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DATING A COPTIC ICON OF ANONYMOUS PAINTER BY SPECTROSCOPIC STUDY OF PIGMENT PALETTE

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ABSTRACT

The scientific dating, using comparative analytical techniques, of an icon which is neither dated nor signed was undertaken. This icon is not attributed to any known painter; therefore one should rely on the pigment palette applied for dating. The icon under study is located in Saint Abanoub church in Samanoud, in Egyptian Delta, representing the equestrian Saint George fighting a dragon. The analytical instruments chosen for this study were; optical microscopy, Raman microscopy and Fourier transform infrared spectroscopy (FTIR). Optical microscopy was used to study the layered structure of the icon which comprised a wooden panel, an imprimatura layer underneath some paint areas, multiple paint layers and a varnish layer. The absence of both the canvas and the white ground layer was apparent. The pigment palette was determined by means of Raman microscopy and the identified pigments were Prussian blue, ultramarine blue, vermilion, chrome yellow, lead white, lithopone and carbon black. These pigments were used solely or combined in complex mixtures to reveal the desired paint shades. The FTIR was used to determine the protected varnish layer as well as the paint medium applied. The identification of chrome yellow and lithopone was the keynote in dating this icon.

KEYWORDS: Raman microscopy, FTIR, Coptic icons, Pigments, Shellac, Linseed oil, dating, Laventine-Melkite, imprimatura, Saint Abanoub, Egypt

1. INTRODUCTION

The dating of paintings is often concerned with confirming their association with a specific painter, or at least a specific date. Eastaugh (2006) reported that the historical practice of an artist, including painting styles and materials used, is not always reliable, due to the presence of imitators and the lack of the complete history of artists' materials. According to Kühn (1973: p. 204), the use of terminal dates of pigments used, which comprise both earliest and latest dates, is the best method for dating paintings. The use of this method may suggest strong, weak or non-existent indications of some pigments or pigment combinations. He also stated that, this method is not effective when pigments with no exact history of use, such as lead white and ochres, were used. In case of Coptic icons, three more problems which may prevent the right and precise dating are apparent. The first is the workshop production, as many famous painters such as Ibrahim el-Nasekh, Yuhanna el-Armani and Anastasi el-Romi ran large workshops, in which the majority of the actual execution of the icons might have been done by assistants and the final retouching and signatures were made by the master painters themselves. The second problem is the possibility of copying some icons by other painters whose icons were mostly with no signatures. The third problem is the repeated use of icons' wooden panels, which was encountered because of the short supply of wood in Egypt (Skalova and Gabra 2003). This phenomenon made the use of radiocarbon dating and dendrochronology is unsuitable for dating icons. Therefore, determining dates of icons should be much relying on the identification of key pigments or techniques whose dates of introduction or disuse are known (Eastaugh 20006). However, the use of pigments over a period of time depends on various considerations. The first is the frequent use of selected pigments in a specific type of paintings. The second is the availability of some pigments in a specific period of time such as Prussian blue which was first manufactured in 1704 and became in use as a pigment in the second quarter of the 18th century (FitzHugh, 2003: p. 20). Meaning that, the detection of these pigments in an icon could set up a scale of time within which the icon could have been executed.

Using lead isotope abundance ratio for dating icons may also be used. ^{210}Pb might provide a useful chronometer for dating the use of lead-containing pigments (Fortunato et al., 2005).

2. THE ICON UNDER STUDY

The icon of Saint George (Mari Girgis) (Fig. 1) is to be found in Saint Abanoub church in Samanoud, in Egyptian Delta. It shows equestrian warrior Saint in Cappadocia (or, according to another tradition, Beirut), fighting the dragon in order to free a young princess (Tribe, 2004).

Figure 1 The icon of "Saint George", showing sampling site numbers.

Saint George is wearing warrior garments (Fig. 2, a) and is mounted on a white horse (Fig. 2, b & c), with the left hand holding the reins. He is holding a spear in his right hand, by which he pierces the dragon beneath his horse (Fig. 2, f). His head, with brown long hair, is surrounded

Figure 2 The detailed images of "Saint George" icon.

by a golden halo with a white dotted outline (Fig. 2, a). To the left, in front of a white castle, a young princess is standing and waving with her right hand (Fig. 2, d). Above in the sky, there is a young figure with wings (Fig. 2, e) which may represent a young Greek believed to have been abducted by pirates from the island of Lesbos, taken to Algeria, and later rescued by Saint George (Tribe, 2004). These figures are depicted against a background of which the upper part is blue and the lower part is yellow. In the right hand side, an Arabic inscription is apparent, saying "Morning planet, the martyr Saint George" "كوكب الصبح, الشهيد ماري جرجس".

The painting technique of this icon, of which the polychrome layer was directly applied on the wooden panel with neither intermediate canvas nor white ground layer, has not yet been studied. The appearance and the touch of the paint layer are different from those executed with tempera technique. This may suggest the application of a different paint medium other than the commonly used egg yolk. The icon condition is fairly good with ageing cracks spread all over the icon (Fig. 2, d-1 & e-1, 2). Deep candle burns are noticeable in the bottom part of the icons' background (Fig. 2, f-1), in addition to the presence of waxy accumulations in some areas.

3. MATERIALS AND METHODS

3.1. Samples and Sample preparation

Paint samples from the very edges of the icons or from damaged areas were taken using a scalpel. The paint samples examined were blue, green, yellow, red, buff tone, white, and black. The fragments 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.

3.2. 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 x100 to x400 depending on the size of the samples.

3.3. 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.

3.4. 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 (Burgio and Clark, 2001; Bell and Clark, 1997).

