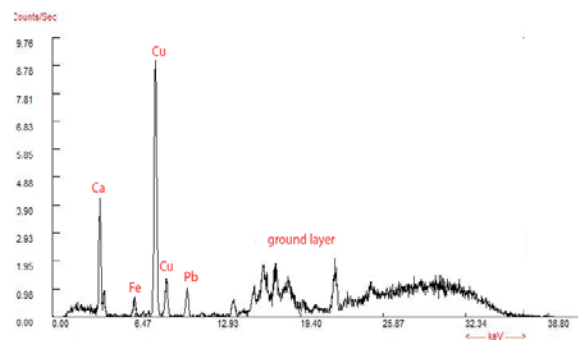


Figure 9 XRF result of the green paint layer indicating the presence of Cu, Ca Fe, and Pb.

EDX analysis revealed the presence of iron (Fe), Calcium (Ca), Aluminum (Al), Magnesium

(Mg), potassium (K), Chloride (Cl), Copper (Cu). These results confirm the presence of green earth, while the ratio of Iron (Fe) to (Mg) would suggest that glauconite was used rather than Celadonite (Figs. 10, Table 1).

**Table no.1: elemental relative percentage resulted from both XRF and EDX analysis of the green sample from Baouit encaustic mural painting.**

XRF analysis		EDX analysis	
Element	Concentration in PPM	Element	Percentage (%)
Sb	51	C	45
Sn	97	O	30
Pb	32	Mg	0.53
As	234	Al	1.22
Cu	2554	Si	3.59
Fe	1820	S	2.62
Mn	97	Cl	0.49
		K	0.40
		Ca	11.78
		Fe	1.37
		Cu	1.76

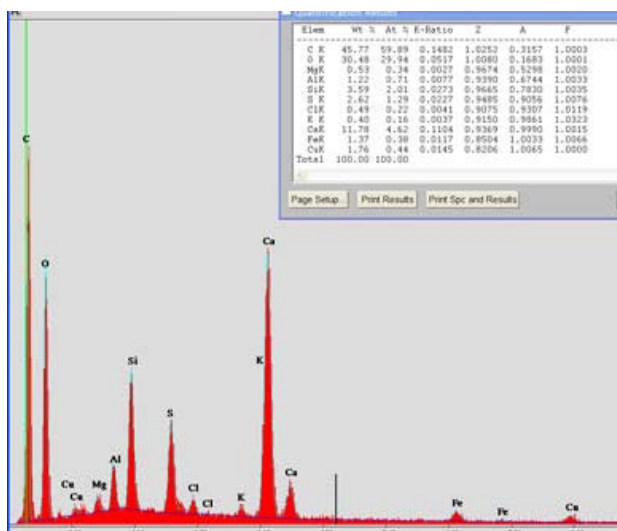


Figure 10 EDX analysis for the green paint layer revealed the presence of Fe, Ca, Al, Mg, K, Cl and Cu.

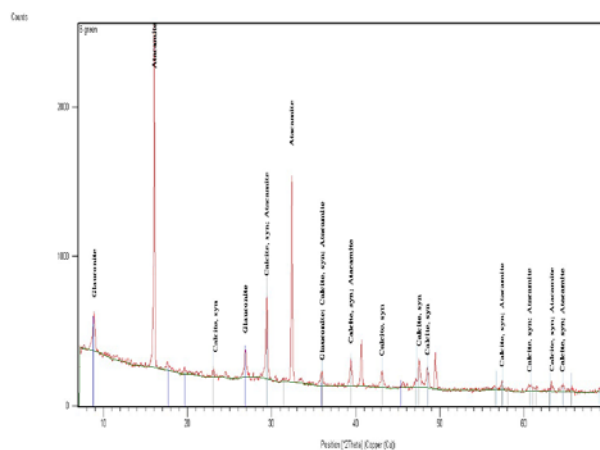


Figure 11 XRD result for the first sample of the green paint layer indicating the presence of glauconite, calcite and attachamite.

