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Archaeometric Investigation of A Triptych Coptic Icon, El-Surian Monastery, Egypt

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HIGHLIGHTS

- The triptych icons are unique icons called traveling icons.
- Several microscopes were used to examine and study the layers of the icon such as stereo, digital and SEM microscopes.
- Different analytical methods such as XRD, Raman, FTIR and SEM-EDX were complementary to each other and helped in identifying the different components of the icon.
- The use of shellac as a varnish, calcium carbonate as a preparation layer, barium chromate, Prussian blue, titanium white and cadmium yellow as pigments are strong results that are not commonly used in icons.
- Spectroscopic studies dated the icon to the end of the 19th century and the beginning of the twentieth century.

GRAPHICAL ABSTRACT

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ABSTRACT

The triptych icon is a unique type of Coptic icons, that has rarely been studied before. The archaeometric investigation helps to reveal the triptych icons importance, composition of the pigment palette and to monitor the manifestations of deterioration to determine appropriate treatment. A triptych icon was chosen from El-Surian monastery in Wadi El-Natron. Cracks, dimming, yellowing and parts loss indicate aging processes and chemical interactions with environmental conditions. The examination techniques are used to determine the stratigraphy of the icon.

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The spectroscopic methods used were Raman spectroscopy (RS), Attenuated total reflectance Fourier transform infrared (ATR-FTIR), Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) and X-Ray diffraction (XRD), which have revealed the basic composition and characteristic bands of pigments and the type of protective varnishes applied. The painting technique was tempera style applied on Abies alba (Silver Fir) wood and cotton canvas, the ground layer was calcium carbonate mixed with animal glue. The medium of pigments was egg yolk. The icon also contained some pigments that were rarely combined with each other, such as Prussian blue, ultramarine, barium chromate, titanium dioxide and cadmium yellow. The shellac was used as a varnish. Spectroscopic studies of pigments helped in the dating process and it was concluded that the icon dated back to the late 19th century.

1. Introduction

The icon, in its secret meaning, is a message that plays an effective educational role in the devotional life of the Church [1]. It is a spiritual church philosophy that helps to consolidate faith and knowledge in the people and in which the educated seek what the literature fails to express [2], as the illiterate who is unable to read books can mention the courageous deeds of the Saints [3]. In the second century AD, the term "iconography" appears, which means the artist's treatment of a subject[4].

The icon was not just surfaces to be painted on, but rather several layers executed in a certain style, with specific materials. The wooden support is the main panel for the icon and it is made of good quality wood, and is equipped with the correct scientific method, where it is treated and reinforced with strips or wooden beams that are fixed from the back with nails or strong glue [5]. Wooden Icons have been executed also on two continuous panels (Diptychs) or three continuous panels (Triptychs).

The artist stretched a layer of canvas, whether it was of linen, hemp or cotton. It was fixed with glue on the wooden support, to protect the icon layer from separation, otherwise these layers might fall, and completely damage the icon. Then the artist place the preparation layer to prevent the wooden support from absorbing the chromatic medium, which must be present in order to perform its function of binding the pigment granules[6]. Then a layer of pigment mixed in medium was added and finally the varnish.[7]

The icon took many different forms [8], as we found some transverse beam panel icons and some rectangular icons. Some icons had a moving cover to protect them when they were moved from one place to another [9]. In the fifth and sixth centuries AD, there were also triptych icons, which were ordinary icons with two wings fixed to the icon itself by moving axes (hinges). There were also four-part icons consisting of four parts, three moving on axes, while the fourth part was fixed [10] .

From all the above, it can be said that: the triptych icon: it is an icon consisting of three pieces [11], the middle piece is the central piece, which represents the largest icon, and on both sides are two wooden slats bearing other drawings that close in the middle piece (enveloping it) in order to protect it (Fig.1).

One of the names given to the diptych and triptych icons is traveling icons, because they were distinguished by the ease of transferring them from one place to another and preserving their drawings and colors [12].Artists used to leave their signatures on it. But this research will contain an icon that is undated and not attributed to any known artist.

The triptych icon will be studied in terms of the method of implementation and the technology of industry, and because these icons were not spared from the damage factors that left their fingerprints on them, we will monitor the manifestations of damage to one of the pieces using the latest examination methods that are compatible with this type of archaeological materials, as well as the latest analytical methods to identify the composition and basic structure of the components of the icon so that we can determine the most appropriate methods of treatment and maintenance.

The study aims to determine the age of the icon through spectroscopic analysis of its pigments. By identifying these pigments and understanding their usage history, it is possible to ascertain the icon's age. This method is

particularly effective for icons as it does not require large samples and can date artifacts from recent centuries.

2. Materials and Methods

2.1. Materials

Icons are rich objects with different materials and different chemical compositions. The characteristics of the materials used in the painting are studied by the method of combinatorial analysis. Imaging microscopy is considered a versatile method that provides information about the morphology and topography of layers without destroying the sample. Infrared and energy dispersive x-ray spectroscopy are spectroscopic destructive methods based on material chemical structure [13].

2.1.1. Icon description

The icon under study, located in the well-known monastery of the Virgin Mary (El-Surian monastery), is a triptych with a central scene depicting the annunciation flanked with two horsemen on each side wing (or side) of the triptych. The central icon of the annunciation, in which the virgin Mary is shown standing to the right of the icon wearing a blue robe and above it a scarlet robe, her hands in a position of reverence, and in front of her there is a wooden table topped by an open book. The other half of the icon is the angel Gabriel who announced the birth of Christ to the Virgin, surrounded by clouds. Above their heads, there is the dove of the holy spirit whose rays are directed at the head of the virgin Mary.

The right icon is of Saint Demetrius riding a horse with spear in his hand and stabbing a black man lying on the ground, while the left icon is of Saint George holding a spear and stabbing the dragon (Fig. 1.a**)**. Metal chains connect the two icons to the central icon. The central icon consists of two wooden panels assembled together, while both icons were made from one piece of wood. To prevent friction, the middle icon contains a wooden cushion on which the two wings rest when closing.(Fig. 1b**).** The Coptic writings on the icon have been monitored and translated (Fig.2**).**

2.1.2. Historic Samples

Very small samples were taken from the edges of the icon or from damaged areas using a scalpel, i.e. wooden samples, canvas, red pigment, blue pigment, brown pigment, black pigment, yellow pigment, and white pigment.

The signs of damage to the icon were monitored (Fig.3a) and samples were collected from all the components of the icon in order to obtain all the information about the object and to build a conservation process on a systematic scientific basis (Fig.3.b).

Some samples were mounted in epoxy resin, polished and prepared for examination.

2.2. Methods

2.2.1. Optical Microscope (OM)

The sections of wood were observed under transmitted light using Optical Microscopy (Italy) equipped with Best Scope digital camera. (The Identification Procedures were conducted by Wadjet for documentation and investigation of cultural heritage).

Samples and cross-sections were studied using a Carl Zeiss C-2000 Stereo Microscope equipped with a digital camera, at The Egyptian Italian Laboratory, Faculty of Archaeology, Fayoum University. It has a 35° binocular tube for convenient sample viewing while providing room for specimen manipulation.

Working distance: 110 mm when no additional objectives are used; 31 to 285 mm when additional objectives are used. It features a built-in magnification changer for manual adjustment with a 1 to 7 continuous zoom range. It is mounted on a heavy metal base stand with a 1 1/4 in. diameter (32 mm) post for optical adjustment.

2.2.2. Field Emission Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (FESEM-EDX)

Microscope (Quanta 3D 200i) conservation lab, Grand Egyptian Museum GEM-CC).

Micrographs were taken using an EDX unit (Energy Dispersive X-Ray Spectrometer,

EDAX Thermos Scientific Pathfinder). The voltage of 20 KV, for the purpose of pigment identification in each pigment layer, and the samples were examined at an accelerating elemental composition was determined using the prepared cross-sections and samples

Fig. 1. The selected undated triptych icon under study a) The triptych icon's two sides are opened b) Th triptych icon's two sides are closed.

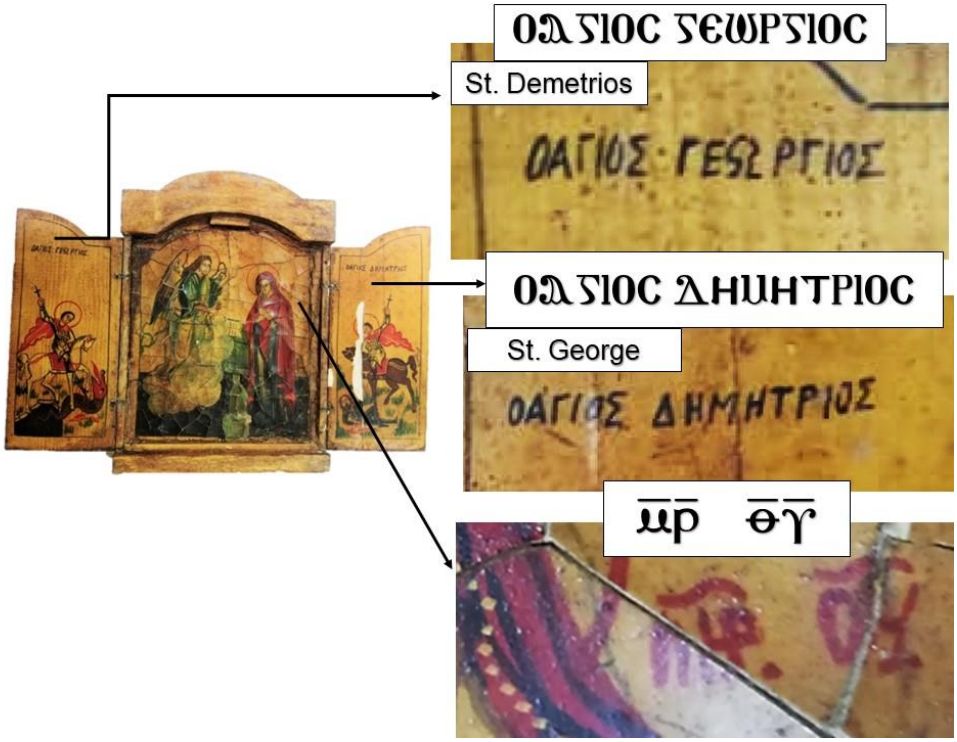

Fig. 2. The Coptic writings on the icon.