4. RESULTS

4.1. The icon's layered-structure

The microscopic observation of St. George icon's cross-sections (Fig. 3) allowed the studying of its layered-structure. The polychrome layer was applied unevenly on the wooden support. It was found to consist of either a single paint layer (Fig. 3, a, c, f) or multiple layers (Fig. 3, b, d, e, g). In some areas, below the main paint layer, a preliminary white imprimatura layer was observed (Fig. 3, b-2, f-1, g-1). This layer, which is thick and translucent, originated between the wooden support and the paint layers to facilitate and support their adhesion and to enhance the saturation and luminosity of the superimposed paint layers (Daniilia et al., 2008). Optical microscope images of the unmounted paint samples are shown in figure 4.

4.2. Composition of the imprimatura layer

The imprimatura layer has never been previously identified in Coptic icons. In our case study, it was detected underneath some paint areas, precisely; red, brown, white and black while was absent under the yellow, green and blue paint areas. It comprised calcium carbonate ($CaCO_3$) as revealed with the Raman analysis with its intense sharp Raman band at 1088 cm^{-1} (Sun et al., 2014) (figure 5). This band is assigned to the $v1(CO_3)^{2-}$ symmetric stretching mode. The band assigned to $v4(CO_3)^{2-}$ symmetric stretching mode is found at 713 cm^{-1} (Shen et al., 2006). Calcium carbonate is admixed with a high proportion of an organic binder which made it appears translucent and caused some difficulties in obtaining the Raman spectrum.

The imprimatura normally comprises binding media, such as oil or egg, and may combine with a pigment. This layer was once detected in a Cretan icon dated back to the second half of the 16th century (Daniilia et al., 2008). Lead white, $[Pb(OH)_2.2PbCO_3]$, admixed with blue coarsely glassy particles composed the imprimatura layer, which was only applied under blue and red paint areas (Daniilia et al., 2008). Optical microscope images of the unmounted paint samples are shown in Fig. 5.

4.3. Identification of pigments by Raman spectroscopy

4.3.1. Ultramarine blue

The Ultramarine blue, $[(Na,Ca)_8(AlSiO_4)_6(SO_4.S,Cl)_2]$ (Plesters, 1993), was identified in the blue sample applied in the princess's dress (Fig. 1, sample 1). The Raman bands attributed to this pigment were detected at 543 and 1091 cm^{-1} (Fig. 6, a). The first band is assigned to the symmetric stretching vibration of the S-S bond (Bruni et al., 2001) while the band at 1091 cm^{-1} is its related overtone band (548 x 2) (Marano et al., 2006).

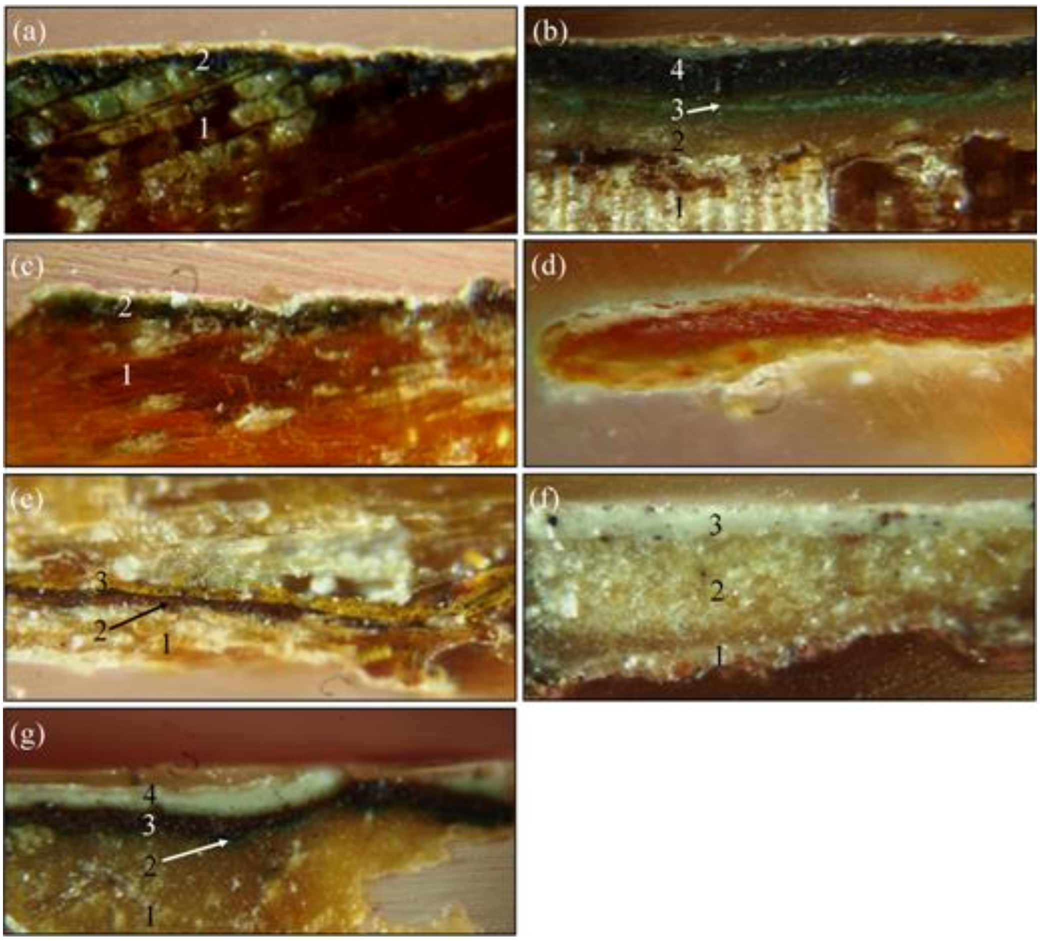

Figure 3 The cross-section images of the paint samples; (a) the blue paint from the icon's background; 1. support 2. blue paint; (b) the blue paint sampled from the Saint's upper garment; 1. panel 2. imprimatura 3. green paint 4. blue paint; (c) the green paint sampled from the dragon; 1. support 2. green paint; (d) the red paint sampled from the chlamys of the Saints' garment; (e) the yellow paint sampled from the horse's saddle; 1. support 2. brown paint 3. yellow paint; (f) the white paint sampled from the castle; 1. support 2. imprimatura 3. white paint; (g) the white paint sampled from the horse's head; 1. imprimatura 2. green paint 3. brown paint 3. white paint. (© by the author and publisher)

