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ANALYTICAL STUDY OF PAINT LAYER IN MURAL PAINTING OF KRABIA SCHOOL (19th c.), CAIRO, EGYPT

Nabil A. Bader[1] & Waeel, B. Rashedy[2]

[1] *Conservation Department, Faculty of Archaeology, South Valley University, Qena, Egypt.*
[2] *Islamic Department, Faculty of Archaeology, South Valley University, Qena, Egypt.*

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Corresponding author: Nabil Bader (drnabil_bader@yahoo.com)

ABSTRACT

Krabia School was decorated with wall paintings which were applied at ceiling and walls of halls and rooms by oil techniques. The Krabia School is dating back to Khediew Ismail period (1875AD/1292Higri). These wall paintings suffered from several deterioration aspects such as flaking, powdering, cracking, discoloration, salt effects and covered with numerous of dirt, stains and insects remains. In this study painting technique has been examined by means of X-Ray diffraction (XRD), observation of samples by transmitted light optical microscopy (LOM), polarized microscope (PM), Scanning Electron Microscope (SEM) attached with EDX and Fourier Transform Infrared Spectroscopy (FTIR) analysis to determine the origins of archaeological raw materials, ascertain the techniques that had been used to apply the plaster and the paint layers used in Egyptian wall paintings during the 19th century and to obtain chemical and physical information about ongoing changes. it was noted that the painting layer consist of two layers and the painter's palette was made up of several pigments as zinc oxide, white titanium (TiO_2), red lead (minium Pb_3O_4), mussicot PbO, barium sulfate ($BaSO_4$), Hematite (Fe_2O_3), vanadium oxide and strontium sulfite $SrSO_4$. In addition, some decay products, such as sodium chlorides and kaolinite were detected.

KEYWORDS: Krabia School, Paint layer, Oil paints, Deterioration, Analysis, Microscope, FTIR. Pigments

INTRODUCTION

Archaeological history of Krabia School

Krabia School is a magnificent building that reflects grandeur and magnificence of the arts together in the period of the descendants of Mohammed Ali's family, located in Sheikh Rihan Street, Tahrir Square, Cairo, Egypt and dating back to the 19th century (There are no researchers that studied its architectural and fine elements before that date. Khediewy Ismail made his great efforts to establish primary schools in Cairo and various capitals, one of these was Krabia School, which had been established for teaching girls. In the Nile calendar for Amin Sami EL-Baroudi (El-Baroudi, 1936), it is mentioned that, in 1292 Hegira many schools were opened in Cairo, one of them was Krabia School for teaching girls with 152 pupils, primary education and handicraft. Through this study we can decide the exact date of the school from studying its architectural and fine elements. We can emphasize the creation date of the school which returns to the end of the 13th Hegira century / last quarter of 19th century AD.

Architectural Description

The school consists of a basement and two floor are all similar in layout (Fig.1). The basement is divided to great Hall shrouded in six rooms, three on each side. The first floor consists of rectangular space (lounge) on the side of it two rectangular rooms, it has the main entrance of the school which leads to a great rectangular hall that has the openings of all units on the first floor. The first floor has six rooms, three to each side, in addition to bathrooms. The layout of the second floor is similar with first floor. It was noted that, the school has large openings, doors, and windows and this undoubtedly is related to the magnitude of this architecture.

Figure 1 The outside view of Krabia School in El-Shech Rehan Street in Cairo.

Wall painting technique

The technological examination of the mural paintings from Krabia School focused on the technical and material elements. This design layer appears to have been executed according to the oil paintings technique on dry plaster, having rough layer (arriccio) made from lime and sand, applied in varying thicknesses and in multiple layers to build up and level the wood and wall which was applied under another white fine layer of plaster (intonaco) varying in thickness from 2-6μ (Fig.2), used as a finishing coat and provided the ground for the mural scheme including in composition lime and inert materials like tow (An analysis and further characterization of these two plaster layers is discussed). Pigments were executed in oil painting. Oil paintings are directly executed on dry plaster. Drying oils have been used as binding media for pigments in wall paintings in the Krabia School. Oils form solid film layers by reacting with the oxygen in the air, this reaction is known as auto-oxidation with air [Gimeno 2001]. In the palette of the wall painting of the Krabia School, many different colors were recognized, white, blue, red, yellow, green, black, and use a mixture of these colors and output them in the implementation of different finishes. The colors that appear are dark, violet, dark red (nbiti), yellow, light green, light blue, beige, lemon yellow, olive green, pink, brown gray and other color.