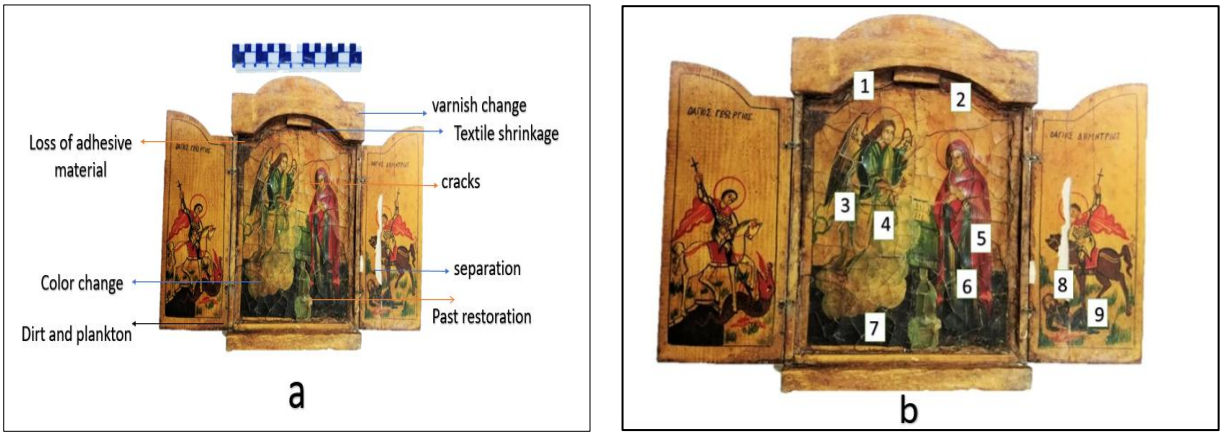

Fig. 3. a) Icon damage symptoms b) samples location.

2.2.3. Raman Spectroscopy (RS)

The Senterra Raman *Spectroscopy* (Bruker), from the Supreme Council of Antiquities-Projects Sector, Lazoghly, was used in the current work, consisting of a confocal Raman microscope (20 × objective lenses) with a spectral footprint of about 2 µm, 4 cm^{-1}. The spectral resolution and the used laser wavelength are both 785 nm.

All compounds were identified by comparing their characteristic vibrational spectra with those in previously published databases. This method is a non-destructive analysis that can identify the compounds of pigments used by the artist and thus reconstruct his palette [14] .

2.2.4. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Sample FTIR spectra were obtained using a Bruker FTIR spectrometer equipped with ATR, model VERTEX 70. at the Supreme Council of Antiquities-Projects Sector, Lazoghly. The IR spectra, in absorbance mode, were obtained from the specimens using an aperture of 20–100 µm, in the spectral region of 600 to 4000 cm^{-1}. The resolution is 4 $cm^{-1}$and the number of additional scans added per spectrum is 64.

The sample's spectra were measured with an ATR (Attenuated Total Reflectance) accessory, which has a crystal diamond, and compares the resulting spectra of a standard without sample preparation. The FTIR was used to determine the protected varnish layer as well as the paint medium applied[7] **.**

2.2.5. X-Ray diffraction (XRD)

Powder X-Ray diffraction (NIS) at the National Institute of Standards was used to identify the different crystalline phases present in pigments and preparation layers and the compounds of pigments. X-ray powder diffraction (XRD) patterns were recorded with a Panalytical x'pert pro diffractometer (Malvern, GH Eindhoven, The Netherlands) with Cu Kα radiation Empyrean, Malvern Panalytical. The condition applied was Step Size 0.0130 2Th, Scan Step Time 3.5700 s, Measurement Temperature 25 °C, Anode Material Cu, K-Alpha 1.54060 Å, K-Alpha2 1.54443 Å, K-Bet 1.39225 Å, K-A2 / K-A1 Ratio 0.50000, Generator Settings, 40 kV, 30 mA.

3. Results and discussion

Traditionally, icons are comprised of five layers: a wooden panel, canvas layer, ground layer, paint layers, and a varnish layer [15].

By examining the cross sections of the studied icon (Fig.4), it was found that the middle icon consists of five layers. The artist placed two preparation layers, and the pigment layer was a thin layer. By examining the sample that was taken from the top of the icon, it was found that the preparation layer was weak and the pigment layer was absent, as the artist was not able to distribute the layer well on the sides. In the case of the right

icon, the absence of the canvas layer was apparent, as the preparation layer was applied directly to the wood.

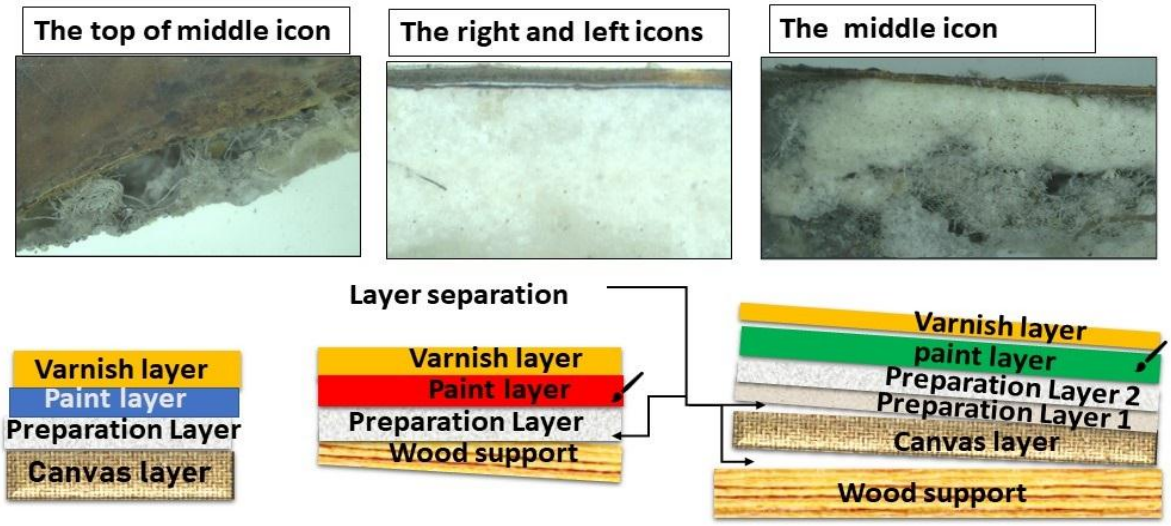

Fig. 4. Layered structure of cross-sections of the triptych icon.

3.1. Wooden Sample

The wooden panel served as a support for other components of icons, and it was frequently made from locally available wood [16]. Thin Sections of the wooden panel were examined microscopically to identify the type of wood used in the panel according to Hoadley [17] . The microscopic investigation indicated that the wooden panel is made of *Abies alba* (Silver Fir).

Transverse section (TS)

Growth ring boundaries conspicuous, generally abrupt, rarely gradual transition from earlywood to latewood- No resin canals.

Radial longitudinal section (RLS)

Ray tracheids commonly present- smooth ray tracheid cell walls. Distinctly pitted end walls of ray parenchyma cells. Distinctly pitted horizontal walls of ray parenchyma cells.

Tangential longitudinal section (TLS)

Rays exclusively uniseriate- Average ray height 15 to 25 (sometimes up to 40) cells. The examination of the wooden panel under SEM pointed out the most characteristics of wood and the perfect condition of the panel (Fig. 5).

3.2. Canvas Sample

Portable digital optical microscopy is a very useful, non-invasive method to examine and document materials' characteristics and to capture the texture and defects of a surface [18]. Canvas Fibers of the icon are observed using a Stereo Microscope to investigate the canvas fibers while the small fragments were investigated using SEM. SEM micrographs of the canvas show that the canvas is comprised of cotton fibers. (Fig. 6).

Microscopic examination of the icon canvas also revealed the differences in the surface morphology related to the materials used and their combination with fibers. The surface appears rough due to the absorption of media.

The presence of a network with cracks and micro-cracks on the canvas may be the result of various deterioration factors that cause discoloration that is more distinctive near the edges.

