Abstract

A comprehensive study has been undertaken into Sabil-Kuttab Umm 'Abbas ceiling (1867 AD/1284 H) in Cairo, Egypt. The study included both organic and inorganic constituents comprising; the pigments, the paint media, the gold layer and the white ground layer. The analytical instruments chosen for the study were Raman microscopy, Fourier transform infra red spectroscopy coupled with attenuated total reflection (FTIR-ATR) and optical microscopy. The pigments identified were ultramarine blue \( \text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Sn}_n \), indigo \( \text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2 \), vermilion \( \alpha\text{-HgS} \), red ochre \( \text{Fe}_2\text{O}_3+\text{clay}+\text{silica} \), barium white \( \text{BaSO}_4 \), lead white \( 2\text{PbCO}_3.\text{Pb(OH)}_2 \) and cobalt yellow \( \text{K}_3[\text{Co(NO}_2)_6] \). The chromate mineral, hemihedrite \( \text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2 \), was detected for the first time as an artistic pigment in this study. The paint media revealed were animal glue admixed with linseed oil and mastic resin. The detection of mastic resin as a paint medium in Egyptian paintings is of interest. The white ground layer was found to consist of calcium sulfate dihydrate \( \text{CaSO}_4.2\text{H}_2\text{O} \) and calcite \( \text{CaCO}_3 \) admixed with animal glue.

1. Introduction

On the occasion of conservation process of sabil-kuttab Umm 'Abbas (Fig. 1, a), analytical investigation on the materials used in the wooden ceiling and the surrounding cornice has been undertaken. The ceiling under study is located in a charitable foundation composed of a sabil, public water dispensary, and a kuttab, an elementary Quranic school for children. The sabil is usually located on the ground floor with the kuttab above it on the first floor. The sabil is roofed by a ribbed dome, with a porch below it, to protect Sabil users from the sun and rain. This foundation could be attached to a mosque or be a separate structure, as the one concerned in this study. Sabil-Kuttab Umm 'Abbas 1867 AD/1284 H was built by Bambah Qadin, the granddaughter of Abbas I, who ruled Egypt from 1848 to 1854 AD, and the mother of Abbas II. "Umm" in Arabic means mother, so the sabil is called (‘the mother of Abbas’). Bambah Qadin was a revered member of
the royal family and was called Umm al-Muhsinin ('mother of charity'), as she gave away so much of her considerable wealth.

The main octagonal façade of the building was decorated with floral and geometrical motifs and garlands, as well as colourful Quranic and poetic inscriptions applied on blue backgrounds [1].

The aim of this investigation is to characterize the paint layers containing pigments and media, and to compare the results achieved with the previous findings from the same period. Both the wooden white ceiling with the relief gilding stucco decorations (fig. 1, b) and the painted cornice (fig. 1, c-d) were studied.

Materials and methods

2.1. Samples and Sample preparation

Small fragments of the paint layers were embedded in a transparent epoxy resin (Buehler® Epo-Thin® low viscosity epoxy resin No. 20-8140-032). Different grades silicon carbide grinding paper was used for grinding and polishing the cross-sections.

The paint samples examined from the wooden ceiling were white and gold (fig. 1, b), while the samples from the cornice were blue, red, brown and yellow (fig. 1, c-d).

2.2. Light microscopy

Paint fragments and cross-sections were studied using a NIKON ECLIPSE ME 600 microscope equipped with an Olympus e-410 digital camera. The magnification varied from ×100 to ×400 depending on the size of the samples.

2.3. Fourier Transform Infrared Spectroscopy coupled with attenuated total reflection (FTIR-ATR)

FTIR spectra of the paint media were obtained using a Bruker FTIR spectrometer, model VERTEX 70 equipped with ATR. The IR spectra, in absorbance mode, were obtained from the
specimens, using an aperture of 20–100 μm, in the spectral region 600 to 4000 cm\(^{-1}\). The resolution was 4 cm\(^{-1}\) and the number of co-added scans was 64 for each spectrum.