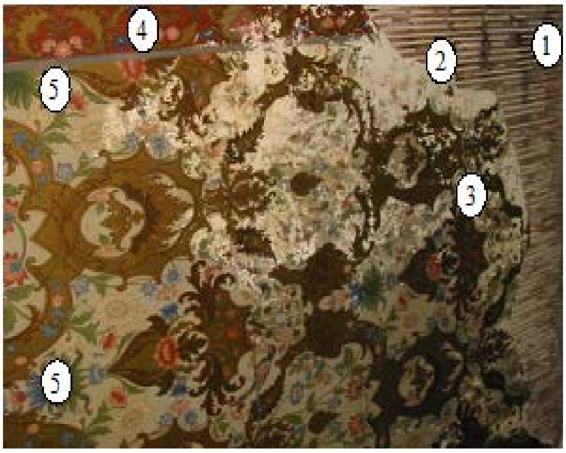

Figure 2: Structure of the wall paintings at Krabia School "1- wooden support 2- preparation layer, 3- olive green color, 4- red color, 5- green 6-blue color.

The figurative elements and the use of pigments

Ceilings are one of the most important architectural elements in the architecture especially in Egypt. It was not only used for structural purposes but it was widely used to add aesthetics and creativity in terms of the building. The celling is the prominent part of the Krabia School and decorated with multiple ornaments in various colors. The ceilings of the rooms, halls and some walls of Krabia School were originally prepared to receive mural paintings with the application of two plaster layers which decorated with amazing paintings, which showed the effects of Islamic art in European artists. Wall paintings have some diversity in the context of the decoration. Units and decorative items were multiple in the celling: beauty and the love goddess "Venus" (Fig.3a), children of love "Kiobid" (Fig.3b), an old man with a mustache and beard (Fig.3c), figurative human drawings painted in the third room to the left of the main entrance on the first floor (Fig.3d), butterflies, animal drawings, birds, doves, eagles, wings painted inside the ceiling of the shed entrance (Fig.3e). Legendary animal drawings were painted and showed a legendary animal with an animal head and a plant body ending in a spiral shape (Fig.3f). Plant drawings frequently showed wrapped branches ending in a spiral shape containing triple paper petals and ending with in a heart shape (Fig.3g).

Chalice-like leaves, Roman alakantes, sheets, equity, and Roman alanthimon, flower God, as bilateral and trilateral exchange, Quartet, Quintet, six, eight, and twelve Hill, grape leaves and his bunch of grapes, the vases out of branches, flowers, sunflowers appeared (Fig.3h). Baroque and Rococo, the flower of the roman alrozet, trees, arabesque and half fans palm (Fig3i,j).

Architectural decoration also appeared in the roof of the School and decoration of frames used in dividing the bishop to spaces and specific regions within which the painters performs his decoration, featured quadrilaterals, Quintet, and forms of assistive devices, circuits, and plagues of the seas, the lobate, contracts, shapes of eight ribs, and forms of stellar dishes (Fig.3k,l). Besides the above-mentioned decoration, other forms and decorations were represented at the ceiling as stick; flames and charges fees of cloudy skies were painted (Fig.3m).

In addition, some landscape represented by River Nile (Fig.3n) or some ancient buildings as Sphinx and pyramids (Fig.3o) and Shrines (Fg.3p) (El-Rashidi, 2010).

Conservation State

The wall paintings on the Krabia School are in a very bad condition. Physiochemical factors and biological agents play an important role in this deterioration causing remarkable amount of aesthetical and chemical damage.