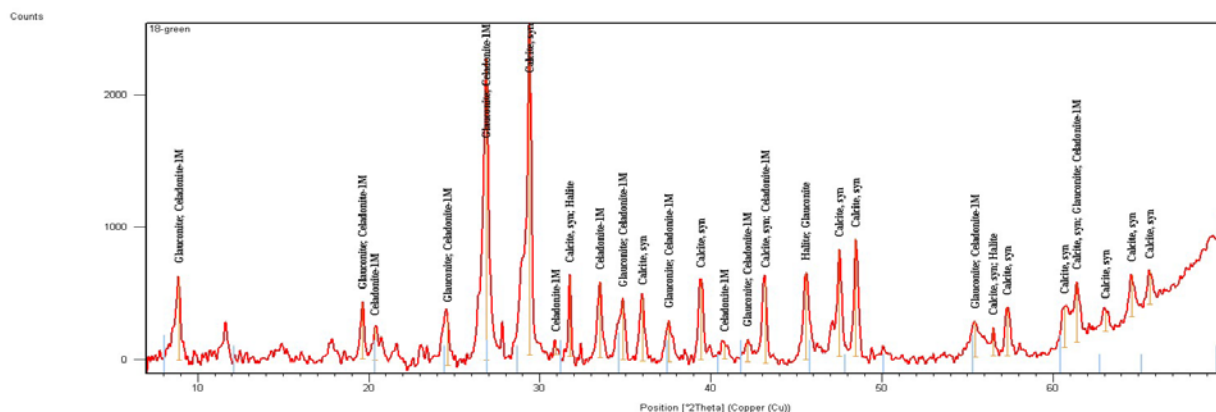


Figure 12 XRD pattern for the second green sample indicating the presence of glauconite, calcite and traces of celadonite

The usage of green earth was conformed using XRD analysis. Two samples were analysed, in one sample glauconite and atacamite were present, and in the second sample both glauconite and Celadonite were present (Figs.11, 12).

### 3.2.4 Blue paint layer

An investigation of the blue pigment in thin section showed the presence of anisotropic crystals with tubular shape, and refractive index less than 1.66. compared to the canada balsam medium used in the sample preparation. these properties are typical of cuprorivaite, the crystal shape was also observed under sem investigation (fig no.13) i.e. egyptian blue. elemental analysis using xrf analysis indicated the presence of copper as a main component; iron also being present. the analysis also indicated the presence of lead (fig no.14). the presence of lead and traces of other elements as tin and zinc is of paramount importance as this may indicate the reuse of bronze alloy as a source of copper for the fabrication of the egyptian blue.

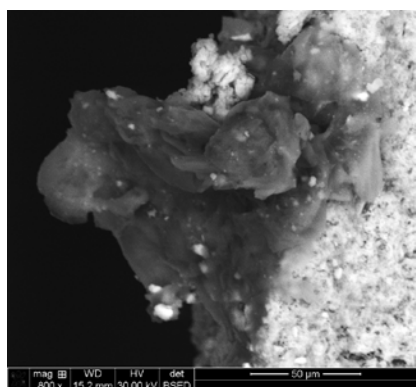


Figure 13 SEM image of the blue paint layer revealed the presence of coarse grains and tubular shaped crystals .

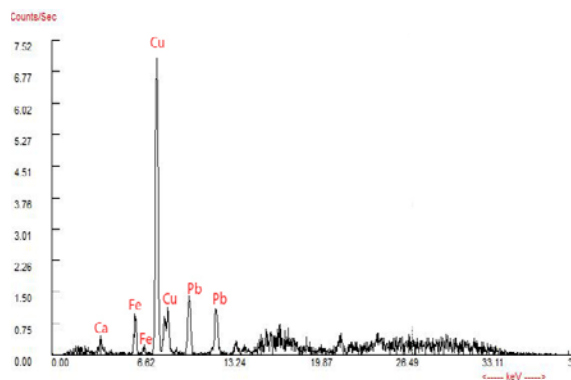


Figure 14 XRF result for the blue paint layer indicating Cu as a major elemental component of the blue pigment

Table 2 relative percentage elemental result using xrf and edx for the blue paint layer.

EDX (%)		XRF(P.P.M)	
Element	Per-centage	Ele-ment	Per-centage
O	44	Cu	13194
Si	13.8	Fe	4916
Ca	30	Pb	1030
Cu	6.4	Zn	891
Fe	1.5	Sn	281
S	0.7	Sb	124
Al	1.44		
K	0.7		

### 3.2.5 BROWNISH RED

The elemental analysis using portable X-ray fluorescence for the brownish red sample indicates the presences of Arsenic (As 26772 ppm) and minor amounts of iron (Fe 3974 ppm) and calcium (Ca 4251ppm). The XRF result may indicate the use of arsenic sulphide, or orpiment (fig no.15). The xrd pattern of the brownish red pigment indicates orpiment, calcite and hematite in the composition of the paint layer (fig no.16). This might explain the dark Chroma of this color, being due to the mixture of orpiment and hematite.