The FTIR spectrum of the white ground layer, in a freshly prepared KBr pellet, was obtained using JASCO FT-IR - 460 plus spectrometer using an aperture of 20–100 μm, in the spectral region 400–4000 cm\(^{-1}\).

2.4. Raman microscopy

A Senterra Raman spectrometer (Bruker) was used in the current work, consisting of a confocal Raman microscope (20× objective lens) with a spectral footprint of about 2 μm, 4 cm\(^{-1}\) spectral resolution and operating with a laser wavelength of 785 nm.

Raman spectra were subjected to baseline correction and smoothed. All compounds were identified by comparing their characteristic vibrational spectra with those in published databases [2, 3].

Results

3.1. The Paint layers of the cornice:

3.1.1. The blue paint sample:

The blue paint was sampled from the background of the inscription in the Cornice (fig. 1, c1). It was applied as a thick layer (fig. 2, a-b) that could be easily separated from the white ground layer underneath in order to be analyzed.

It was examined by means of the Raman analysis, and the spectrum achieved (figure 2, c) revealed the vibrational characteristic bands of ultramarine blue, Na\(_6\)Al\(_6\)Si\(_6\)O\(_{24}\)Sn [4]. The well defined bands of ultramarine, found at 545 and 1091 cm\(^{-1}\), are attributable to the totally symmetric stretch of the radical anion S\(^3-\) and S\(^2-\) [5] [6].

The natural ultramarine is the blue pigment extracted from lapis lazuli, mainly the mineral lazurite, comprising a complex sulfur-containing aluminium silicate [7]. It is suggested that lapis lazuli occurs in the Uweinat oasis in south east Egypt [8].

Artificial ultramarine was first reported in 1827 and was extensively used as an artistic pigment in the second half of the 19th century [7]. In order to manufacture ultramarine blue pigment, anhydrous sodium carbonate or sulfate is mixed with china clay, silica, in the form of sand or quartz, and sulphur in reducing atmosphere. All the ingredients are mixed, finely ground and heated in a furnace at red heat for several hours in the absence of air. The product obtained is green in colour and known as primary or green ultramarine, which is heated again at above 500°C to be converted to a blue colour. The final product is ground and washed to get rid of soluble salts and then dried.

3.1.2. The red paint sample:

The fragment image of the red paint sample taken from the cornice (fig. 1, d2) showed a red pigment, weakly distributed on the ground layer (fig. 3, a). The cross-section image (figure 3, b) showed an uneven thin layer of the red paint. The Raman spectrum (figure 3, c) yielded a complex mixture of cinnabar (α-HgS) and a chromate pigment. Cinnabar revealed its characteristic bands at 342, 285, 253 and 140 cm\(^{-1}\) and the chromate pigment...
Figure 3: the red paint sample taken from decorated cornice; (a) the fragment image, (b) the cross-section image, (c) the Raman spectrum.

Figure 4: The Raman spectrum of the brown paint sample taken from the decorated cornice.

gave triple Raman bands at 846, 864, 825 and two other bands at 380 and 340 cm$^{-1}$. Lead white [2PbCO3. Pb(OH)2] was also detected in the light areas of the red and gave a weak band at 1050 cm$^{-1}$.

These Raman bands of the chromate pigment are assigned to a complex chromate mineral, hemihedrite (ZnPb$_{10}$(CrO$_4$)$_6$(SiO$_4$)$_2$F$_2$) [9], which has never been identified as an artistic pigment before. This mineral was discovered at the Florence Lead-Silver mine in Pinal County, Arizona [10]. It derived from the oxidation of galena, sphalerite, pyrite, and tennantite. The resulting minerals from the oxidation process are hemihedrite, wulfenite, willemite and cerussite [11].

The Raman bands appear at 847, 837 and 824 cm$^{-1}$ are attributed to the CrO stretching and the other four bands are assigned to v4 bending modes (376, 351 and 337 cm$^{-1}$) and v2 symmetric bending modes (319 cm$^{-1}$) [12].