3.3. Preparation Layer

The SEM-EDX results of the double ground layers show that the elemental composition of the grounds are as follows:

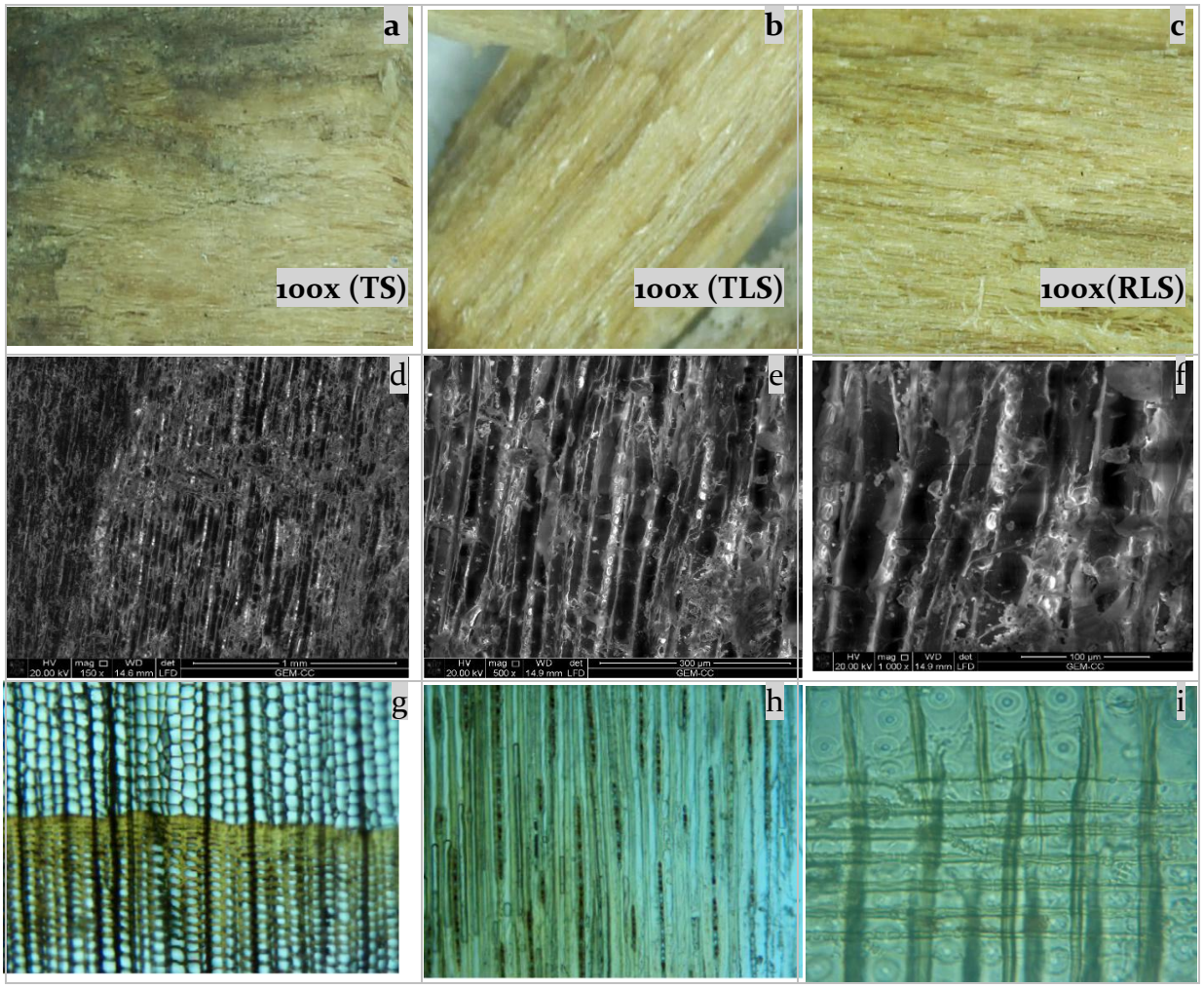

Fig. 5. Wooden sample examination using stereo (a-b-c) and SEM microscope (d-e-f) Transverse section, Tangential longitudinal section (TLS) and Radial longitudinal section (RLS) under transmitted light using optical microscopy(g-h-i).

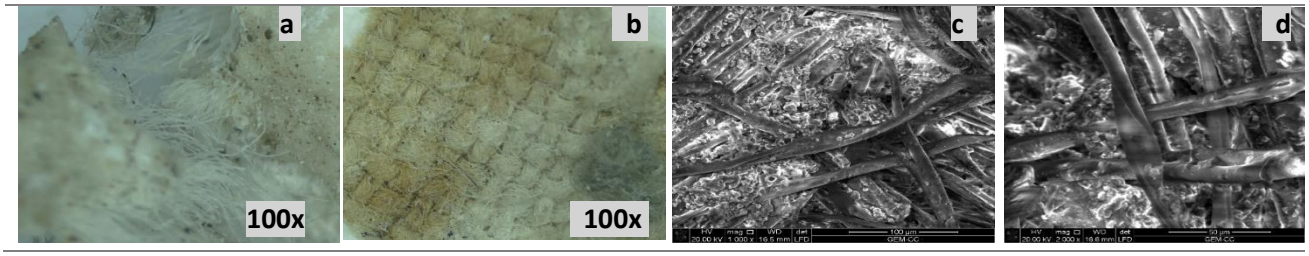

Fig. 6. Examination of canvas samples using a stereo (a-b) and SEM microscope(c-d) .

Ground layer 1: Ca, C, O, Na, Cl, Al, S, K. These results suggest that the ground layer was primarily composed of calcium carbonate, $CaCO_3$.

Ground layer 2: Ca, C, O, Al, Cl, Ba, S, Si. These elements indicate that the ground layer was primarily composed of calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$) (Fig. 7).

Both layers consisted of calcium carbonate mixed with animal glue. The FTIR spectrum of the preparation layer was compared with the reference samples of animal glue and Calcite, indicating the presence of animal glue at 3273-3295 cm^{-1} bands. The Amide group (-NH-CO-) characterizes this group [19]. This group belongs to the N-H stretching. A faint band at 2927 cm^{-1} was assigned to the C-H stretch (Methylene)[20]. The presence of the band at 1642 $cm^{-1}$was also attributed to the amide I group at 1417 cm^{-1}, there is also a band representing the amide III Group 1230-1238 cm^{-1}. FTIR spectra also showed an intense stretching vibration bands at 1796, 1396, 872, 711 cm^{-1}, attributed to the characterization of calcium carbonate [21] [22]. (Fig. 8.b-c).

3.4. Binding media of pigments

The results showed that the medium used in pigments is egg yolk. It was found that the egg yolk functional groups as below : -CH-stretch 2926 cm^{-1}, C=O stretch 1650 cm^{-1},C-H bending 1388 cm^{-1}[23]. The animal glue sharp peak at 3325–3330 cm^{-1}. In the IR spectrum was due to the N-H stretching of –$CONH_2$ in protein. The special characteristic peaks of protein Amide-I (C=O stretching vibration in amide group) at 1637 cm^{-1} and amide-IV (N-H plane bending vibration in amide groups) at 1535–1541 cm^{-1} [24] (Fig.8.a). This provide that the medium was egg yolk, while the presence of animal glue is because the sample has grains of preparation layer which incorporates the animal glue medium.

3.5.Varnish Samples

Layers of varnishes are used by painters to protect paint layers from adverse environmental conditions such as dirt, dust, and pollution that may change the optical effect of the varnish surface and increase color saturation. Photo-oxidation of these resins produces short carbon-chain compounds [25]**.** Photo-oxidation of top organic resins that protect paintings is caused by adverse environmental conditions [26] (Fig.9). The FTIR spectrum revealed the typical absorbencies of a natural resin. It contained bands at 3373 cm^{-1} due to O-H stretching bands,2919 and 2851 cm^{-1} due to -CH_2/CH_3 stretching modes of the hydrocarbonated chains, 1710 cm^{-1} due to carboxylic acid C=O stretching, and 1634 cm^{-1} due to C=C stretching. Additional band at 1463 cm^{-1} attributed to CH_2 group bending or scissoring and 1368 cm^{-1}attributed to CH_3 group asymmetric and symmetric stretching vibrations. The band at 1146 cm^{-1} is thought to be a signature of shellac resin photodegradation **[27]**. The obtained spectrum corresponded well to the reference spectrum of shellac resin (Fig.8.d).

3.6. Pigments

The identification of pigments is essential to understand the techniques and to solve all the problems of conservation process [28]**.**

3.6.1. Red pigment

By examining the sample of the red pigment under the stereo microscope, it was found that it displays different degrees, ranging from light to dark, in addition to some black particles. The presence of the black particles may indicate; the lack of pigment quality or it may be intentionally added by the painter to give the red a darker shade.

The examination under the Scanning Electron Microscope revealed that there are cracks in the paint layer, as well as the heterogeneity of pigment particles (Fig. 10). SEM-EDX analysis of the red pigment. It can be interpreted as (Table 1).

Red ocher is always composed of hematite mixed with clay minerals such as hydrated alumino silicate: kaolinite and illite. It also contains some impurities of quartz and calcite[33]. This result was confirmed by Raman spectrum (Table 2) (Fig.11.b). As for the x-ray diffraction analysis, it was clear that the compounds found in the sample were hematite and clay minerals (Fig. 11.c) (Table 3). Thus, it can be said that the red pigment used in the icon is (red ochre). Red ochre has been in use since prehistoric times until now **[34].** The presence of chromium and barium indicated that the artist utilised a base layer of lemon yellow (BaCrO4 barium chromate) beneath the red to create varying shades.