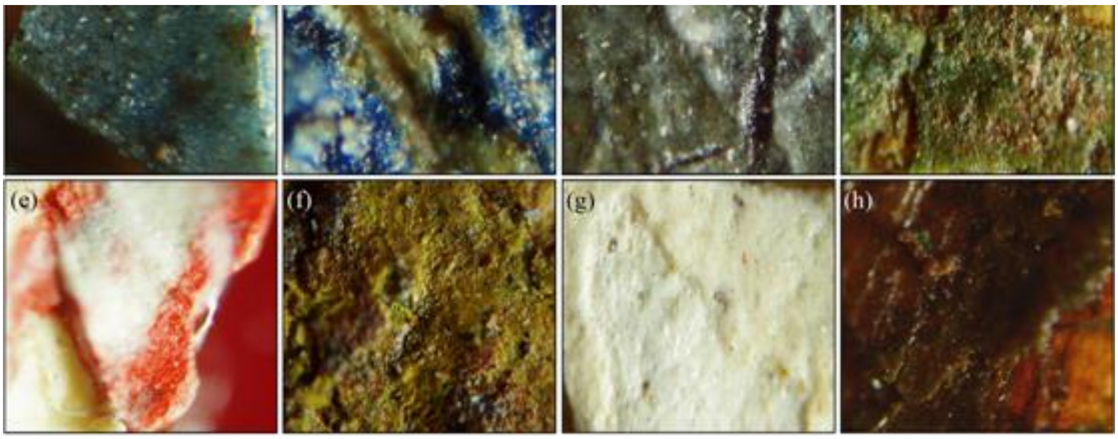

Figure 4 The unmounted paint fragments: (a) the blue paint sampled from the princess' dress; (b) the blue paint sampled from the icons' background; (c) the blue paint sampled from the Saints' garment; (d) the green paint sampled from the dragon; (e) the red paint sampled from the Saint's chlamys; (f) the yellow paint sampled from the horse's saddle; (g) the white paint sampled from the horse's head; (h) the brown paint sampled from the Saint's hair. (© by the author and publisher).

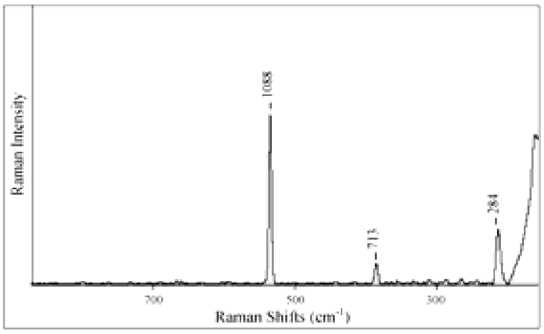

Figure 5. The Raman spectrum of the imprimatura layer.

Ultramarine is a term which refers to a pigment, lazurite, derived from the semi precious stone known as *lapis lazuli*. Other blue minerals may also contained with lazurite such as hauyne $(Na,Ca)Al_6Si_6O_{24}(SO_4)_{1-2}$, sodalite $[Na_8(Al_6Si_6O_{24})Cl_2]$ and noselite $[Na_8Al_6Si_6O_{24}(S0_4)]$, in addition to, mineral impurities like calcite ($CaCO_3$), pyrite (FeS_2), diopside ($CaMgSi_2O_6$), sphene ($CaTiSiO_4$) and zircon ($ZrSiO_4$) (Desnica et al., 2004).

Ultramarine blue is also applied as a term to describe artificially prepared pigments of similar composition to lazurite. Therefore, the words ʻnatural' and 'synthetic' are frequently used to differentiate these two types (Eastaugh et al., 2004: p. 375).

Lapis lazuli was mainly used as a semi-precious stone and a decorative building stone in Dynastic Egypt. However, there are limited cases where lapis lazuli powder was used as a pigment (Berke 2007; Edwards et al., 2004).

Ultramarine blue has not yet been identified in Coptic icons. Instead, Prussian blue, indigo and azurite were the pigments previously identified. Azurite was revealed in a Post-Byzantine Coptic icon dated to the 13th century (Abdel-Ghani et al., 2009a) while indigo and Prussian blue were detected in 18th and 19th century Coptic icons respectively (Abel-Ghani et al., 2012, 2008). Latter applications were also found in a wooden ceiling (Abdel-Ghani and Mahmoud 2013) and a wall painting attributed to Mohammed Ali Era (Darwish 2013).

4.3.2. Prussian blue

In St. George icon, Prussian blue pigment was detected in three paint samples, of which two are blue (figure 1 sample 2 and 3) and the third is green (Fig. 1, sample 4). It was established by its characteristic Raman bands at 530, 2091, 2117 and 2152 cm^{-1} with its strongest band at 2152 cm^{-1} ascribed to ν(CN) (figure 6, b and figure 6, c). Lead white, with its well-defined band at 1049 cm^{-1}, was found in admixture with Prussian blue in the blue samples to give a lighter shade (Fig. 6, b). The green sample was accompanied with chrome yellow as confirmed by the characteristic bands at 356 and 835 cm^{-1} (Fig. 6, c).

