ORIGINAL PAPER

EXAMINATION AND ANALYSIS OF AN EGYPTIAN COPTIC FRESCO FROM SAINT JEREMIAH MONASTERY

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Manuscript received: 16.10.2018; Accepted paper: 10.01.2019;
Published online: 30.03.2019.

Abstract. *In the present study, a comprehensive investigation has been undertaken into an Egyptian Coptic fresco dating to the 4th century and painted by Saint Jeremiah . It was initially located in saint Jeremiah monastery in Saqqara, in Egypt and currently it is found at the National Museum of Egyptian civilization - Fostat city - Cairo.The analytical instruments used for investigation were optical microscopy, scanning electron microscopy , X-ray Florescence , X- ray diffraction and Fourier transform infrared coupled with attenuated total reflectance "FTIR-ATR". The analysis revealed that the pigments used in this fresco were hematite, goethite and malachite. The ancient ground layer comprises calcium carbonate with silicon dioxide and the added modern ground layer comprises calcium sulphate dihydrate admixed with animal glue .*

Keywords: *Mural paintings, Saint Jeremiah, Portable optical microscope, Raman, XRF, XRD, FTIR.*

1. INTRODUCTION

The 4th century is considered the most important period in the Coptic art which distinguished with the fresco paintings. In this century, several fresco paintings were applied as its requirements are available in the surrounded environment of the church and monastery [1].

1.1. DISTINCT LAYERS OF FRESCO

A first layer of rough coating, applied on the wall support of mud bricks , this mortar is a mixture of hydrated lime - calcium hydroxide and coarse sand, the second layer consists of hydrated lime and well-filtered fine sand, the third layer is the pictorial layer made of pigments and pure water applied in several coatings with a brush [2]. The calcified layer results from the carbonation of the lime mortar, while drying, produces a transparent protective crust (outer membrane that forms as a result of carbonation of lime). This pellicle includes the pigments and fixes them definitively [3]. In this study, an Egyptian Coptic fresco painting was fully investigated. The purpose from this research is to set, beside the technical

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information about this type of painting, the knowledge about both organic and inorganic materials used. The study comprised the examination of the pigments, media, ground layer and the modern added layer.

1.2. THE EXAMINED FRESCO PAINTING

This fresco painting has a registration number (7968), at the National Museum of Egyptian Civilization in Fostat City, Cairo (Fig. 1), its dimensions about 110 cm x 119 cm, the thickness about 4 cm. It dates back to the 4th Century and was discovered in 1907 by Qubille in Saqqara [1].

Figure 1. The Egyptian Coptic fresco painting and the sample locations.

1.3. THE FRESCO PAINTING CONDITION

The analysis of this painting was carried out in the occasion of the restoration treatment. From the visual inspection and the cross section images, the condition of the fresco painting is poor; failure in paint layers is the most apparent deterioration phenomenon. Another type of deterioration of the pictorial layer is the candle burns (Fig. 2 A-C, E, F).

Figure 2. The condition assessment of the Coptic fresco painting: A - detachment in the body of painting; B - failure in paint layers; C - vital cracks; D - losses in painting layers; E - candle burns; F - resins materials from old conservation treatment.

This phenomenon is due to placing candles in front of paintings with the absence of glass protection [4]. Therefore, the pictorial layer suffered from severe loss and color change [5-10] around the lost areas [11]. Soot accumulations are also found over the paint layer around those burnt areas, and resins materials from old conservation treatment.

2. MATERIALS AND METHODS

2.1. SAMPLING

Samples were collected carefully from the destroyed edge, using a micro scalpel, to identify the constituents and degree of deterioration of the fresco paintings. All the analyzed and investigated samples were carefully collected from areas without aesthetic value or from severely damaged parts.

2.2. ANALYTICAL TECHNIQUES

Portable optical microscopy (POM)

This examination applied directly on fresco paintings in the site without taking any samples. The Coptic fresco painting was examined with portable optical microscope to identify the samples refraction coefficient, shape and crystals of color, as well as internal disconnect and color change. In addition, it helps us identify the aspects of damage within the samples from the minute cracks.

Raman spectroscopy

Raman spectra were recorded using a triple grating spectrometer (Dilor XY) equipped with a Charge Coupled Device (CCD) liquid nitrogen cooled detector system. The red line (632.8 nm) spectra were excited from a 35 mW air- cooled He–Ne laser (Spectra Physics, mod.127). The spectral resolution of the system was ~3 cm^{-1}. The laser was focused on the sample through the system's microscope equipped with a standard objective lens 100x. In order to avoid damaging of samples, the laser power was kept at 0.1-0.3 mW [12].