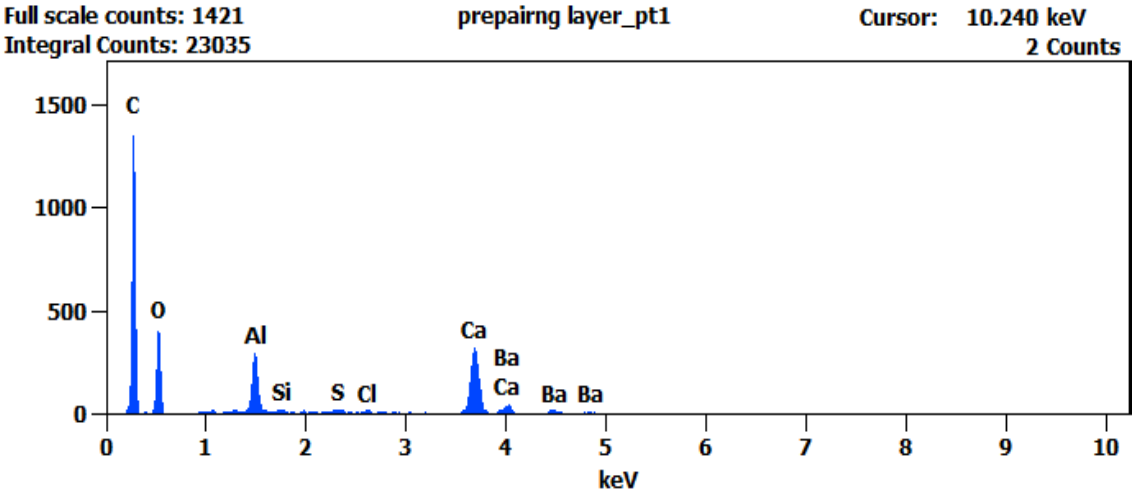

Fig. 7. EDX of the preparation layer indicates the elemental composition of the used material.

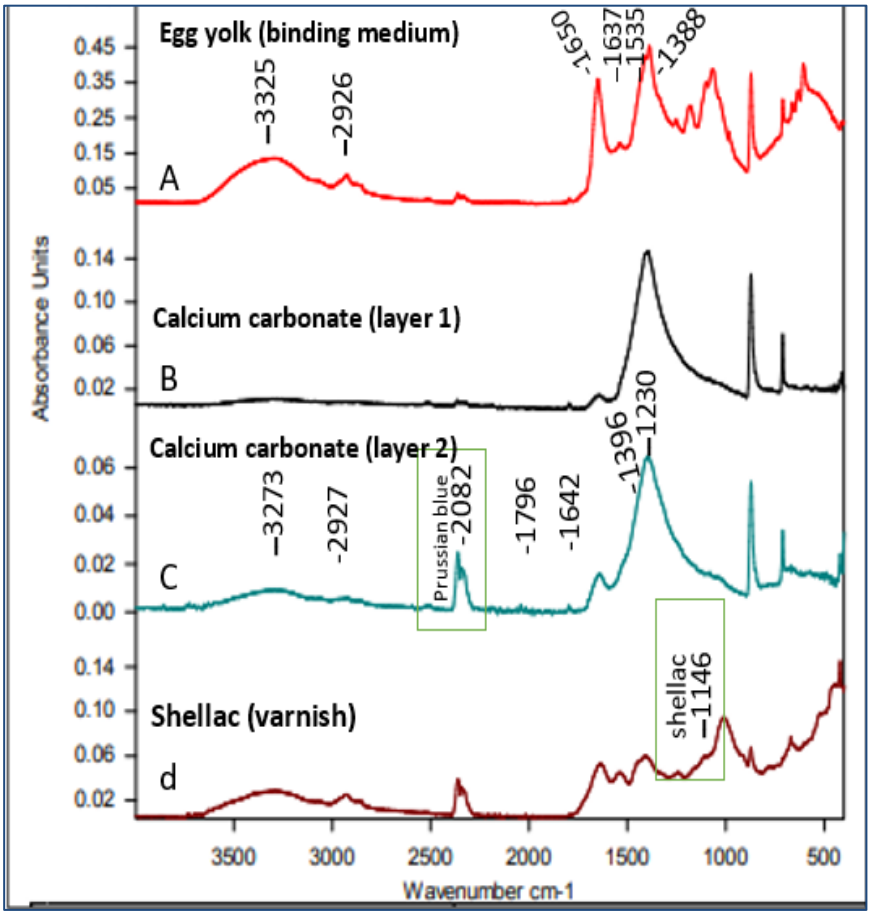

Fig. 8. FTIR results. a) FTIR analysis of (Egg yolk) as a binding media of pigments. b-c) FTIR analysis of the medium of the preparation layer indicates the animal glue. c)FTIR of preparation layer containing blue pigment d) FTIR analysis of shellac varnish .

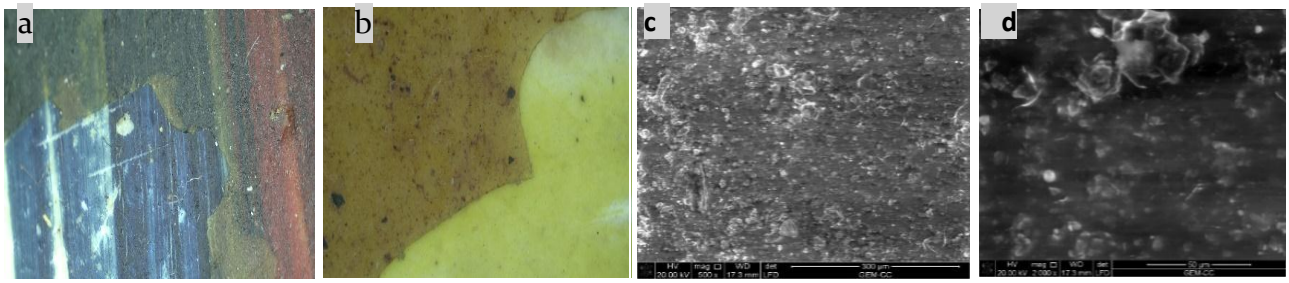

Fig. 9. The examination of the varnish layer under stereo microscope (a-b), and SEM microscope (c-d)

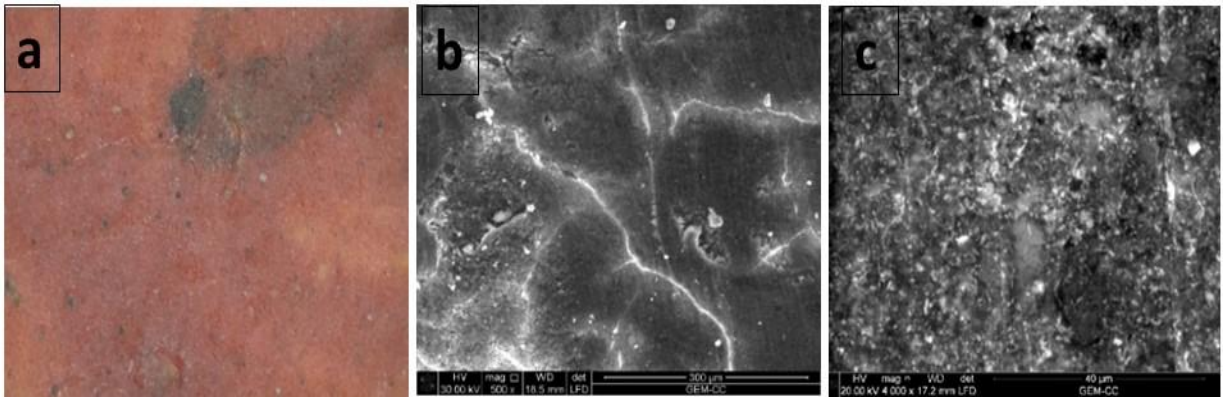

Fig. 10. Red pigment examination a) Stereo microscope photograph of red pigment, b) SEM microphotographs show cracks in red pigment sample, c) SEM microphotograph of red pigment shows heterogeneity and fragility of pigment grains.

Table 1. The EDX elements of pigments.

Pigment	EDX Elements								Result
Red	Fe	Cr Si	O Al	K N	Mg Ca	Cl C	Na Ba	S	Red ochre
Black	**C**								Carbon black
Blue	Ba	O Cl	Zn Al	N Na	Ti S	Ca	C	Si	Ultramarine
Brown	Fe	O Cl	Ti Mg	Ca Al	C Ba	K Cr	Si	Na	Red ochre + Carbon
Yellow	Cd	S Cl	Ba Al	Si Mg	O Cr	C	Ca	Na	Cadmium yellow +barium yellow

3.6.2. Black pigment

The black pigment appears homogeneous and its grains are well interconnected[35]. Examination using a scanning electron microscope at a magnification of 500 x showed fine interconnected grains of pigment and some very light cracks appeared at a magnification of 2000 x. (Fig. 12). The EDX results show a high amount of carbon element in the sample (Table 1) (Fig. 13.a). By comparing the obtained results from the EDX with the Raman spectrum as shown in (Table 2), it was found that the black pigment is lamp black (Fig. 13.b).