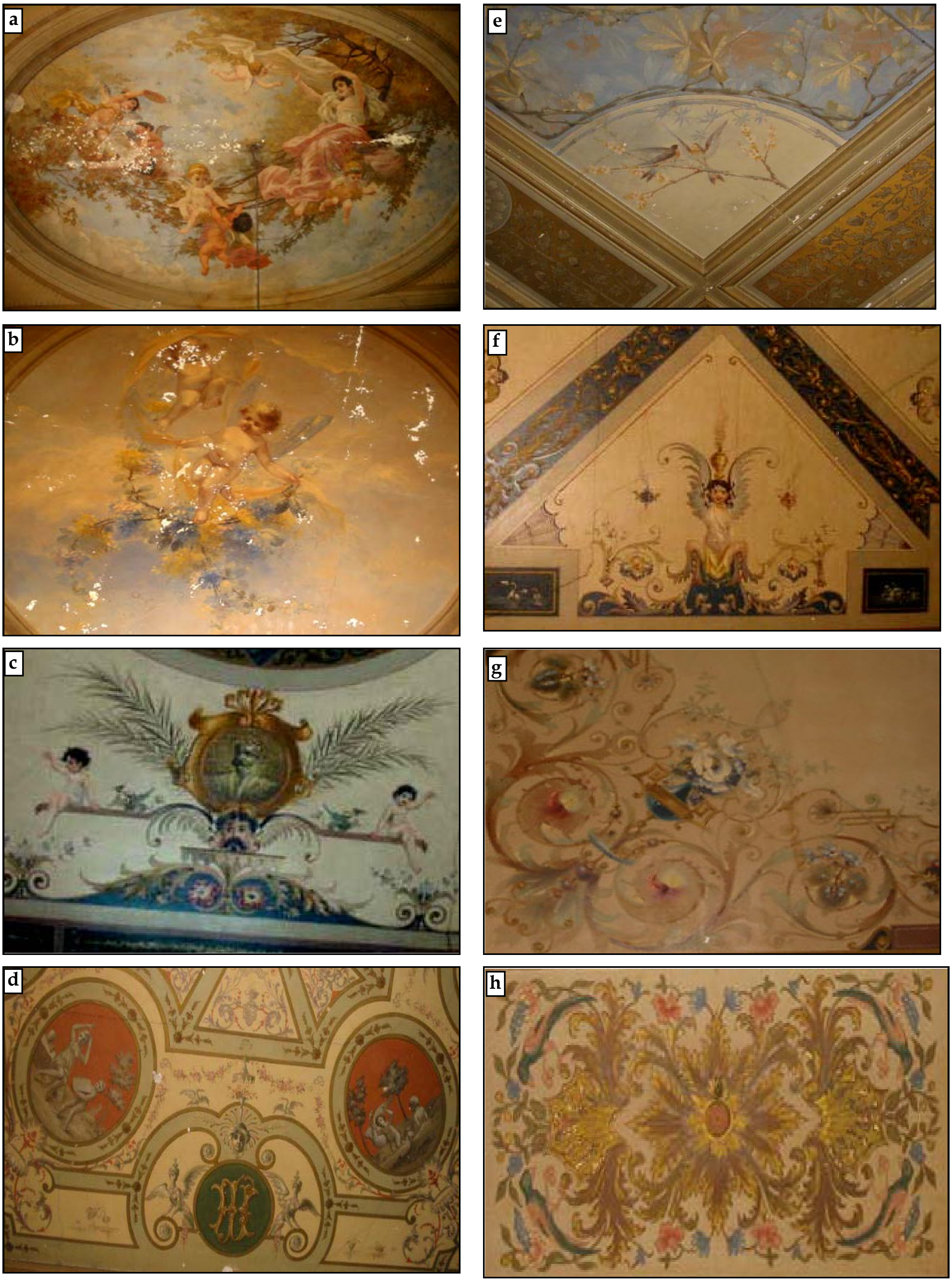

Figure 3. Details from the wall paintings at the Kerabia School (Continued next page)