Two bands arise at 276 and 988 cm^{-1} were detected in the three spectra which may attribute to the white pigment lithopone ($BaSO_4$ + ZnS). Prussian blue was normally sold with fillers (Berrie, 1997: p. 194) such as; alumina, quartz and calcium carbonate (Ionescu et al., 2004). In this case study, the presence of lithopone was of interest as it could be added either as filler or as a white pigment. However, with the presence of lead white, being filler might be more sensible.

Prussian blue, hexacyanoferrate $Fe_4[Fe(CN)_6]_3.14\text{-}16H_2O$, is an artificial pigment that has been called the first of the modern pigments. Two formulae of Prussian blue are given; $KFe[Fe(CN)_6]$ and $Fe_4[Fe(CN_6]_3$. Modern formulations are $M(I)Fe(III)Fe(II)(CN)_6.nH_2O$, Where M can be K, Na or NH_4 and n = 14-16 (Eastaugh et al., 2004: 308-9). The pigment is made by mixing ferrous sulfate, sodium ferrocyanide and ammonium sulfate with an oxidizing agent such as potassium bichromate and sulfuric acid. The resulting pigment is deep blue with a fine grain size, which is washed, filtered and dried (Eastaugh et al., 2004: p. 308-9; Gettens and Stout, 1966: p. 149).

Prussian blue was first invented in Germany in 1704 and was commercially produced by 1724 (FitzHugh, 2003: p. 20; Berrie, 1997: p. 193). It was used in Egyptian paintings not a long time after its production date (Abdel-Ghani et al., 2009a). It has also been detected in Coptic icons dated to the 19th century. Prussian blue has been applied in Greek icons; as a main paint layer in an icon dated to the 18th century (Burgio et al., 2003) and as a new addition on an overpainted icon dated to the 20th century mixed with chrome yellow in the form of chrome green (Daniilia et al., 2002).

4.3.3. Vermilion

Cinnabar (mercury (II) sulfide, α-HgS) was the red pigment occurred in the studied icon. It revealed its three characteristic Raman bands at 254, 286 and 345 cm^{-1} of which the band at 254 cm^{-1} is assigned to the Hg—S stretching vibration.

Vermilion was extensively found in various paint areas. For instance, in the red paint sample (Fig. 1, sample 5), vermilion was found either solely (Fig. 6, d) or admixed with lead white in lighter red areas. It was also identified along with carbon black (Fig. 7, b) (1558 and 1320 cm^{-1}) in the brown paint, sampled from the Saint's hair (Fig. 1, sample 6). The same combination was identified as an under paint layer (Fig. 3, g) in the white paint sample taken from the horse's head (figure 1, sample 10).

Admixed with chrome yellow pigment (Fig. 7, a), lead chromate (VI) ($PbCrO_4$), (358, 404, 606, 803, 839 cm^{-1}), vermilion was also applied to reveal the buff tone of the Saint's neck (Fig. 1, sample 7).

Cinnabar is a soft red mercury (II) sulfide mineral with ideal composition of α-HgS, although impurities of bitumen and members of the clay minerals group are often present (Eastaugh et al., 2004). It was introduced to the Egyptian palette in the Greco-Roman period (Lucas 1962: p. 348) and has been widely used in several artefacts (Edwards et al., 2004). Vermilion is the name given to the red artist's pigment based on the artificially made mercury (II) sulfide which commenced to be used in Arabic countries as early as the eighth century. It was reported that Jaber, the Arabic alchemist, mentioned a red compound formed by the union of mercury and sulfide (Gettens et al., 1993). To be used as a pigment, the mineral was broken into small pieces and ground in a small mortar. Then it was washed several times to get rid of the impurities. There are two ways to prepare the artificial analogue of cinnabar "vermilion". One of these is the dry process in which 100 parts by weight of mercury are added to 20 parts of molten sulfur in an iron pan to produce black mercuric sulfide which is then transferred into earthenware retorts and heated to above 580 ◦C. The sublimated product is condensed on earthenware pots and it converted into a red crystalline mercuric sulfide (α-HgS) which is then heated with a strong alkali solution to remove any free sulfur. The last step is to wash and grind it under water and it is ready as a pigment.

In Coptic icons, cinnabar is the most widely used red pigment which was used by its own or in admixture with red lead. This combination was used either to increase the orange shade of the vermilion or to reduce the cost, since vermilion is the most expensive red pigment. It was sometimes accompanied with lead white to reveal the buff tone (Abdel-Ghani et al., 2012).

4.3.4. Lead chromate

Two detections of chrome yellow, lead chromate ($PbCrO_4$), in this icon were found. The first was in the yellow paint taken from the horse's saddle (figure 1, sample 7) where it was solely applied (figure 7, c). The second detection was found in the buff tone paint sample executed in the saint's neck (figure 1, sample 8) admixed with vermillion (figure 7, a). It gave its featured Raman bands at 358, 400 and 838 cm^{-1} in which the intense band at 838 cm^{-1}, located in the CrO_4 stretching region, is assigned to the v1 symmetric stretching vibration. The bands at 358 and 400 cm^{-1} are assigned to v4 and v2 bending modes (Frost 2004).