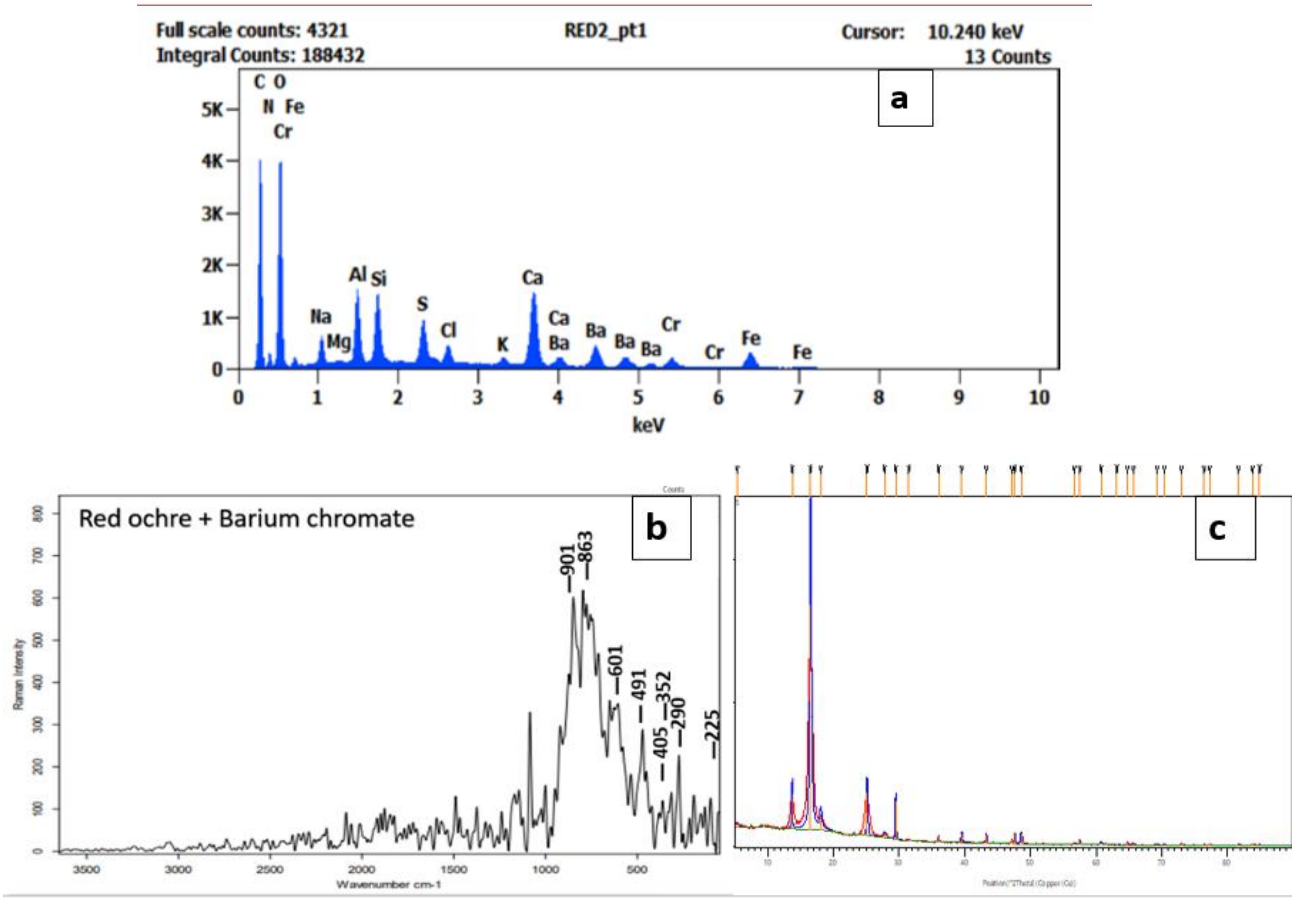

Fig. 11. a) EDX of red pigment spectrum b) Raman spectrum of red pigment c) XRD pattern of red pigment.

XRD analysis is a unique method to discover qualitative properties such as crystallinity, type, fingerprint, and quantitative material [36].

The main peaks appear at 10–30 $^{2\theta}$. Most references show a high similarity between these peaks, especially the first strong peak. (Fig. 13.c) The first peak on the left has very high intensity and a smaller width compared to the peak on the right. The length and width of the peaks are often used to characterize the crystal size[37]. In general, for carbon, the first peak on the right refers to a crystalline or amorphous nature; therefore, the width increases with decreasing intensity or length, indicating that they are in the amorphous crystalline form. Carbon black is the soot produced by burning oil or other combustible organic materials. Soot is basically pure carbon, sometimes containing small amounts of unburned material or other combustion products[38]. Like all carbon historic times and is one of the oldest pigments[39]. It should be noted that using lamp black with other pigments increase the shade.

3.6.3. Blue pigment

As a result of the yellowing of the varnish layer, the sample seemed green. Once the varnish was removed, the blue color appeared. The painter used the blue pigment in different shades, from dark as the color of the robe to the light, heavenly color as the color of clouds and the angel. Using SEM, the blue pigment appeared in the form of strong-covering clumps with fine cracks, the pigment particles and the method they interconnected began to appear more clearly (Fig. 14). Two blue samples were analyzed. The first was examined using FTIR and Raman microscope. FTIR analysis of the blue revealed the presence of Prussian blue ($Fe_4[Fe(CN)_6]_3$) as its strong band at 2082 cm^{-1} appeared (Fig.8.c).

Table 2. Results of Raman spectroscopy for compounds of pigments.

Sample color	Color of the paint layer	Structure and Composition	Raman shifts cm^{-1}	Ref
Layer	Calcium carbonate (chalk)	$CaCO_3$	1085, 280, 152 cm^{-1}	[29]
Red	Red Ochre	Fe_2O_3 + clay minerals	225,290,405, 491, 601 cm^{-1}	[29] [30]
	Barium Chromate	$BaCrO_4$	352,863,901 cm^{-1}	[31]
Brown	Hematite	$SiO_2+Al_2O_3+Fe_2O_3$	224,293 cm^{-1}	[29]
Black	Carbon	C	1333, 1598 cm^{-1}	[29]
Blue	Prussian blue Iron(III)hexacyanoferrate(II)	$Fe_4[Fe(CN)_6]_3$	282, 538, 2102, 2154 cm^{-1}	[32]
	Ultramarine [natural, sulfur-containing sodio-silicate], Lapis lazuli	$Na8\text{-}10Al_6Si_6O_{24}S_{2\text{-}4}$	364, 548, 583, 808, 1096, 1346 cm^{-1}	[29]
	Zinc white	ZnO	438 cm^{-1}	[29]
Yellow	Cadmium yellow	CdS	131, 615 cm^{-1}	[29]
	Barium chromate	$BaCrO_4$	352,863,901 cm^{-1}	[31]
White	Titanium dioxide	TiO2	142, 236, 449, 614 cm^{-1}	[29]

This result was confirmed by Raman analysis as shown in **(**Table 2) (Fig.15.b). The second sample was analyzed by EDX (Fig. 15.a) and XRD (Fig.15.c) (Table 3) and was found to be ultramarine blue. Using XRD, the main compounds were ultramarine and zinc oxide which were used during the 18th century. The presence of some elements in EDX, such as titanium and zinc, in addition to the presence of oxygen, is explained by the fact that the artist used white pigment mixed with blue pigment to give a gradation of colors. Prussian blue appeared in some analysis while ultramarine appeared in others. This imparts rich results, as the artist has combined the two pigments in the icon in order to create different shades of luster for the blue pigment. Prussian blue is a synthetic pigment consisting of hexacyanoferrate $Fe_4[Fe(CN)_6]_3.14\text{-}16H_2O$. There are two formulae for Prussian blue, K $Fe[Fe(CN)_6]$ and $Fe_4[Fe(CN_6]_3$ [7] **.** It is the oldest modern synthetic pigment and has been in use since its discovery in 1704[40]. The synthetic ultramarine blue was used as a reference pigment in an artwork created around 1917 [41]**.**

3.6.4. Brown pigment

Usually, the iconographer choose a brown pigment in his icon, and sometimes he used a mixture of a group of pigments such as red, blue, and green to produce a reddish-brown pigment. When examined by stereomicroscope, the brown pigment appeared to be

mixed with black to give darkness and shade in some places. When examined with a scanning electron microscope at a magnification of 500 ×. It showed that certain areas in the pigment have different lighting, and this suggests the use of a mixture of pigments. When magnifying 2000×, it became clear that there are bulges and graininess in the pigment as a result of its exposure to damage. (Fig.16) Analysis of the elements of the pigment was done using EDX (Table 1) (Fig. 17.a). A Raman analysis of the brown pigment revealed the characteristic spectra of iron compounds (Table 2) (Fig.17.b**)** This means that the pigment used was hematite. And to verify this, a sample was taken, and XRD was performed to identify the compounds (Fig. 17.c). The results revealed the presence of the compound hematite.