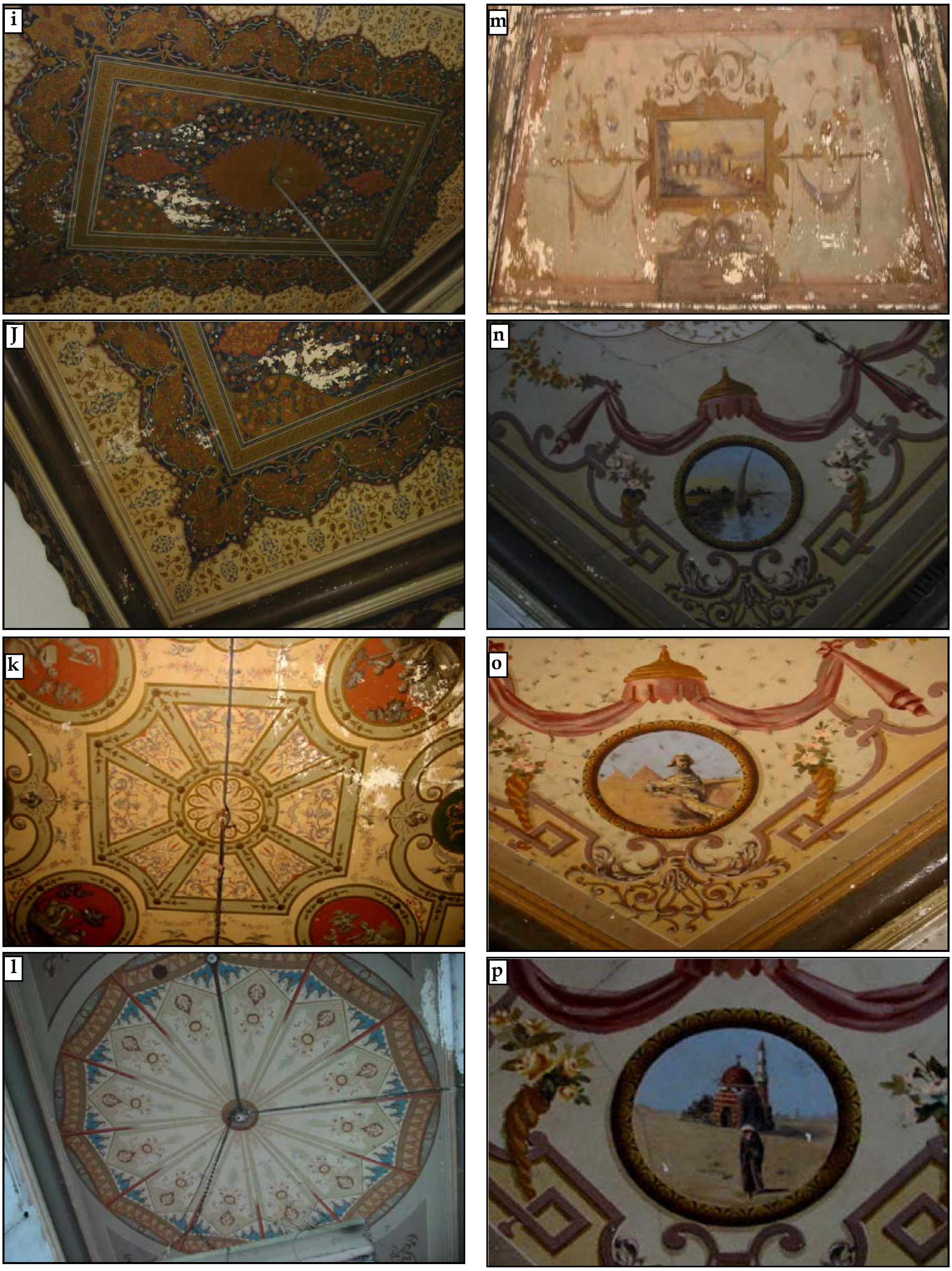

Figure: 3 Details from the wall paintings at the Kerabia School

The most common alterations of the mural painting were is found in the paint layer as a result of moisture with constant water infiltration, due in part to failing roof drains; missing window panes and damaged impermeable roof membrane, the evaporation front now migrates through the interior of the ceiling roof (fig.4a). Paint layer suffer from sever deterioration such as, detachment of the paint layer and some pieces were lost (Fig.4b,c). Discoloration of the paint layer was noticed (Fig.4d). Different types of dirt accumulate, such as dirt, dust, stains, insect's remains and house fly specks are deposited on the painting surface (Fig.4e) which can cause the painting to deteriorate further and it is affect the painting visibility. In addition to crumbing in some parts of paint (fig.4f) and fine network of cracks is present through the paint and ground layers. Obviously salts effect can be seen (Fig.4g,h), widespread presence of salts, visible as a whitish irregular film in several places in Krabia School wall paintings. The nature of the salts has been determined by XRD and EDX analysis. In the present study, the work of a prolific, respected and noteworthy wall painting and decorator is ceiling presented for analytical interpretation as a result of some restorative procedures. The present study concerns itself with disclosure and classification of its painting techniques used in the wall paintings, identify the composition of the materials used in the construction and decoration of the wall painting which consists of ground layer, pigments and binding media and to examine the alteration processes in wall painting from it. In fact, only through a profound knowledge about the nature and conditions of constituent materials, suitable decisions on the conservation and restoration measures can be adopted and preservation practices enhanced. It is interesting that no previous analytical study has been performed for these decorations, so the results are not only novel but essential for the future restoration project.