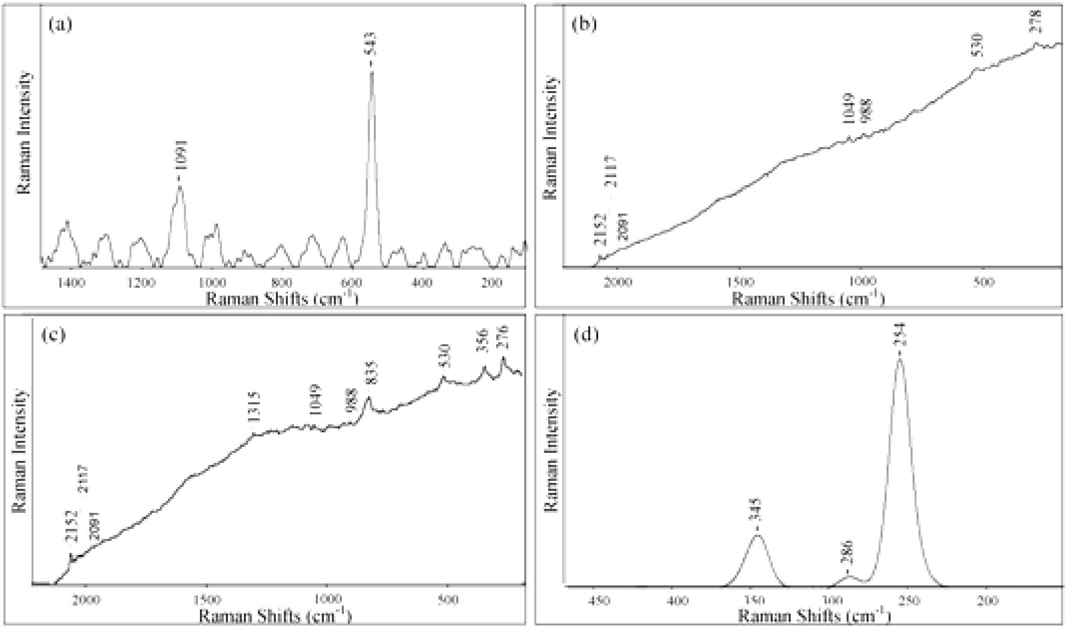

Figure 6. The Raman spectra of: (a) the blue paint sampled from the princess's dress (b) the blue paint sampled from the icon's background (c) the green paint sampled from the dragon (d) the red paint sampled from the chlamys of Saint George.

It is well known that chrome yellow pigments are those which their composition is lead chromate (VI) ($PbCrO_4$), or lead chromate sulfate ($PbCrO_4.xPbSO_4$) (Eastaugh et al., 2004: p. 99). The colour of these pigments varies from light to orange-yellow depending on the amount of lead sulfate ($xPbSO_4$). The natural analogue of chrome yellow pigments is the rare mineral crocoite ($PbCrO_4$) which was first recognized by Lehman in 1766 (Parkes, 1967: 866). This was first synthesized in 1804 and was used as a pigment from the second quarter of the 19th century (Kühn and Curran, 1986: p. 188).

Commercial lead chromate pigments according to the American Society for Testing and Materials 1977 (ASTM 211-67) comprises three different types. These types are classified according to their lead chromate ($PbCrO_4$) content. It is reported that when $PbCrO_4$ present in the pigment is >50%, the lead chromate is type I primerose pigment, when $PbCrO_4$ is >65%, lead chromate is type II "lemon or light pigment and when $PbCrO_4$ is 87%, lead chromate is type III "medium" pigment.

The pigment identified in this icon is a chrome yellow type which consists of lead chromate ($PbCrO_4$) with no additions. Other types of chromate pigments were previously identified in Egyptian artefacts. For instance, chrome orange, which is a combination of lead chromate and lead oxide ($PbCrO_4.PbO$), was identified in a 19th century Coptic icon (Abdel-Ghani et al., 2008) and the mineral hemihedrite, $ZnPb_{10}(CrO_4)6(SiO_4)_2F_2)$, was detected in a wooden ceiling dated to 1867 (Abdel-Ghani and Mahmoud 2013).

4.3.5. Chrome green

Chrome green was the green pigment identified in the green paint applied in the icon as a main paint and as an under paint. It was revealed in the paint sampled from the green dragon (Fig. 1, sample 4) and as an under paint of the blue of the saints' upper garment (Fig. 1, sample 3). The green pigment in this icon is not a green chromophore but a mixture of chrome yellow ($PbCrO_4$) and Prussian blue, $Fe_4[Fe(CN)_6]_3$, known as chrome green (Fig. 6, c).

Chemically, chrome green is a composite pigment consisting of a combination of chrome yellow and Prussian blue. In some instances, barite ($BaSO_4$) and gypsum ($CaSO_4$. $2H_2O$) may also be detected (Desnica et al., 2003). In our sample, the Raman bands attributed to Prussian blue were recognized at 530, 2092, 2117 and 2147 cm^{-1} and the bands of chrome yellow were found at 356 and 835 cm^{-1}. Neither barite nor gypsum was detected in these samples. Raman bands were identified at 966 and 276 cm^{-1}. These bands are attributed to lithopone, which is a mixture of zinc sulphide and barium sulphate ($ZnS + BaSO_4$). It was first synthesized in 1850 and became commercially available in 1874. Lead white (1049 cm^{-1}) was also revealed in this green paint.

Chrome green was previously identified in two 19th century overlapping Coptic icons (Abdel-Ghani et al., 2008). The lead chromate detected in these icons was found to be chrome yellow deep; lead (II) chromate admixed with lead oxide, $PbCrO_4.PbO$.

The recipe for preparing chrome green is stated by Salter in 1869. 'To a solution of Prussian blue in oxalic acid, first chromate of potash is added, and then acetate of lead'; he then addresses the deterioration problem just mentioned and adduces a method of making similar compound pigments substituting 'chloride of barium or nitrate of bismuth' for the lead acetate commonly used thus making 'superior and more permanent chrome greens' (Eastaugh et al., 2004: 97).

4.3.6. Lead white

Two white paint samples were analyzed in this study. The first was sampled from the column of the castle (Fig. 1, sample 9) and the second from the horse's head (Fig. 1, sample 10). The identified pigment in both samples was found to be lead white [basic lead (II) carbonate (hydrocerussite), $[Pb(OH)_2.2PbCO_3]$, which showed its Raman band signature with a characteristic band at 1049 cm^{-1} (Fig. 7, d).

Lead white was the common pigment used in Coptic icons, in addition to some other white pigments; such as calcite, dolomite, gypsum and barite that were used as fillers. The advantage of lead white on the other whites is its high covering power (Edwards and Benoy, 2006).