Table 3. XRD analysis results of *pigments.*

Sample	[°2Th]	d-spacing [Å]	Rel. Int. [%]	JCPDS Card No.	Compound
Red pigment	16.5183 25.1437 13.6301 29.5394	5.36675 3.54187 6.49676 3.02406	100.00 18.75 27.50 45.14	41-1493	Red Ochre
Black pigment	37.3565 63.3543 76.3111	2.40727 1.46808 1.24788	100.00 40.22 31.81	41-1487	Carbon
Brown pigment	13.6241 16.4257 29.5441 37.0856	6.49961 5.39680 3.02359 2.42423	29.60 100.00 23.61 14.91	41-1493	Hematite
Blue pigment *sample 1* *sample 2*	37.0830 43.1182 62.9260 75.8567 37.0830 43.1182 62.9260	2.42440 2.09801 1.47704 1.25422 2.42440 2.09801 1.47704	100.00 30.26 22.99 13.24 100.00 30.26 22.99	73-0687 20-1087	Prussian blue Ultramarine
Yellow pigment	29.0738 39.1124 42.8166 47.1999 57.168 64.3614 72.6422	3.07142 2.30315 2.11209 1.92566 1.88831 1.61266 1.44752	48.86 34.17 58.01 100.00 93.88 60.46 47.08	89-0440 15- 376	Cadmium yellow Barium chromate
White pigment	Not identified (N.D)				

3.6.5. Yellow pigment

The yellow pigment appeared in some areas of the icon, and it was also found mixed with the blue pigment to give a green luster. Examination using the stereo microscope, it appeared homogeneous and fine-grained. The lemon-yellow pigment appeared with a slight blue luster. When examining it with scanning electron microscope at a magnification of 500 ×, the homogeneity and accuracy of the grains appeared with the presence of some dark spots as impurities of the pigment, and with magnifying 1000 ×, the pigment grains were interconnected and formed a light film covering the ground layer (Fig.18). To determine the elements of the pigment, the yellow pigment sample was analysed using EDX and the results are displayed in (Table 1) and (Fig. 19.a). In Raman, the characteristic spectrum is displayed in (Table 2) and (Fig.20.a).

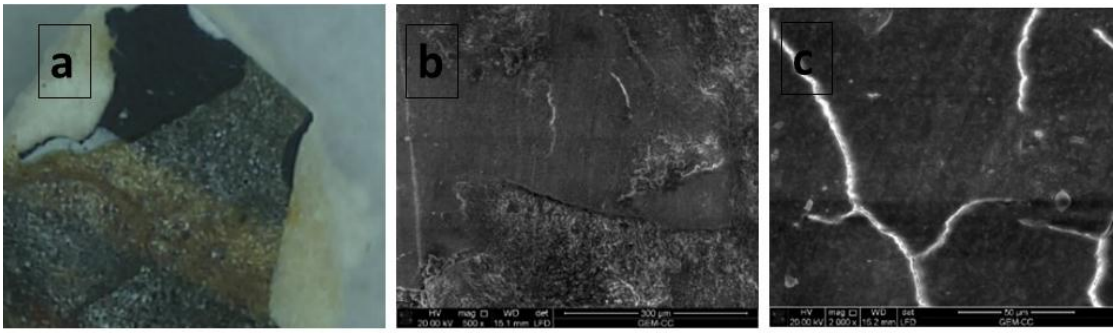

Fig.12 a) Stereo microscope photographs of black pigment, b) SEM microphotographs showed fine interconnected grains of pigment c) SEM microphotograph of black pigment shows cracks.

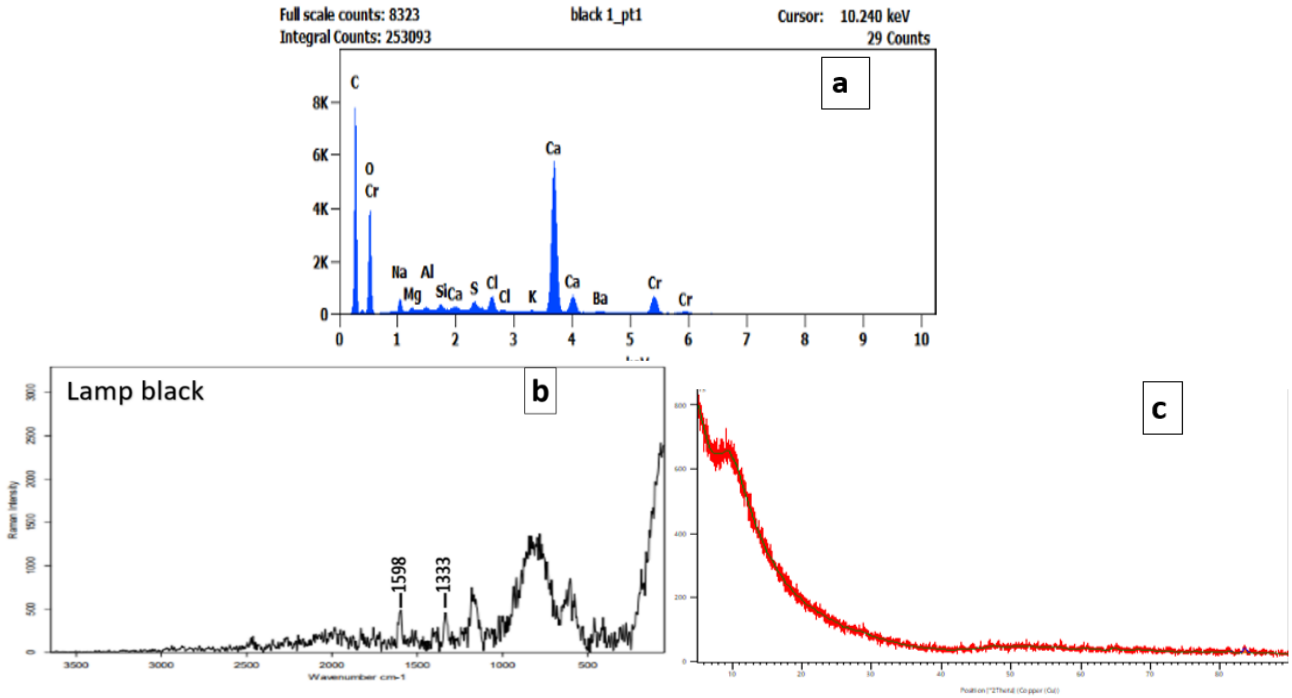

Fig.13 a) EDX of Black pigment b) Raman spectrum of black pigment c) XRD pattern of black pigment

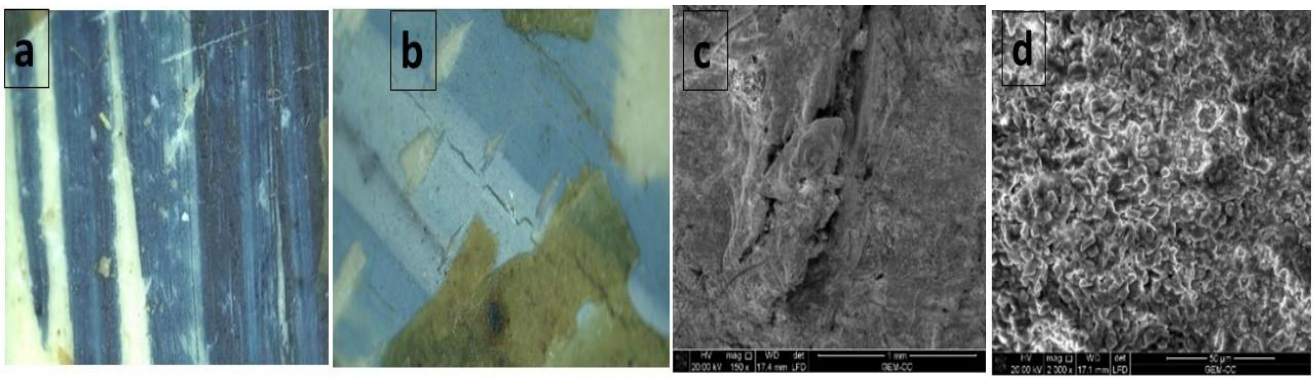

Fig.14. a, b) Stereo microscope photographs of dark blue as the color of the robe to the light, heavenly color as the color of clouds c) SEM microphotograph indicates cracks of blue pigment sample d) SEM microphotograph of blue pigment appeared in the form of strong-covering clumps.