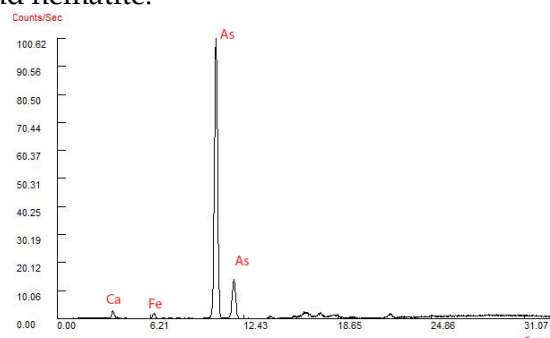


Figure 15 XRF result of the brownish red paint layer indicating the presence of As and traces of Fe.

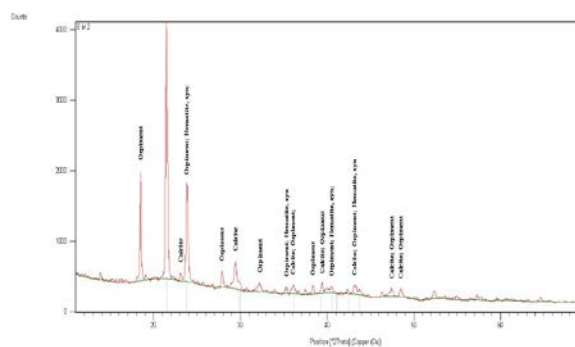


Figure 16 XRD pattern for the brownish red paint layer indicating the presence of orpiment, hematite and calcite.



### 3.3 Organic binding medium

The identification of the organic binding medium was based on the vibrational signature of the functional groups for beeswax, using both Fourier transform infrared analysis, and gas chromatography mass spectrometry analysis. Further information obtained using these two methods enabled us to understand the original technique used for the execution of the encaustic technique and the alteration of the material over time.

#### 3.3.1 FTIR analysis

Two samples were analysed by means of FTIR analysis, from the red and green paint layers. The results were compared to two control samples of bees wax - molten and Punic beeswax (fig no.17) were prepared- in order to compare the results with the archeological samples in order to identify both the presence of the wax and the technique used.

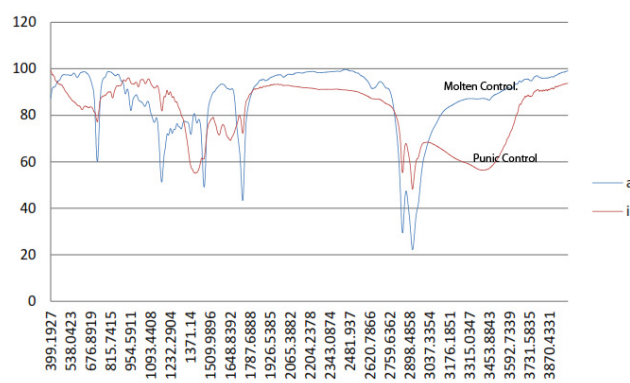


Figure 17 FTIR pattern for two control samples of molten and Punic (saponified) wax

The main functional groups obtained from the contemporary beeswax sample were two main doublets representing stretching in plane and out of plane in the region of 2950 and 2850  $\text{cm}^{-1}$ , as well two other sharp doublets at 1460 and 1470  $\text{cm}^{-1}$ . The peak in the region of 715 – 720  $\text{cm}^{-1}$  indicates the  $\text{CH}_2$  torsion bend; the C-O of the wax ester usually appears in the 1165 – 1170  $\text{cm}^{-1}$  region; C=O of the organic fatty acids appears in the 1715 -1720  $\text{cm}^{-1}$  region.

The FTIR results of the paint layers showed two strong and sharp methylene stretching symmetrical and asymmetrical bands at 2919 and 2849  $\text{cm}^{-1}$  respectively, as well as two bands at 721  $\text{cm}^{-1}$ , 874  $\text{cm}^{-1}$  and 922  $\text{cm}^{-1}$ , a strong C=O at 1735  $\text{cm}^{-1}$  and C-O at 1169  $\text{cm}^{-1}$  of the

ester (Fig.18). The band at 1512  $\text{cm}^{-1}$  could be assigned to carboxylate salts or fatty acid salts (Mirghani, Che Man, Jinap, Baharin, & Bakar, 2002), while alcohols bands are present in the OH stretching at 3407  $\text{cm}^{-1}$  and the alcohols OH bending at 1122  $\text{cm}^{-1}$  and 1056  $\text{cm}^{-1}$ .