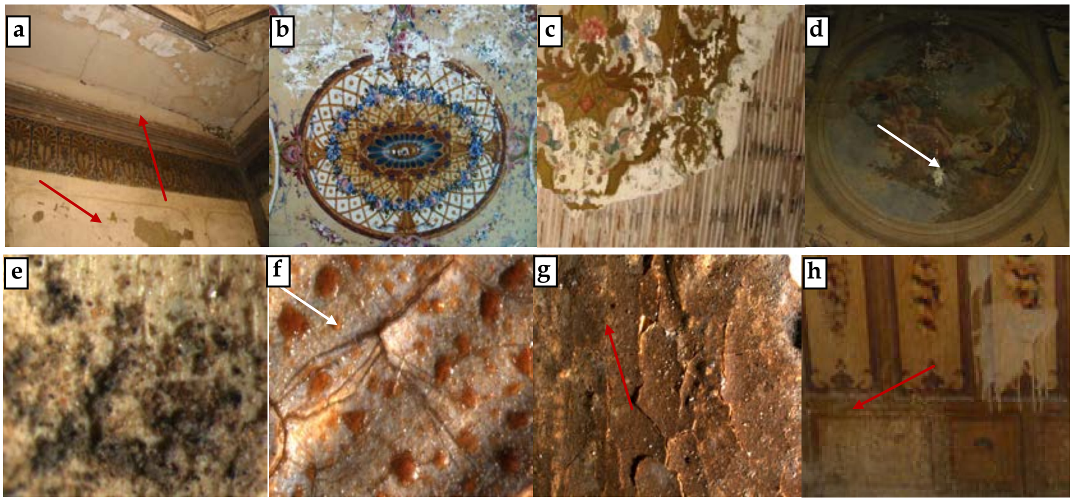

Figure 4: Details of deterioration features of wall painting at Krabia School a: filtration of moisture from the ceiling b: c: detachment of the paint layer from the ground layer and other pieces of paint layer and ground layer were missing chromatic alterations d: discoloration of the paint layer e: dust, stains and insects remains f: crumbing in some parts of paint layer g: cracks and salt deposits at the paint layer.

2. MATERIALS AND METHODS

Samples

In theory, samples should be taken from the most representative area (Maryse, 2009) but due to the minimum invasiveness requested, several samples were generally collected from pre-existing cracks, lacunas or edges and submitted to complementary analyses. The samples under investigation were acquired from a variety of scenes and zones in the school and were chosen for the purpose of identifying the material elements that make up the plaster, pigments, binding media and the residual salts on the surface. The sampling of pigments for the analysis was collected as powder or fragment detached parts of the paintings, it was cared to collect samples as small as possible in size. These samples can give interesting information which can be validated by further analyses.

Methods and instrumentation

The compositional analysis of paint plays a vital role in our understanding of techniques. The compositional analysis of paint, in conjunction with a condition survey, is the starting point for any intervention whether it is cleaning, consolidation or documentation. This study highlights analytic techniques used in the identification of the paints of the Krabia School as:

Light Microscopy

Optical microscopy techniques include reflected light used with opaque samples such as those prepared as cross sections or it may be used in combination with transmitted light for pigment dispersion [Silva 2006]. This technique allows their stratigraphic characterization under visible light. Numbers of layers, color of paint layers, the particle size, presence of pigments' mixtures and presence of organic substances can be determined; also it can provide information on the damaged layers. An optical microscope Leica DM 1000 has been used for the dark field observation and photomicrographs recorded with a Leica EC3 camera.