X-Ray Diffraction (XRD)

The X-ray diffraction patterns of the Coptic fresco painting were obtained using a diffract meter (Philips PW 1840), operated at 40 kV and 25 mA, using Cu Ka radiation and a receiving slit of 0.2 mm. The measurements were made at room temperature. Preparation of each sample consisted of grinding it in the dry form, by using a mortar and pestle to obtain a fine powder.

X-Ray Fluorescence (XRF)

Samples were analyzed by XRF to determine the chemical composition of the stucco samples. The apparatus used is a Philips PW1400. The investigated samples were prepared in the form of pellets, using a manual press under a 20 tons load, and were analyzed using an Rh-Ka (rhodium) radiation tube at 50 KV and 50 mA. The chlorine ion was analyzed by potentiometer titration. The loss on ignition (LOI) of the samples was determined by igniting 1 g of the sample in a weighted platinum crucible heated to 950 ^{o}C in an electric furnace for 30 minutes (first time) and then for 15 minutes (second time). The crucible and samples were cooled for 10 minutes before each weighting, performed after heating and was observed. Weighting were repeated until constancy of weight.

Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR)

Samples were analyzed with a FTIR spectrometer (Model 6100 Jasco, Japan). Spectra were obtained in the transmission mode with TGS detector.

3. RESULTS AND DISCUSSION

Portable optical microscopy (POM)

After examining Coptic fresco painting of Saint Jeremiah monastery investigation of the samples revealed that the samples of reddish color composed mainly of fine to medium-grained of quartz, iron oxides embedded in very fine-grained groundmass admixed with considerable amounts of iron oxides giving the reddish color of the sample, homogenous of ground layer, red color mixed with a percentage of fine black color, micro cracks in the green color (Fig. 3 A-F).

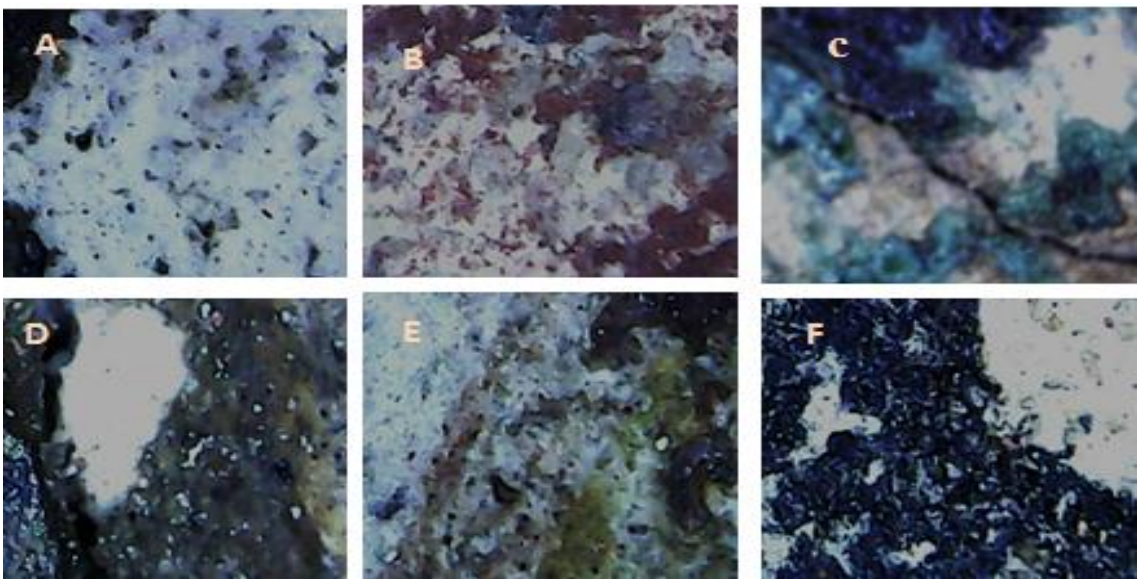

Figure 3. Portable optical microscopic structure of fresco painting: A - the crystals of ground is big and seems to be homogenous; B - red color mixed with a percentage of fine black color; C - micro cracks in the green color which mixed with black color; D - a small gap in the yellow color; E - the mixture of colors and crystals of silica; F - the fine black color.