The ftir spectrum of the green sample represents a wax based paint layer, in which a partial saponification process is indicated by the presence of the carboxylate and alcohol functional groups. This could be due to natural aging of wax, as the Punic process of saponification will result in the complete saponification of wax. The small peak at 958 may indicate the presence of Si-O, which could be from the green earth pigment.

The FTIR analysis of a sample from a red flaking paint layer proved the presence of wax as a binding medium; this is demonstrated by the presence of the methylene group of the wax hydrocarbon, as well as the carbonyl group of the wax ester.

A significant broad and large band could be seen in the region of 3450  $\text{cm}^{-1}$  due to the OH group, probably indicating the presence of triglyceride alcohols. A small band at 1107 and 1028  $\text{cm}^{-1}$  for the long chain alcohols indicates that small quantities of alcohol could be in the sample.

Crystallized areas of wax represented by the small band for C=O at 1735  $\text{cm}^{-1}$  and another one for the C-O at 1170  $\text{cm}^{-1}$ , indicates that certain alterations could have occurred in the sample composition.

Inorganic materials were indicated by the presence of a secondary absorption band of the  $\text{CO}_3^{2-}$  group of calcium carbonate in the region of 2516  $\text{cm}^{-1}$ , 1793  $\text{cm}^{-1}$ . A broad band at 1458  $\text{cm}^{-1}$  overlapped the CH band in the same region and bending of the  $\text{CO}_3^{2-}$  is seen at 874  $\text{cm}^{-1}$  (Derrick, stulk, & Lundry, 1999). Small peaks in the region of 1107 and 1028  $\text{cm}^{-1}$  indicated the presence of long chain alcohols (Mirghani, Che Man, Jinap, Baharin, & Bakar, 2002), and could be connected to the broad band of the OH at 3454  $\text{cm}^{-1}$ .

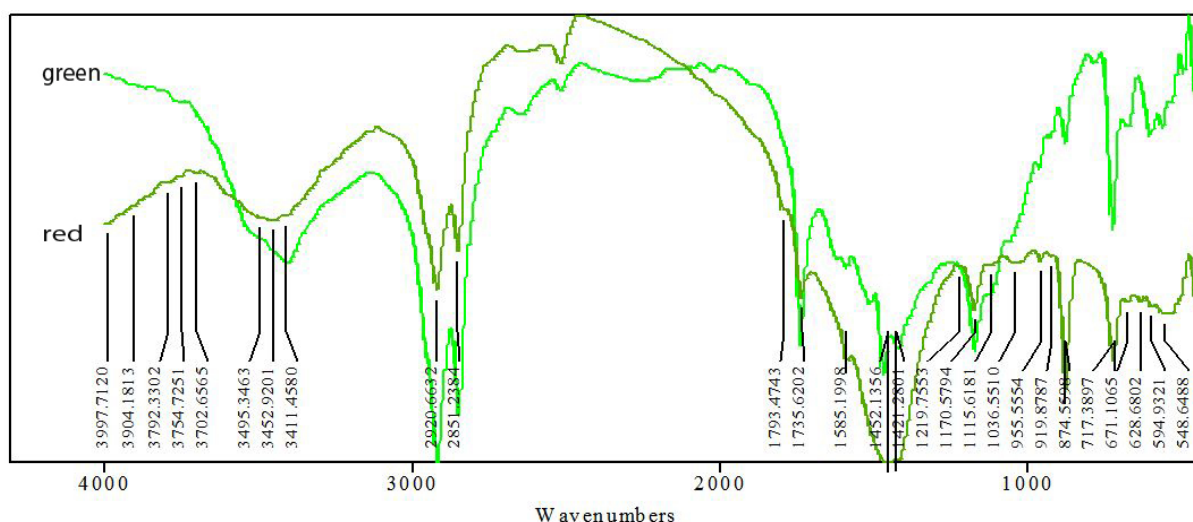


Figure 18 FTIR pattern of two samples from green and red paint layer, Baouit encaustic mural painting.