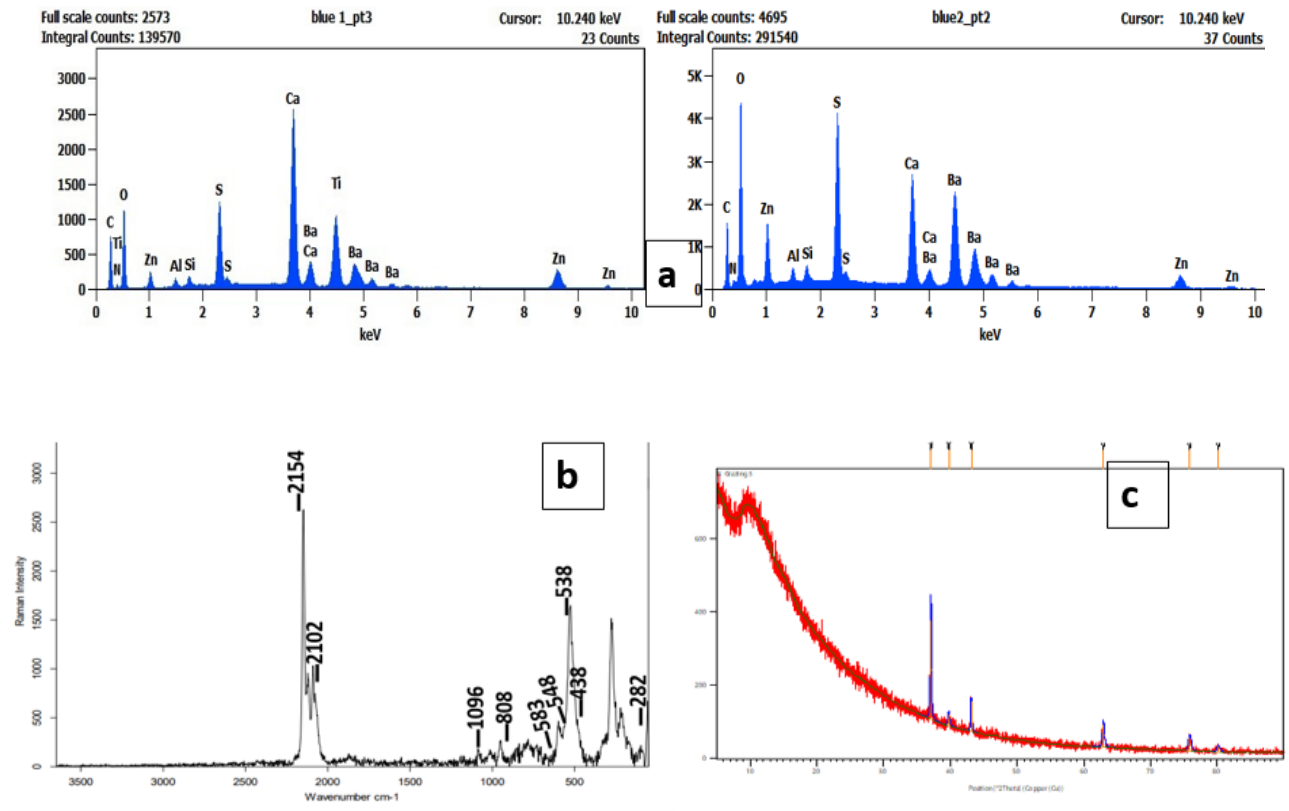

Fig. 15. a) EDX of blue pigment b) Raman spectrum of blue pigment c) XRD pattern of blue sample.

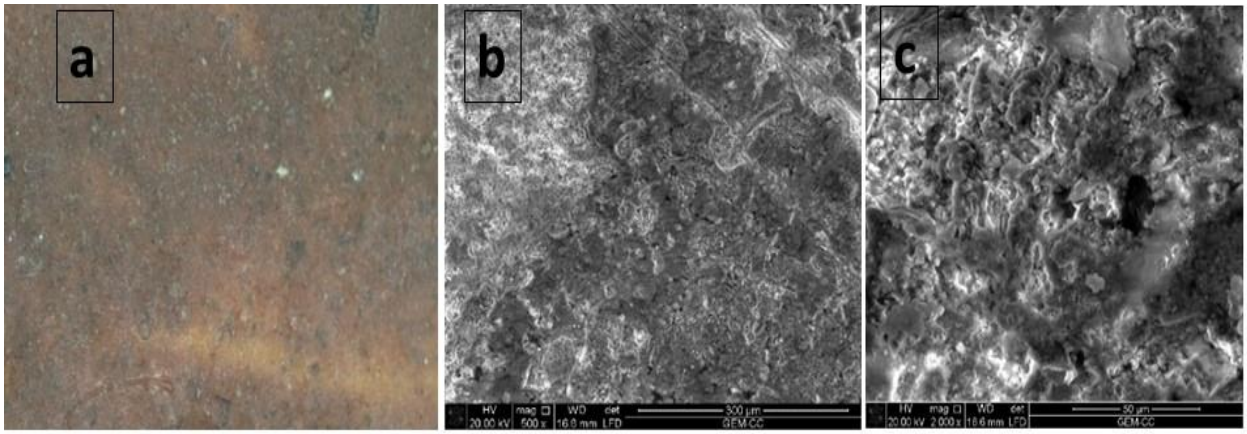

Fig. 16 a) Stereo microscope photograph of brown pigment b, c) SEM microphotographs of brown pigments show bulges and graininess in the pigment as a result of its exposure to damage.

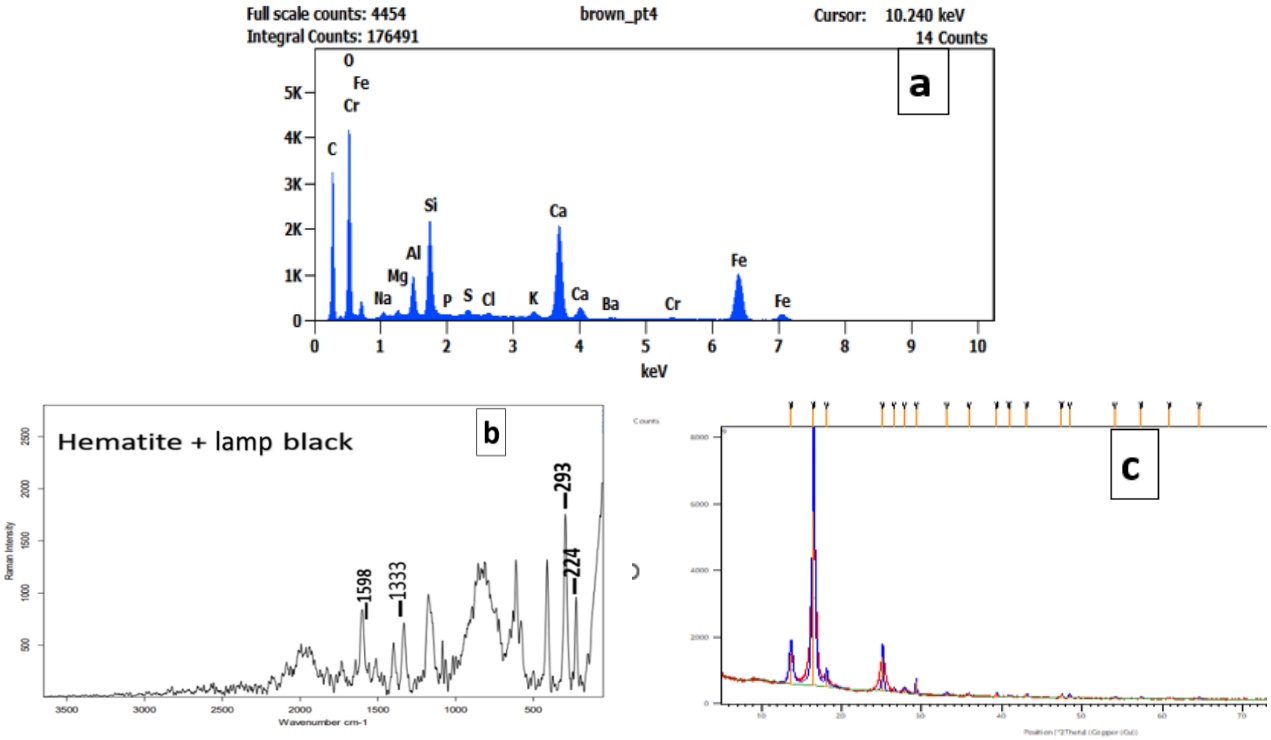

Fig. 17. a) EDX of brown pigment b) Raman spectrum of Brown pigment c) XRD pattern of brown sample.

3.6.6. White pigment

The white pigment was used alone on a small scale in the icon. It was also added to some pigments for the purpose of lighting. By examining the white pigment under the stereo microscope, its grains are very weak and interconnected with each other in the medium in the form of a light film over the preparation layer, and there are many impurities present in the pigment, perhaps as a result of exposure to damage.

Upon examination with a scanning electron microscope at a magnification of 300 ×, the light pigment layer appeared swollen and peeled. (Fig.18.d, e)

Using EDX, the element appeared in the form of strong spectra characteristic of the element Ti. (Fig.19.b) Using Raman 785 nm, it was found that the main peaks are 1085, 280, 152 cm^{-1} for calcite) and there are weak peaks for titanium dioxide (TiO_2). Its bands are 138, 230, 450, 609, and 831 cm^{-1}. (Fig.20.a) Titanium dioxide white has been used by a multitude of painters since its first production date between 1910 and 1920 [44](Fig. 20b)

Painting dating often involves confirming the association with a specific painter or date. However, the historical practice of an artist, including styles and materials used, is not always reliable due to the presence of imitators and the lack of a complete history of materials. Coptic icons face three problems: workshop production, the possibility of copying icons by other painters, and the repeated use of wooden panels due to a short supply of wood in Egypt. Radiocarbon dating and dendrochronology are not suitable for determining the dates of icons, so identifying distinguishing characteristics is crucial. The usage of pigments over time depends on factors like their frequent application and availability during a specific historical period. Lead isotope ratios and ^{210}Pb can help to determine the time an icon was made if the icon contains lead in one of its compounds. Kühn suggests using terminal dates of pigments used, which may suggest strong, weak, or non-existent indications of certain pigments or pigment combinations. However, this method is not effective when pigments with no exact history of use, such as lead white and ochres, are used [7]. The best method for dating paintings is to look at the pigments used, which include both the earliest and latest dates. Determining the dates of icons should rely heavily on identifying key pigments or techniques whose dates of introduction or disuse are known. However, the use of pigments over time is determined by a variety of factors. The first is the frequent use of particular pigments in particular types of paintings .The second factor is the availability of certain pigments during a specific time period.[7] The date of some pigments are given in Table 4.