4.3.7. Lampblack

Lampblack, amorphous carbon [C], was the black paint applied in this icon (figure 1, sample 11). It is characterized with its broad bands located approximately at ~1590 and 1320 cm^{-1} (not shown), corresponding to the G and D modes of sp2 and sp3 hybridised carbon (Edwards and Benoy, 2006). Lampblack was the black pigment used in Coptic icons in most cases (Abdel-Ghani et al., 2012, 2009a, 2008). However, in some instances, pyrolusite, manganese dioxide MnO, was used instead, where a pigment with higher covering power was needed (Abdel-Ghani 2009: p. 179). According to the colour measurements, manganese dioxide has more chromaticity than other black pigments including carbon black (Guineau et al., 2001).

4.4. Identification of the organic constituents by FTIR spectroscopy

4.4.1. The varnish layer

The varnish layer was yellow and brittle, from which a tiny sample was easily collected for analysis.

The FTIR spectrum (Fig. 8, a) showed the characteristic absorbencies of a natural resin. It comprised bands at 3395 cm^{-1} due to O–H stretching bands, 2919 and 2850 cm^{-1} attributed to –CH2/CH3 stretching modes of the hydrocarbonated chains, 1703 cm^{-1} from C=O stretching of carboxylic acid and 1621 cm^{-1} from C=C stretching. Additional band at 1461 cm^{-1} attributed to the bending or scissoring of the CH2 groups and 1385 cm^{-1} attributed to the asymmetric and symmetric stretching vibrations of the CH3 groups (Favaro et al., 2005). The band at 1171 cm^{-1} is suggested to be a characteristic sign of shellac resin photo-degradation (Azémard et al., 2014). The achieved spectrum matched well with the reference spectrum of shellac resin (Fig. 8, b) (Derrick et al., 1999, p. 190).

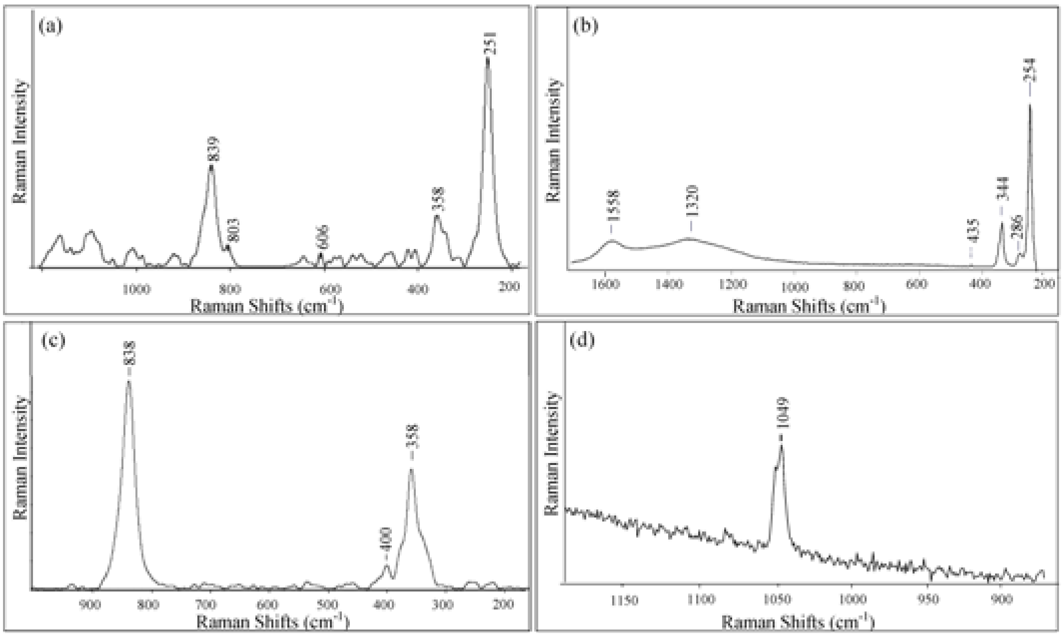

Figure 7. The Raman spectra of: (a) the buff tone paint sampled from the Saint's neck (b) the brown paint sampled from the Saint's hair (c) the yellow paint sampled from the horse's saddle (d) the white paint sampled from the castle.

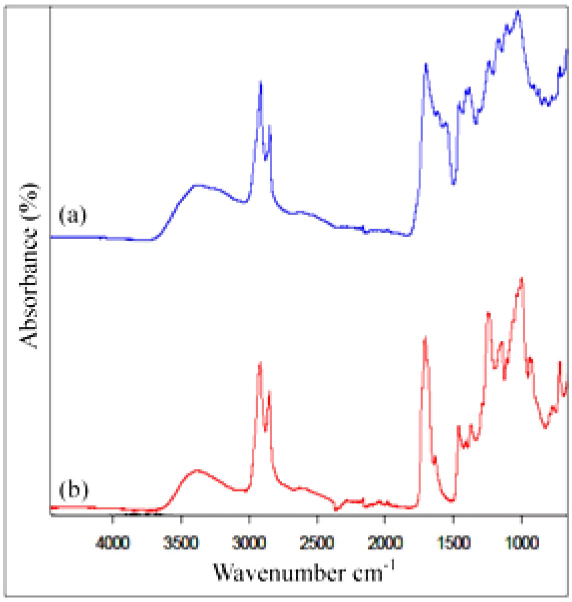

Figure 8 The FTIR spectra of (a) the original varnish (b) the shellac resin reference sample.