The green sample was compared to both a molten bees wax sample and a Punic bees wax sample. The comparison of the ftir charts (Fig.19) proved that the archeological samples were similar to a large extent to the molten controlled sample. Some alterations appear in the archeological paint layer profile, but it does not resemble totally and intentionally saponified wax (Punic sample), which means that the presence of small bands related to long chain alcohols or carboxylates, could be interpreted as a result of natural aging and alteration of wax due to oxidation and water hydrolysis in an arid and exposed environment.

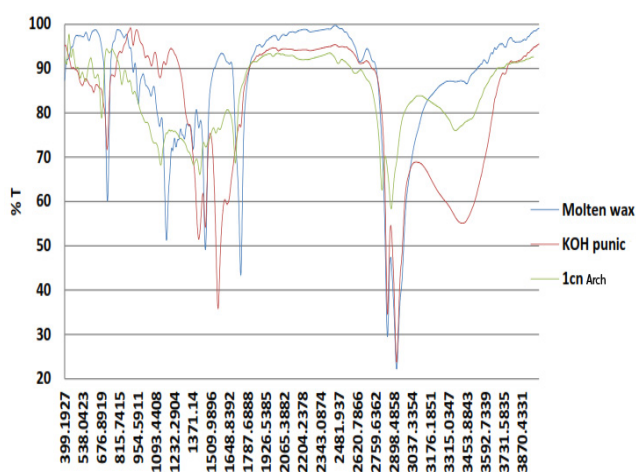


Figure 19 comparison between FTIR pattern of the green archaeological paint layer with the two control samples of the molten and Punic wax.

### 3.3 GC-MS analysis

The GC-MS analysis for one of the wax based paint layers indicates the state of alteration that the binding medium had reached. The fragmen-

tation and the separation of the main organic components of the wax identified as seen in (Fig.20) mainly hydrocarbons, esters and fatty acids, clearly represent the wax alteration. The alteration is shown by:

- Presence of long chain alcohols.
- Depletion of hydrocarbon profile of wax.
- Presence of phenolic compounds.
- Alteration of esters and appearance of glyceride esters and fatty acids.

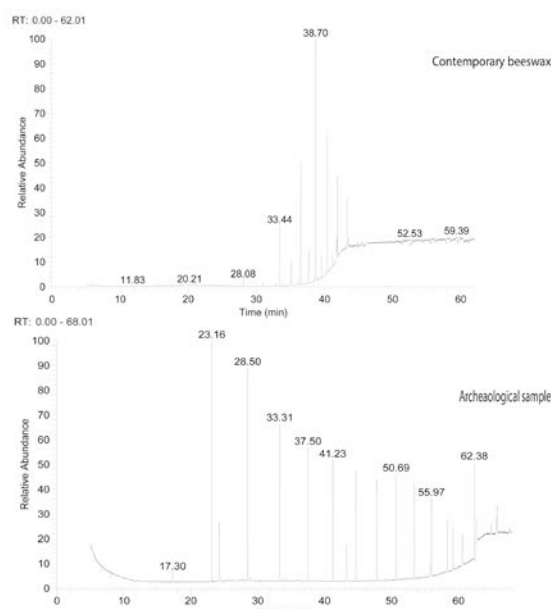
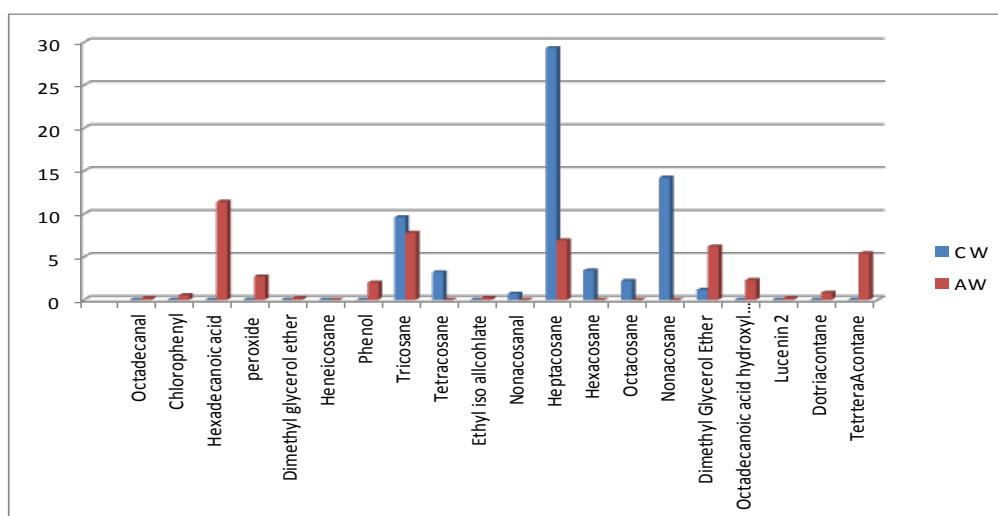