3.1.3. The brown paint sample:

The Raman spectrum of the brown paint taken from the cornice (fig. 1, d3) gave the characteristic bands of red ochre (Fe$_2$O$_3$ + clay + silica) [13]. It gave its strong vibrational bands at 224, 291 cm$^{-1}$ while the medium and weak bands were shown at 407, 494, 610, 660 cm$^{-1}$. Three bands, attributed to the blue indigo pigment (C$_{16}$H$_{10}$N$_2$O$_2$), were also detected at 673, 1014 and 1123 cm$^{-1}$. The presence of indigo may originate from an adjacent blue paint area that was not examined in this study.

Red ochres are by far the most commonly reported red pigment from ancient Egypt starting from the pre-Dynastic period. They naturally occur in the Oases of the Western desert and near Aswan [14] and were prepared by washing, levitating and grinding.

3.1.4. The yellow paint sample:

The yellow paint area studied from the cornice (fig. 1, d4) revealed the Raman bands of complex mixture of cobalt yellow (fig. 5), aureolin (Potassium cobaltinitrite K$_3$(Co(NO$_2$)$_6$), [15] as the predominant pigment in addition to calcite and gypsum. The bands assigned to cobalt yellow revealed at 278 and 307 cm$^{-1}$ while the bands of gypsum was found at 418, 669 and 1007 cm$^{-1}$ and of calcite at 712 and 1085 cm$^{-1}$.

The principal preparation method of chrome yellow was by the acidification of solutions of cobalt salts with acetic acid followed by addition of a concentrated potassium nitrite solution. Cobalt yellow would then slowly precipitate as a yellow crystalline mass. It was first synthesised by N.W. Fischer in 1831 and was first introduced as an artist’s pigment in 1861. It does not be widely used in paintings because of its expensiveness [16].
3.2. The Paint layers of the wooden ceiling:

3.2.1. The white paint sample:

The white pigment was sampled from the background of the ceiling (figure 1, b5). The Raman bands at 986, 460 and 435 cm\(^{-1}\), which are assigned to barium white (barium sulfate, BaSO\(_4\)) (fig. 6), were revealed.

Synthetic barium sulfate, BaSO\(_4\), has been used since the early nineteenth century as a white pigment and an extender. The naturally occurring mineral analogue is barite which normally used as a starting mineral for producing the synthetic analogue and its synthetic version is prepared by using barite as a starting mineral which is heated with coal, forming the sulfide and gaseous by-products. After dissolving the resultant barium sulfide in water and filtering it, the sulfate can then be precipitated by adding sodium sulfate; it is filtered, washed and dried to complete the process [15]. Barium sulfate was also commonly called blanc fixe, process white and permanent white.

3.2.2. The gold sample:

Figure 7 (a–b) shows the fragment and the cross-section images of the gold layer. The thick bole layer underneath is apparent in the cross section image (fig. 7, b, 1). The gold failed to give any Raman spectrum, suggesting it being real gold. The gold was applied on an orange bole layer, consisting of hydrated iron oxide and a large amount of kaolinite. The bole layer gives a warm red tonality to the hue of the gold surface and allows further treatments of the gold leaf by burnishing [17].

The FTIR spectrum of the bole layer gave the characteristic bands assigned to the OH groups at 3698 and 3619 cm\(^{-1}\). The strong bands between 900 and 1100 cm\(^{-1}\) are attributed to the Si—O, Si—O—Si, Si—O—Al and Al—OH groups. The bands at 1653 cm\(^{-1}\) along with the strong bands at 2852 and 2918 cm\(^{-1}\) attributed to methylene groups of animal glue [4].