Shellac is a sesquiterpenic resin secreted by a scale insect Laccifier lacca, Coccus lacca or tacchardia. The crude lac is gathered from the tree (sticklac) which is then crushed and graded. The largest particles called seed-lac from which the best varnish quality is made (Gettens & Stout, 1996: p. 60). Stick-lac contains about 70-80% of resin, 4-8% of colouring dyestuffs and 6-7% wax (Mills and White, 1994: p. 116). In nature, lac resin comprises polyester structure but under chemical treatment for commercial use it gives aliphatic acids such as aleuric and butolic acids and acyclic acids derived from sesquiterpens such as jalaric and shellolic acids (Marinach et al., 2004).

As a varnish, shellac resin has not yet been identified in Coptic icons. Colophony, pinaceae resin, which was sometimes accompanied with vegetable oil and beeswax, was the varnish normally applied. It was identified in a 13th century Coptic-Byzantine icon (Abdel-Ghani et al., 2008), two 18th century and two 19th century Coptic icons (Abdel-Ghani et al., 2012; 2009a).

4.4.2. The paint medium

Before performing the FTIR-ATR analysis, a surface of the green paint fragment (Fig. 1, sample 4) was carefully treated with organic solvents to remove the varnish layer applied over the paint. The spectrum achieved (Fig. 9, a) shows the main bands of drying oils. It comprises; the sharp carbonyl band (vC=O) of the triglyceride ester linkage at 1708 cm^{-1}, due to the half esters of the dicarboxylic acids associated with the partial oxidative degradation of fatty acid chains during aging (Mannino et al., 2013). This band is normally identified at ~1750 cm^{-1}. However, due to admixture with some pigments, the carbonyl band may be shifted towards lower wavenumber (Derrick et al., 1999: p. 103). The two methylene bands of symmetric and antisymetric stretching bands attributed to fatty acids were found at 2919 (asymmetric stretching CH2) and 2850 cm^{-1} (symmetric stretching CH2) and the bands assigned to C-O bands was identified at 1165 and 1103 cm^{-1}. The absorption band at 1584 cm^{-1} may be attributed to carboxylates formed during the degradation reaction of the oil with metal cations from the paint layers (Egel and Simon, 2013). Fig. 9 shows the FTIR spectra of both the green paint sample (Fig. 9, a) and the reference sample of linseed oil (Fig. 9, b).

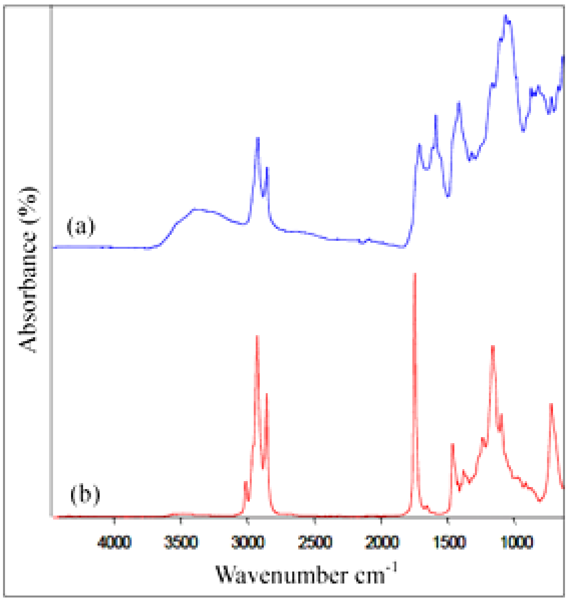

Figure 9 The FTIR spectra of (a) the paint medium (b) the linseed oil reference sample.

Chemically, vegetable oils are classified into three groups; drying oils which dry to a solid film when exposed to air, semi-drying oils which form tacky films and non-drying oils which do not form viscous material when exposed to air. Among all oils found in Egyptian artifacts, linseed oil (Serpico and White, 2000: p. 413) and flax seed oil (Ali and Darwish 2011) are the only detected oils in paint matters.

The properties of the drying oils depend on their chemical composition. The main component of oils is triglycerides, small amount of diglycerides, saturated and unsaturated fatty acids (Serpico et al., 2000: p. 412; Polard et al., 2007: p. 150).

Detection of vegetable oils as paint media in Coptic icons is pioneering, as egg yolk is the commonly used paint medium (Abdel-Ghani et al., 2012, 2009a, 2008).

4.4.3. The waxy material

Quite thick, soft and easily scraping layer was found on the paint layer in some areas. FTIR analysis for this layer was performed and FTIR spectrum revealed (Fig. 10, a). The predominant absorbencies of this spectrum were the methylene bands at 2916 and 2848 cm^{-1} which assigned to the stretching vibration of asymmetric and symmetric vibrations of C–H groups. In addition, two strong bands at 1735 and 1710 cm^{-1} attributing to the stretching carbonyl ester and acid groups, and two bands at 729 and 1462 cm^{-1} of the rocking vibration of methylene groups (rCH2) (Ganitis et al., 2004). These absorbencies are similar to those of beeswax (figure 10, b). This result agrees with the observation and the softness of the analyzed material.

This wax layer could not be a part of the varnish, as it only covers some scattered areas located at the bottom part of the icon. Accordingly, it could be suggested that,

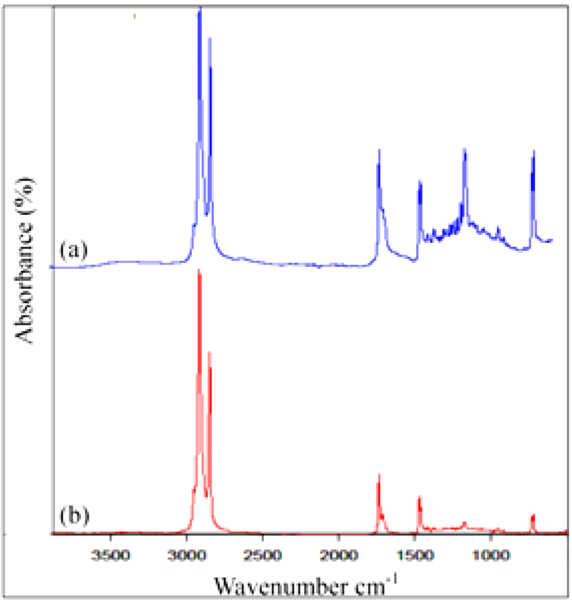

Figure 10 The FTIR spectra of (a) the waxy substance (b) the beeswax reference sample.

beeswax was present either as a result of candle lighting in front of the icon in praying ceremonies with the absence of a glass protection or as an earlier conservation treatment product.