Figure 20 GC-MS result for the beeswax contemporary sample and the archaeological green sample.

The four previous aspects are shown in the following Table 3, taking into consideration the relative intensity of the separated compounds:

**Table 3 GC-MS analysis results including Retention time and compounds identified from both control beeswax sample and the archaeological green sample.**

No	Rt	Compound	Chemical formula	Area %	Comments
1	5.20	3Oxo20methyl hydroxyconanine1,4diene	C22H31NO2	0.42	Steroid compound result from the reaction of lipid with heavy metal as lead
2	7.99	Octadecanal	C18H34O	0.17	Long chain alcohol
3	17.29	2-4Chlorophenyl thiazolyamino,benzoxazine	C17H10ClN3O2S	0.52	1. Phenolic compounds
4	23.16	Hexadecanoic acid	C16H32O2	11.48	2. PALMITIC ACID
5	24.24	2,5Dimethylhexane 2,5dihydroperoxide	C8H18O4	2.78	Peroxides
6	27.83	Dimethyl glycerol ether	C27H56O5	0.20	Ether accompanied with carboxylic acid
8	28.08	Heneicosane	C21H44	1.3	hydrocarbons
9	28.68	PHENOL, 2,6BIS (1,1DIMETHYLETHYL) 4METHYL	C15H24O	0.24	Phenol based compound
10	33.31	Tricosane	C21H44	7.8	Hydrocarbons
11	33.44	Tricosane	C21H44	9.6	Hydrocarbons
12	35.14	Tetracosane	C24H50	3.2	Hydrocarbons
13	35.94	Ethyl iso allcoholate	C26H44O5	0.21	
14	36.18	Nonacosanal	C29H60O	0.7	Fatty Alcohol
15	37.4	Heptacosane	C27H70	6.9	Hydrocarbons
16	37.6	Hexacosane	C26H54	3.4	Hydrocarbons
17	38.7	Heptacosane	C27H70	29.3	Hydrocarbons
18	39.5	Octacosane	C28H58	2.28	Hydrocarbons
19	40.43	Nonacosane	C29H60	14.2	Hydrocarbons
20	41.23	Dimethyl Glycerol Ether	C27H56O	6.28	Ether accompanied with carboxylic acid
21	41.20	Dimethyl Glycerol Ether	C27H56O	1.16	Ether accompanied with carboxylic acid
22	41.77	Dimethyl Glycerol Ether	C27H56O	5.8	Ether accompanied with carboxylic acid
23	43.2	Octadecanoic acid hydroxyl ester	C20H40O	2.38	caprylic acid
24	47.8	Dimethyl Glycerol Ether	C27H56O	5.8	Ether accompanied with carboxylic acid
25	53.15	Ethyl Iso allcoholate	C26H44O5	0.2	Alcohols
26	55	Dotriacontane	C32H66	0.8	Hydrocarbons
27	62.3	TetrteraAcontane	C44H90	5.44	Hydrocarbons

**Figure 21 Comparison between the main component of contemporary beeswax and the archeological sample from Baouit**

#### 4. DISCUSSION

The analysis performed on the samples from the unique encaustic painting from the monastery of Baouit explains the formation of the painting palette. The pigments identified were mainly types identified previously from the roman period, only the brownish red is an exception. The palette shows the variety of sources where these pigments were obtained; both natural and artificial sources were used.

The integrated elemental analysis using EDX and XRF confirms the usage of a green earth based pigment in combination with a copper pigment, the XRF shows major amounts of Fe and Cu as well as minor amounts of Sb, Sn, Pb and As, while the EDX gives major Ca peaks with minor percentage of Al, Fe, Cu, as well traces of Mn, K, Cl and S. The results match those of green samples from different periods (pharonic and roman period green samples) from an ancient shrine, analysed by Berry (Berry, 2002) as well mineralogical identification and description for green earth (both glauconite and celadonite) in the literature (Buckley, Bevan, Brown, & Johnson, 1978) (Bearat, 1996).