Raman spectroscopy

The micro Raman spectrum obtained on a yellow spot in the sample Fig. 4 (a) show the main strong bands at 1158- 1086-21.8- 278 cm^{-1} with weak ones at 711-852-464-278-940 cm^{-1} In accordance to Barbara stuart, the main peaks for goethite are present at 118-203-241-299-393-533. The micro Raman spectrum obtained on a red spot in the sample Fig. 4 (b) shows the main characteristic strong bands at ~225, 297 cm^{-1} with the weaker ones at 411 and 497 cm^{-1}.

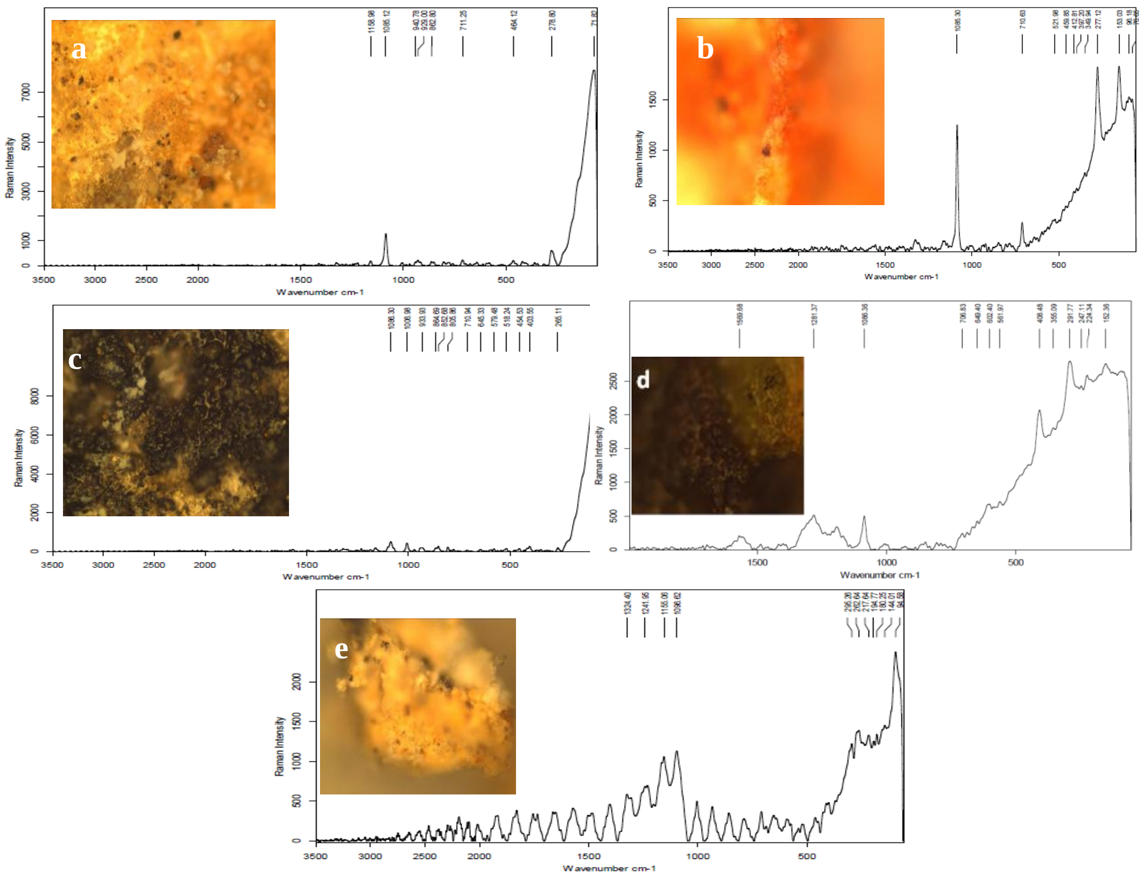

Figure 4. The Raman spectra of: a - yellow color with fine crystals with spots of black colors; b – red color with fine crystals; c - black color with fine crystals; d - green color with fine crystals; e - the modern added layer of gypsum.

In accordance with Stuart B.H. [13] the main peaks for hematite are present at 224, 291, 407, 494, 610,630, also 247, 412, 226, 246 cm^{-1}. The micro Raman spectrum obtained on a black spot in the sample, Fig. 4c shows the main strong band 450-1005 cm^{-1} and the weak ones at at 411 and 497 cm^{-1}.