It can be concluded that the icon dates back to the end of the nineteenth and the beginning of the twentieth century.

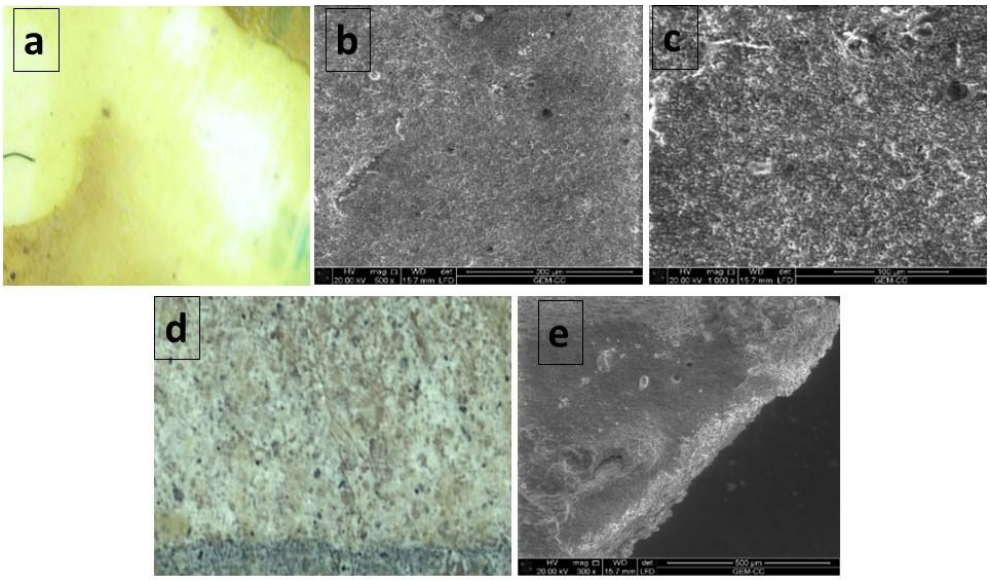

Fig. 18. a) Stereo microscope photograph of yellow pigment b, c) SEM microphotographs of yellow pigment show grains with the presence of some dark spots as impurities of the pigment, d) Stereo microscope image of white pigment, e) SEM microphotograph of white pigment

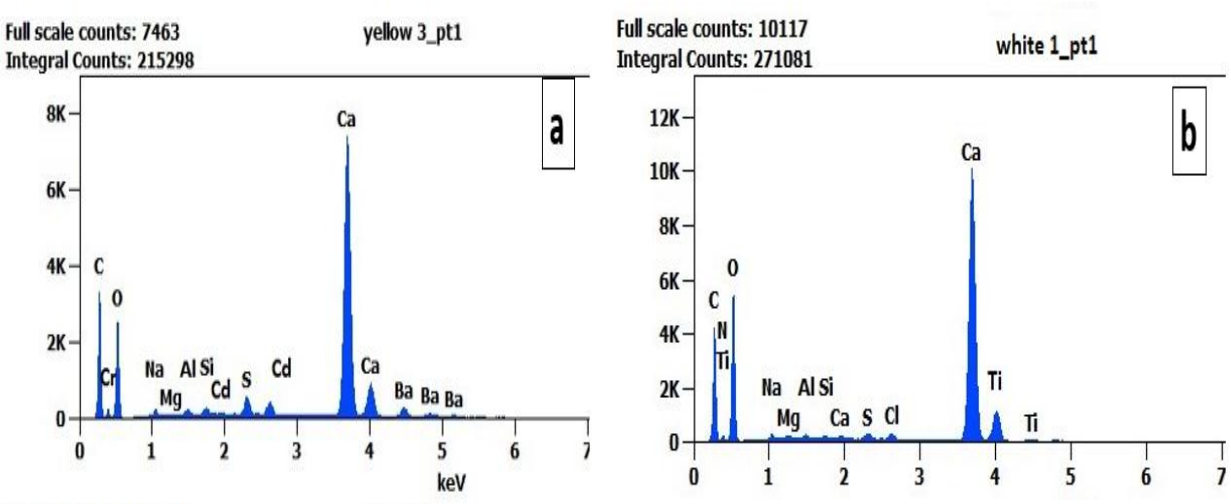

Fig. 19. a) SEM-EDX spectrum of yellow pigment b) SEM-EDX spectrum of white pigment.

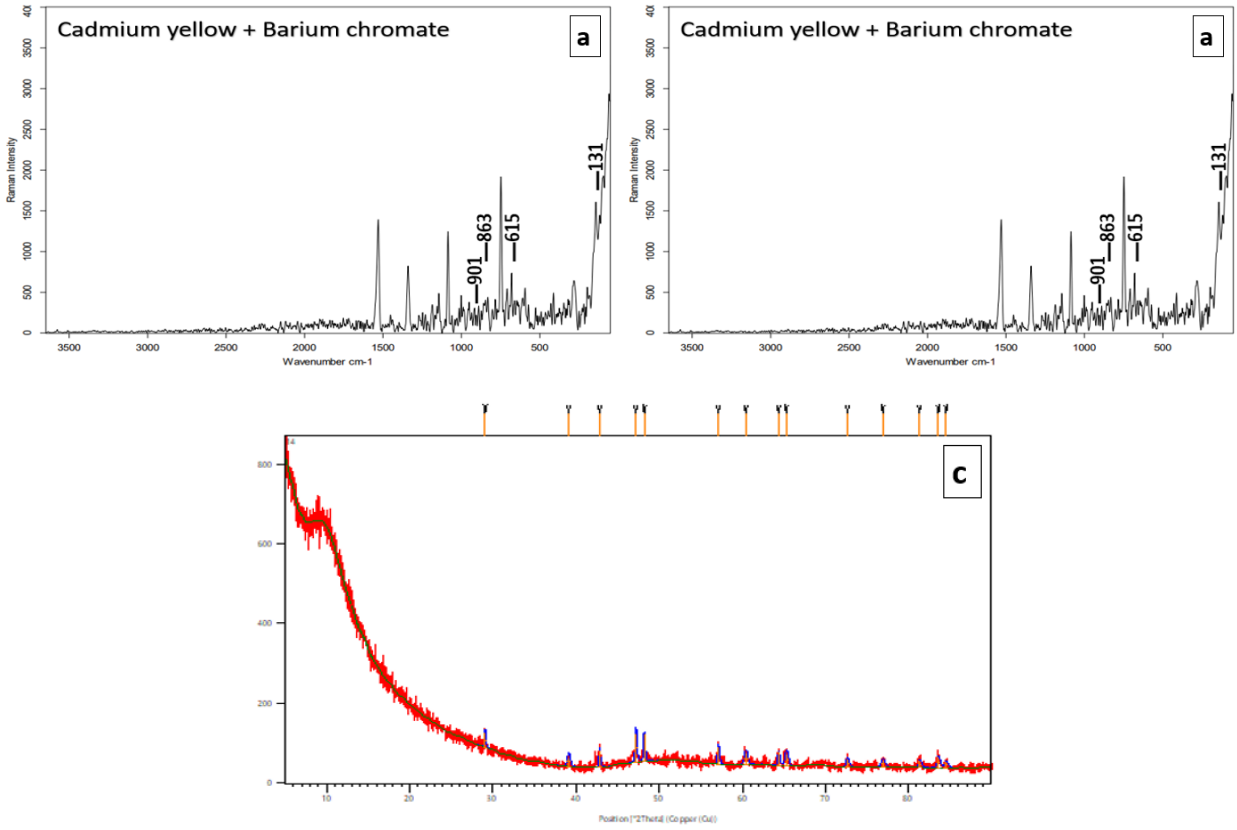

Fig. 20. a) Raman spectrum of yellow pigment, b) Raman spectrum of white pigment, c) XRD pattern of yellow pigment.

Table 4. The discovery or usage date of some pigments

Pigment	Discovery or usage date
ultramarine blue	1917
Prussian blue	1704
Cadmium yellow	since about 1845
Titanium dioxide	1920
Zinc oxide	Within 18 century
Chromium yellow	1797

4. Conclusion

The study of triptych icons yields significant archaeological insights. The icon under examination comprises three-in-one, featuring diverse, layered compositions on a support made from Abies alba wood. .The use of preparation layer made of calcium carbonate mixed with animal glue is something very rare in Coptic icons. The Coptic iconographer used different types of varnishes, but shellac was not widely used, and therefore its presence here confirms the icon's modernity. Although the style of painting was egg yolk tempera, and the way the artist depicted his subject was through simple drawings, the pigments used were of a unique range of colors such as Prussian blue, ultramarine, cadmium yellow, barium chromate, and titanium white. Spectroscopic studies of pigments were able to determine the age of the icon in a professional and accurate manner, which is difficult compared to other common dating methods. Identifying all the pigments and studying the history of their discovery and usage, the icon was dated to the end of the nineteenth century and the beginning of the twentieth century.

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