4. The white ground layer:

The FTIR analysis of the white ground layer of the ceiling (fig. 7, c) revealed calcium and gypsum, admixed with animal glue. The absorbance bands shown at 3541, 3405 and 1621 cm\(^{-1}\) are attributed to water molecules [4] [18] while the band at 1137 cm\(^{-1}\) is assigned to the sulfate group (SO\(_4^{2-}\)) [4]. The characteristic features yielded at 1428, 875, 711 cm\(^{-1}\) are attributed to normal modes of vibration of the calcite’s CO\(_3^{2-}\) [19]. In addition to bands at 2927 and 2855 cm\(^{-1}\) which are ascribed to the methylene groups of animal glue [4] [18] [20].

5. The paint media:

Two paint samples were studied by FTIR-ATR in order to determine the paint media used. The first was the blue paint taken from the inscriptions’
Figure 7: (a-b) the gold layer taken from the relief stucco motif of the ceiling; (a) the fragment image, (b) the cross-section image, (c) the FTIR spectrum of the white ground layer.

background and the second was the red sample from the decorated cornice.

5.1. The blue paint sample:

The FTIR spectrum of the blue sample (fig. 8, a) showed characteristic bands at 2935 and 2871 cm\(^{-1}\), which are assigned to C-H stretching and 1700 cm\(^{-1}\) of carbonyl group (C=O). These bands are most probably attributed to a tree resin. According to Derrick protocol for distinguishing tree resins in accordance to the position of the carbonyl and hydrocarbon absorption bands, mastic resin gives spectrum with a strong carbonyl (C=O) stretch band between 1715-1695 cm\(^{-1}\) and hydrocarbon (C-H) bands between 2958-2930 cm\(^{-1}\) and 2875-2865 cm\(^{-1}\) [21]. When comparing mastic resin reference sample (figure 8, b) with the spectrum of the blue paint sample (fig. 8, a), more bands were identified at 1387, 1020, 982, 757 and 629 cm\(^{-1}\).

Mastic resin attributed to the genus Pistacia sp. (family Anacardiaceae) which has four recognized species found in Mediterranean area, namely Pistacia atlantica, Pistacia khinjuk, Pistacia Lentiscus and Pistacia terebinthus [22] [23]. Pistacia atlantica (Chios turpentine) and Pistacia lentiscus (mastic resin) were used as a varnish in ancient Egypt [24] [25]. However, Pistacia khinjuk is the only source of pistacia resin in modern Egypt [26]. On the other hand, Stern et al., (2008) [27] pointed out that the analysis of the resin cannot be used to distinguish the species due to degradation and confusion between species.

5.2. The red paint sample:

The FTIR spectrum of the red paint sample (fig. 9, a) revealed that animal glue admixed with linseed oil was used as a paint medium. The bands attributed to animal glue shown at 1621, 1537, 1443, 1382, 1235, 1029 and 851 cm\(^{-1}\), while the bands of linseed oil yielded its fatty acids (CH\(_2\)) at 2922, 2854 cm\(^{-1}\) and esters (C=O) at 1727 cm\(^{-1}\). Figures 9, b and 9, c showed the FTIR spectra of animal glue and linseed oil reference samples compared to the spectrum of the red paint sample (fig. 9, a).

The results obtained from the FTIR analysis of the two samples suggest that, animal glue and linseed oil were used as a paint medium in the decorated cornice. Mastic resin could be added to the blue paint, as a paint medium, to give a different texture and thickness needed to hold the gilded inscriptions.

6. Discussion

Three studies have been performed on wall paintings and ceilings in archaeological palaces and cemeteries dated to Mohammed Ali Era [28] [29] [30]. The blue pigment identified in Sabil-Kuttab Umm Abbas was ultramarine blue which had been previously identified in the Royal family graveyards [28]. In El-Safa palace, the blue pigment identified was Prussian blue (Ali and Darwish 2011). Another blue pigment, indigo, was identified in the brown paint sample and could originate from an adjacent blue paint area of the cornice. This pigment has not been identified in Mohammed Ali artefacts but had been found in Coptic icons dated to the 18th century [31].