The presence of both copper based pigment and green earth in the XRD pattern, explains the result of the investigation of the thin sectioned sample for the green paint layer, with large green particles embedded in very fine green matrix.

The EDX and the XRF elemental analysis of the red pigment indicates lead as a main element, with traces of iron and calcium, which could be traces from the white wash. The mineralogical composition of the pigment was identified using XRD qualitative analysis as Minium ( $Pb_3O_4$ ), as well as calcite indicating the lime based render.

The absence of wallastonite in the qualitative XRD result of the blue pigment indicates the temperature used in the manufacture of the Egyptian blue was lower than 950 °C (Riederer, 1997). As no green particles could be observed in the stereo microscopic investigations, the theory is supported by well identified sharp edge crystals observed under the SEM-BSSED investigations.

The identification of pigments like natrojarosite and mixture of orpiment and hematite high-

light richness of the byzantine palette used for the encaustic painting in Egypt, during the 6<sup>th</sup> century.

The FTIR analysis in the mid-range (400-4000) for five archaeological samples, proved the presence of methylene and ester functional groups identical to those for the wax ftir profile. This result confirms the usage of wax and more likely beeswax as a binding medium in the mural painting of baouit.

The samples indicate evidence of hydrolysis or partial saponification of the organic medium, the presence of OH vibration bands in the 3400 region as well as 1035 to 1060  $cm^{-1}$  region indicates the presence of long chain alcohols or glycerides. One should also mention the observed depletion of the methylene or the hydrocarbon from the weakness of the peak of the characteristic group which may be due to the sublimation of the lower molecular hydrocarbons. The same is true for those peaks representative of the ester functional group, as they were shifted and weakened, and sometimes the intensity of the carbonyl peak increased, which indicates the occurrence of hydrolysis and formation of carboxylate, for which some small representative peaks were observed in the archaeological sample charts.

It's hard to say whether the saponification identified on the ftir spectrum for the archaeological samples was intentionally made by the artist in order to prepare the water soluble encaustic, or that the presence of the saponification was due to the water hydrolysis as well as other alteration processes, which could have taken place in the wax composition during rancidification.

It's well known that rancidification is the decaying of unsaturated fatty acids by an oxidation process; this process could be promoted by the presence of trace metals as Ca, Cu, Fe, and Zn (Megahed, Nashy, & Ashkar, 2011), which already exist in the paint layer from the pigments, as well as the presence of heat. These two factors existed within the context of the mural painting at baouit.

The Chromatogram of the archaeological wax based paint layer shows the highly deteriorated pattern of the wax medium. This was demonstrated by the presence of long chain alcohols, palmitates and mainly the glycerols of the

hydrolysed triglycerides represented by the ester of fatty acids.

Oxidation or photooxidation may be one of the main reasons for the alteration of the wax; other components found in the archaeological sample such as phenolic compounds may indicate that this process took place.

The profile of the hydrocarbon was also strongly altered. The main hydrocarbon heptacosane concentration was 29 % in the contemporary wax sample but only 6.9 % in the archaeological wax. This indicates that the hydrocarbons which represent the main backbone of the wax were totally depleted and changed as a result of aging starting with the lower molecular weight hydrocarbons.

One of the interesting pieces of information that came from the GC-MS analysis, is the presence of luteolin, which is a luteolin flavone glycoside found in the sunflower family (Bohm & Stussey, 2002) with a molecular composition (Luteolin 6, 8-di-glucoside), which informs us

that the honey and its wax were naturally formed by bees which fed on sunflowers.

## 5. CONCLUSION

The painting palette of the encaustic mural painting at Baouit was identified as: lead red (minium), Egyptian Blue, natrojarosite, a mixture for the brownish red (red ochre and orpiment), and green (glaucosite and atacamite with traces of celadonite). The mixtures highlight how the ancient artists adapted their materials to obtain the colors.

The identification of beeswax proves the existence of the encaustic technique as an ongoing tradition for painting in Egypt during the Byzantium period. The analysis shows also that the wax was probably not treated with alkali in order to prepare the punic; the presence of long chain alcohols could be a result of alteration through natural water hydrolysis and oxidation as a part of the aging process.

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