In accordance with Stuart B.H. [13] the main peaks for Pyroluosite are present at 4801-7250 cm^{-1}. The micro Raman spectrum obtained on a green spot in the sample Fig. 4d shows the main strong bands at 579-418-454-403.5-265.11-71.5 cm^{-1} which approved that the green color is the malachite and the micro Raman spectrum obtained on a white spot in the sample from the modern added layer Fig. 4e shows the main strong bands at 1132-1007-670-619-493 cm^{-1} which approved that the modern added layer consisted of gypsum.

X-Ray Diffraction (XRD)

The XRD patterns of the samples of the Egyptian Coptic fresco painting indicate the following results which are resumed in Table 1 and Fig. 5:

1. the modern added layer to support the fresco painting consists of gypsum (Fig. 5a);
2. the existence of calcite in the ground layer in a percentage too high assured that the binder in that painting depended on the calcium hydroxide carbonation (Fig. 5b);

3. the colors which were used in the painting are among the most common and available pigments in the surrounded environment [14]. The red color is hematite, the yellow color is goethite, the green color is the malachite, and the black color is the perollosite (Fig. 5c-f);
4. the halite constitutes 5.3% of the modern layer, 4.5% of the original layer, and 21.3% of the black color sample that result assured the occurrence of deterioration which can cause detachment in the future [15], which caused the detachment of painting layer [16].