The red pigment, cinnabar, was identified in this study mixed with hemihedrite and lead white. The mineral hemihedrite has not been previously identified as a pigment. Was it deliberately added
by the painter or accidentally (geologically) accompanied lead white by origin? To answer this question more studies should be carried out, but the presence of hemihedrite in some red paint areas that has no lead white, could assist the first hypothesis.

In our case study, cinnabar, lead white and Barium white were first detected in Mohammed Ali Era. Instead, haematite and zinc white had been used in both Abdeen palace [30] and Gawhara palace [29]. Cobalt yellow was detected in the yellow paint sample while massicot (PbO) was identified as the yellow pigment in both Abdeen palace ceiling [30] and the Royal family graveyards [28].

The white ground layer on which the decorations were applied was found to consist of gypsum and calcite. The same combination was found in Abdeen place and the Royal family graveyards with addition of quartz in both instances [28] [30].

The main paint medium identified in the decorated cornice was found to be animal glue admixed with linseed oil. The same ingredients had been previously identified in the studies performed on wall paintings attributed to Mohammed Ali Era. Ali and Darwish (2011) stated that animal glue, admixed with flux seed oil, was used as paint medium in the ceiling of Abdeen Palace [30] while, in a different occasion, animal glue alone was used in the wall painting of the Royal family graveyards [28] and linseed oil was also detected in the wall paintings of El-Gawhara palace in Cairo [29].

The discovery of mastic resin as a paint medium in the blue background of the inscription is pioneer and could have been applied to obtain different properties of the blue paint, such as mechanical strength and thickness.

Historically, mastic resin has not yet been detected as a paint medium in Egyptian paintings. It used to be applied as a varnish layer in ancient Egyptian funerary artefacts, precisely in the Graeco-Roman period and in the New Kingdom. In the New Kingdom, it was applied as a transparent varnish on top of funerary artefacts and mixed with bitumen or applied over a base of bitumen to imitate the appearance of the black ebony [32]. It was also used in the Graeco-Roman period (2200 BC) on a decorated sarcophagus coffin-lid as reported by Edwards et al., (2007) [33].

7. Conclusions:

The analytical investigation of paint layers applied on sabil-kuttab Umm 'Abbas ceiling was undertaken. Both organic and inorganic constituents were subjected to examination including pigments, media, ground layer and gold layer. The analytical instruments used in this investigation were Raman microscopy, Fourier transform infra red spectroscopy coupled with attenuated total reflection (FTIR-ATR), and optical microscopy. Ultramarine and indigo were the blue pigments identified. Ultramarine was applied in the inscriptions’ background while indigo was identified in the brown paint area. It most probably came from an adjacent blue area in the decorated cornice, not examined in this study. Three red pigments were detected; the first was cinnabar, which was used as a predominant pigment in the red paint area, while red ochre was used in the brown paint area. The mineral hemihedrite, which has not been previously detected as a pigment, was
admixed with cinnabar to reveal the red paint. Cobalt yellow was the yellow pigment identified in this study. It was used along with calcite and gypsum to comprise the yellow paint applied in the cornice. The white pigments identified were barium sulphate and lead white. The former was used as the main pigment to obtain the white paint area of the cornice while the latter was identified in the red paint area. The white ground layer was found to consist of calcium sulfate dihydrate and calcite admixed with animal glue. Real gold leaf was used to decorate the relief stucco motifs and to paint the ornaments in the ceiling. It was applied over an orange bole layer using proteinaceous material, most probably animal glue. The paint medium identified in the cornice decorations was animal glue combined with linseed oil. This finding is not so far from the results achieved in the previous studies performed on wall paintings from Mohammed Ali Era. The interesting finding in this research was the detection of mastic resin in the blue paint sample taken from the inscriptions’ background. This paint layer was completely different from the others applied in the decorated cornice in both texture and thickness. These differences may attribute to the application of mastic resin as a paint medium.

Figure 9: The FTIR spectra of (a) the red paint sample taken from the decorated cornice (b) the reference sample of animal glue (c) the reference sample of linseed oil.
References:


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