5. DISCUSSION

In accordance with the pigment palette determined in Saint George icon (Table 1), the icon could be positioned in the last quarter of the 19th century. In the identified pigment palette, some of the pigments have been used since the Greco-Roma period, such as α-HgS, lead white and Lapis lazuli. Artificial ultramarine was first reported in 1827 and was extensively used as an artistic pigment in the second half of the 19th century (the artificial was much cheaper than the natural, meaning that the icon was painted before 1827). Prussian blue was first invented in Germany in 1704 and was commercially produced by 1724 (FitzHugh, 2003: p. 20; Berrie, 1997: p. 193). Chrome pigments were discovered in Paris in 1797 and were well recognised as pigments around 1804 (Castro et al., 2004). It is supposed that the industrial production of chromate pigment pigments started ten years later with the discovery of the chrome mineral, chromite ($FeO.Cr_2O_3$), in France.

Chrome yellow has been detemined in Coptic icons in 1846 (Abdel-Ghani et al., 2009a) in Anastasi el-Romi's icons. The pigment lithopone, which was accompanied Prussian blue in the blue and green paint samples was commercially produced in 1874. This may verify the attribution of the icon to the last quarter of the nineteenth century.

The painting technique, which is different from the traditional one, raises another argument. The traditional technique comprised from bottom to top; wooden panel, canvas layer, white ground layer, polychrome layer executed with egg tempera and varnish layer of Pinaceae resin. In the icon under study, the canvas and the white ground layer were absent and an imprimatura layer was detected underneath some paint areas. In addition, both the paint medium and the varnish layer were completely different from the previously identified.

Skalova and Gabra (2004: p. 144) mentioned that Anastasi el-Romi, the Greek icon painter worked in Egypt between 1836 and 1871, was the last painter who maintained the traditional iconography and technique of Coptic icon painting. After the mid-nineteenth century, a new school, Levatine-Melkite, was established by incoming Levantine, Greek and Armenian icon painters from Jerusalem; such as Yuhanna Salib Al Urushalimi, Yussef Dimitry Al-Rumi and Nicola Tadrous Al-Qudsi. In addition, some Coptic painters imitated them and copied their painting style and technique. The Priest Yohanna and Mina Bastawly were considered from those painters.

To sum up, according to the artistic and the technical styles, as well as the materials used in this icon, it could be suggested that the icon of Saint George was painted at the end of the 19th century by either a Levantine-Melkite painter or a local imitator who copied their characteristic style.

Table 1: the examined samples; their colour, location, structure, composition and Raman shifts

Sample colour	Sample location	Structure	Composition	Raman shifts (cm^{-1})
Blue	Saint's dress		Ultramarine blue	548, 1096
Blue	Icon's background		Prussian blue & lead white & lithopone	520, 2091, 2117, 2152 & 1049 & 276, 899
Green	Dragon		Prussian blue & chrome yellow & lead white & lithopone	520, 2091, 2117, 2152 & 358, 400, 838 & 276, 899
Red	Saint's chlamys		Cinnabar	254, 286, 344
Buff	Saint's face		Cinnabar& chrome yellow	254, 286, 344 & 358, 400, 838
Brown	Saint's hair		Cinnabar & carbon black	254, 286, 344 & 1320, 1558
Yellow	Horse's saddle	(1) Yellow (2) Brown	(1) Chrome yellow (2) Cinnabar & carbon black	(1) 358, 400, 838 (2) 254, 286, 344 & 1320, 1558

White	Castle	(1) White (2)Imprimatura	(1) Lead white (2) calcium carbonate	(1) 1049 (2) 284, 713, 1088
White	Hours' head	(1) White (2) Brown (3) Green (4) Imprimatura	(1) Lead white (2) Cinnabar & carbon black (3) Prussian blue & chrome yellow & lead white & lithopone (4) calcium carbonate	(1) 1049 (2) 254, 286, 344 & 1320, 1558 (3) 530, 2091, 2117, 2152 & 356, 835 & 1049 & 276, 899 (4) 284, 713, 1088
Black		(1) Black (2) Imprimatura	(1) Carbon black (2) calcium carbonate	(1) 1320, 1558 (2) 284, 713, 1088

6. CONCLUSIONS

Scientific dating of a Coptic icon which is neither signed nor dated was undertaken by means of vibrational spectroscopic techniques, namely; Raman and FTIR analysis. The icon is located at Saint Abanoub church in Samanoud, in Egyptian Delta and represents the equestrian Saint George fighting a dragon.

The pigments identified were ultramarine blue, Prussian blue, chrome green, vermilion, lead chromate, lead white, lithopone and carbon black. The medium used was found to be linseed oil and the varnish is shellac resin. The layered structure comprises wooden panel on which the polychrome layer was directly executed with the presence of the imprimatura layer underneath some paint areas. Waxy accumulation found on the bottom part of the icon was analyzed and found to be bees wax.

According to the pigments, the medium and the varnish applied on this icon, in addition to the technique of application, it could be suggested that the icon dated to the end of the 19th century and was painted by a Levatine-Melkite painter or a local imitator.

The icon of Saint George could be considered as the first icon to be analyzed from its type. Therefore, further work should be carried out on similar icons, in order to set the technique and materials commonly used in this type of icons.

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