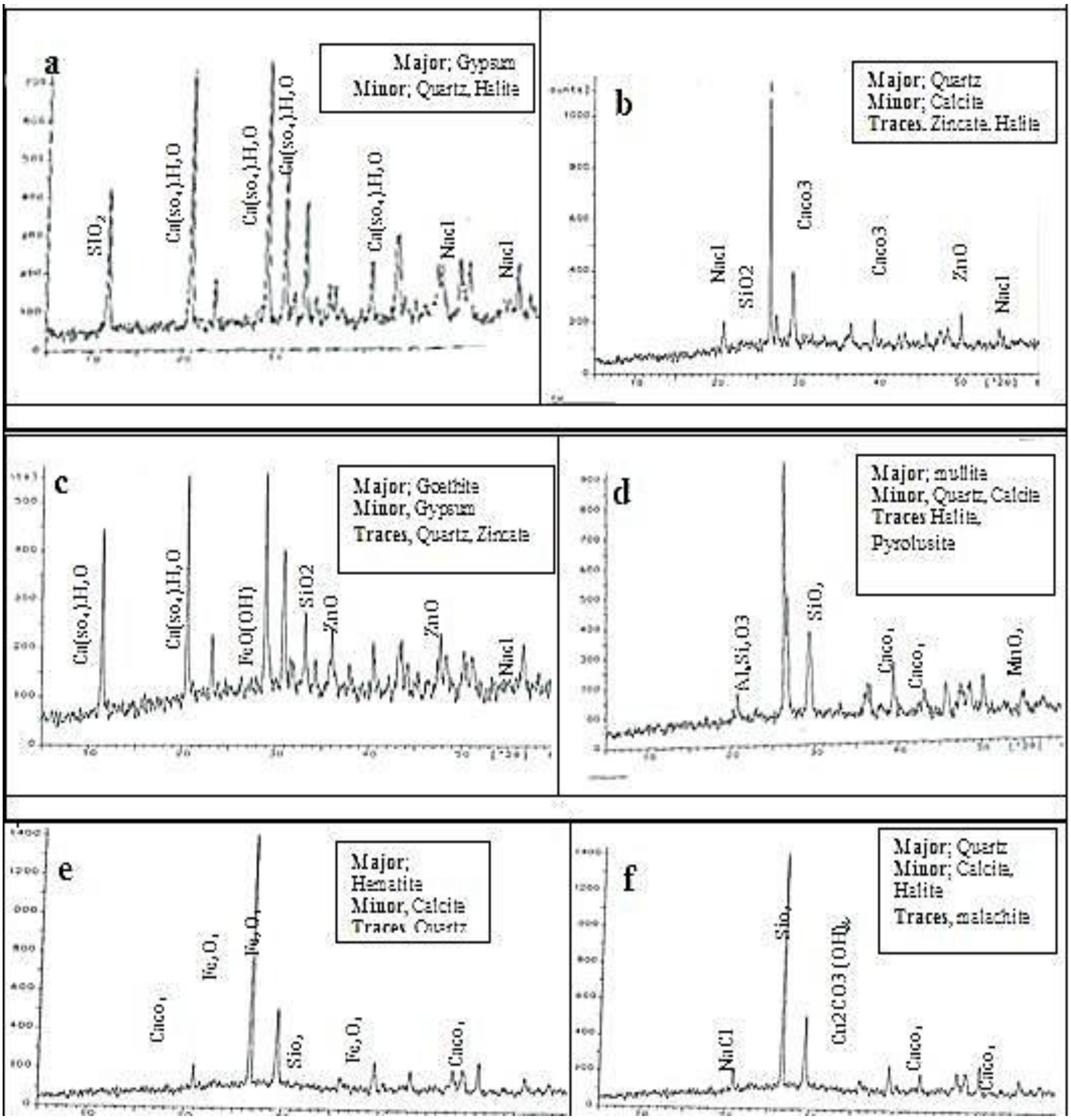

Figure 5. a) X-Ray diffraction patterns of sample of the modern added layer the results proved that the sample consists of gypsum and halite; b) the original ground layer consisted of calcite and quartz and a little percentage of zincate and halite; c) X-Ray diffraction patterns of sample of the yellow color is goethite with little percentage of gypsum and quartz and zincate as the original ground layer; d) the black color is Pyrolusite or manganese dioxide with calcite and silica as the original ground layer; e) X-Ray diffraction patterns of sample of the red color is hematite or iron oxide with calcite and quartz as the original ground layer; f) the green color is malachite with quartz and calcite with a little percentage of halite.

Table 1. X-Ray Diffraction data.

Compounds [%]	Samples					
	1s	**2s**	**3s**	**4s**	**5s**	**6s**
Gypsum	100	-	-	-	-	-
Calcite	-	20	29.5	34.7	37.8	15.5
Silica	41.9	100	10.6	100	9.8	22.8
Goethite	-	-	-	-	100	-
Hematite	-	-	100	12.4	-	-
Malachite	-	-	-	5.4	-	-
Purollusite	-	-	-	-	-	5 1
Halit	2.9	3.2	-	-	3.3	9.9
Zincate	-	6.6	-	-	9	-
Mulite	-	-	-	-	-	100

X-ray Fluorescence (XRF)

The XRF patterns of the Coptic fresco paintings samples from saint Jeremiah indicate the following results which are resumed in Table 2, the results of X-ray Fluorescence assured all the results of XRD and Raman spectroscopy and assured that the black color is purollosit not magnetite as the percentage of manganese is more than the percentage of iron.

Table 2. X-Ray Fluoresce data.

Samples	Elements [%]								
	Mg	**Al**	**Si**	**S**	**Ca**	**Mn**	**Fe**	**Cl**	**Zn**
1s	-	-	1	35	36	-	-	-	1
2s	1	1	24	1	52	-	-	1	-
3s	2	-	-	-	24	5	38	1	-
4s	1	-	1	46	31	-	-	-	1
5s	2	1	31	2	44	-	1	-	-
6s	2	1	22	5	46	-	1	1	-

Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR)

The samples were placed inside a spectrometric analysis, the device is running to give the analysis as a chart graph paper [17-19], the paint layer was covered with a layer of glue to support it as it wasn't popular to use glue with calcium hydroxide so the presence of glue is due to the its addition to the surface of the fresco painting and it was also mixed with the gypsum in preparing the modern added layer.

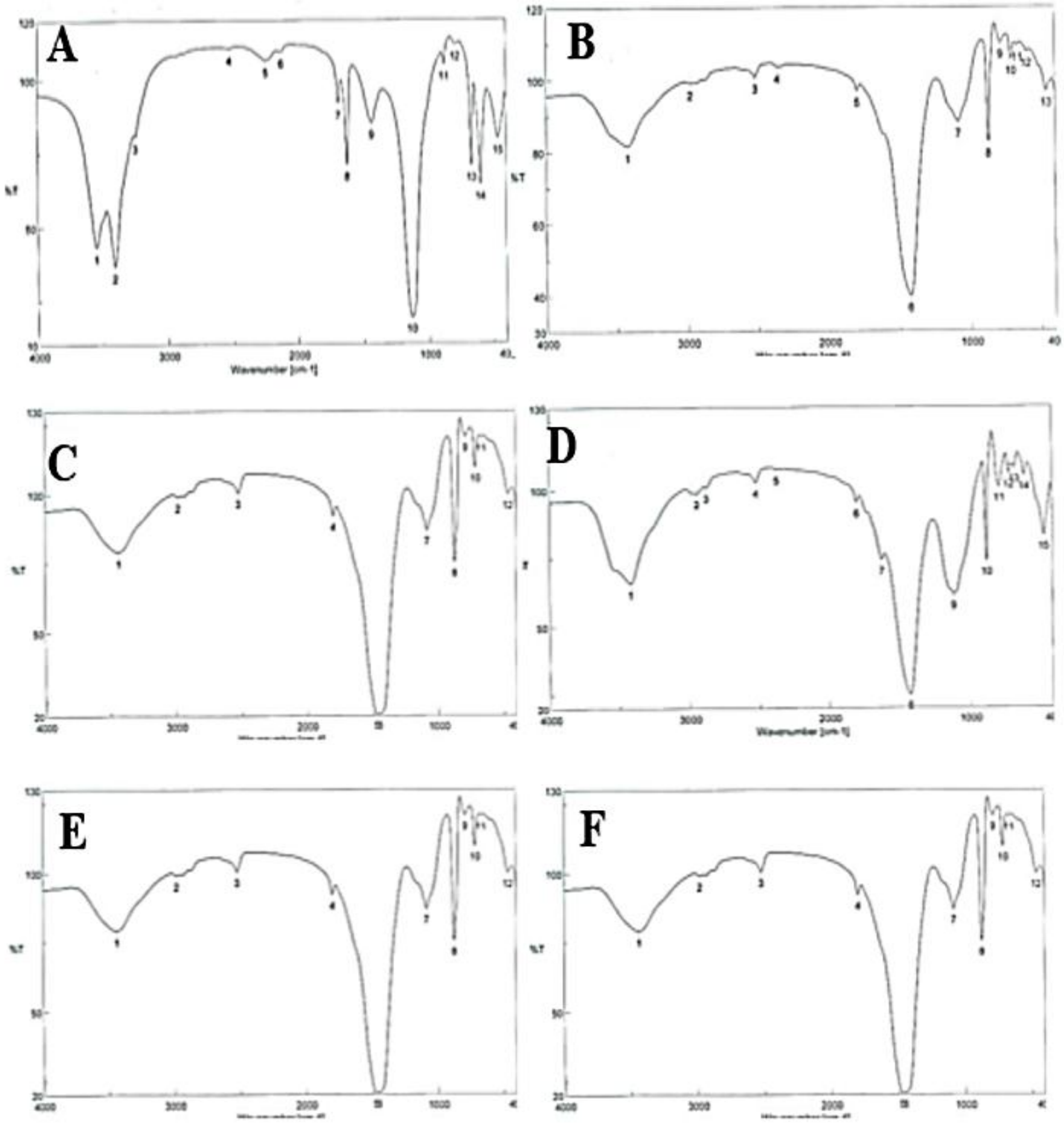

Figure 6. Infrared spectra of samples to assured that the fresco painting was covered with a layer of animal glue : A) the modern added layer was mixed with glue; B) the original ground layer; C-F) assured that the fresco painting was covered with a layer of animal glue for two reasons first supporting the fresco painting , and second reason the detachment of the fresco painting from the mud brick wall in order to transferee it to the museum.

4. CONCLUSIONS

This paper is presenting the initial stages for restoration of an Egyptian Coptic fresco painting, this study focused mainly on the physical and chemical properties of the fresco compound and the main changes happened for the fresco material which caused deterioration and fall down of the painting parts, so it can find the best and optimum restoration ways for this project.

Based on the analysis and testing results below are the findings and conclusions:

1. The modern added layer consisted of gypsum mixed with animal glue it's thickness more than 5 cm;
2. The main chemical components of the ground layer are Calcite, Quartz, and little percentage of gypsum;
3. The main reason for deterioration and fall down of the painting layers was the halite which was the main reason of its crystal erosion;
4. All colors which used in painting the current fresco painting were from nature and surrounded environment so: the red color is hematite; the yellow color is goethite; the green color is malachite; the black color is pyrolusite;
5. The presence of glue in all pigments because of adding layers of glue for consolidation in the past treatments and for the detachment from the mud walls to transfer them to the museum.

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