Scanning electron microscope

Scanning Electron Microscopy (SEM) is an imaging technique more common in conservation and measuring small features. This is a technique used to more precisely describe the morphological features of a pigment. The samples were coated with gold in order to increase their low conductivity. SEM is often used in combination with EDX, which identifies the elemental composition of a sample in a scanning electron microscope. This technique measures emitted X-rays and generates fluorescence from atoms in its path. The elemental composition has been determined using a JEOL JSM 6400 scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDX) system, detector model 6587, analyzer at an acceleration voltage of 5-50 keV, lifetime>50sec, CPS _4000 and working distance 7mm.

X-ray diffraction (XRD)

This technique is used to identify crystallography of a material as well as identify minerals and chemical compounds using the random powder method for the bulk sample using a Philips X-ray PW 1840 diffractometer for semi-quantitative mineralogical analyses using CuK radiation, 40kV/25mA divergence and detector slits of 1.54056°, 1.54439° 2 step size, and time for step of 1s. The XRD profiles were measured in 2θ goniometer steps for 0.300s.

FTIR analysis

FTIR in the study of pigments can be particularly useful for identifying organics that are missed using techniques such as EDS and XRD. FTIR is able to recognize inorganic compounds containing complex anions (such as carbonates, sulfates, silicates) but it is unable to identify simple anions (such as oxides and sulfides) (Michele et al 2002). Many of inorganic compounds and organic substances show characteristic absorptions in the mid-IR range 4000–600 cm^{-1}, FTIR represents one of the first analytical techniques applied to cultural artifacts. The samples were analyzed as KBr pellets by JASCO FT-IR–460 plus spectrometer, in the transmission mode (400–4000cm^{-1}, at a resolution of 4 cm^{-1}).

RESULTS AND DISCUSSION

The paint ceiling is composite structures; its incorporate varying species of wood as support, preparation layer, different types of paints and binding medium. The objective of substrate analysis for this project was to determine the constituents of the plasters and paints.

The plaster

Macroscopic investigation of the wall paintings surface at points of extensive damage and detachment permitted the detection of two layers of plaster shows that, the painted layer were applied on two different techniques. The 1st starting from the bottom layer was as follows, wooden support, coarse layer, fine layer and paint layer (Fig.5a), the 2nd starting from the bottom layer, was as follows, wooden support, coarse layer, canvas, fine layer and paint layer (Fig.5b). SEM examination of the canvas fiber proved that the fibers are from Linen (Fig. 6a). From a detailed examination of the FTIR spectrum (Fig.6b), the area 2918cm^{-1} of C-H stretching, O–H stretching in the region 3404cm^{-1} and the area 1620cm-

1 of C=O stretch lead to characterize the canvas as Linen. XRD was used to analyze the mineralogical composition of the fines portion of the selected samples. The fine and rough plaster were separated and crushed. XRD patterns of the inner layer in contact with the wood support (coarse layer) indicated that it was mainly consists of calcite as a major component mixed gypsum, quartz, halite and small amount of zinc (Fig.7a) , the fine plaster layers composed of calcite ($CaCO_3$), quartz (SiO_2), halite (NaCl) and little quantities of zinc (Fig.7b). EDX mapping of a fine layer (Fig.7c) illustrates the presence of high amounts of zinc (Zn), calcium (Ca), sulphide (S), low amount of silicone (Si), chloride (Cl) and lead (Pb). The FTIR analysis of the white ground layer of the ceiling (Fig.7d) revealed calcium and gypsum. The absorbance bands shown at 3543 and 3404cm^{-1} due to the O–H stretching, 1619 cm^{-1} due to O–H bending, 1141cm^{-1} due to S–O stretching [Daniilia et al 2008]. The characteristic bands of calcite are present also; yielded at 2562cm^{-1} due to (CO_3^{2-}), overtone and combination 1419.71 cm^{-1} due to CO_3^{2-}, stretching, 669cm^{-1} CO_3^{2-} bending. In addition to bands at 2919.7-2850.27 cm^{-1} which is ascribed to the methylene groups of animal glue. Considering the results, the two layers analyzed had very similar characteristics such as color, texture and binder, suggesting that they are both part of the same campaign or at least utilizing similar technologies. It can be claimed that plaster layers were made mainly of calcite ($CaCO_3$) attributed to lime binder, Gypsum ($CaSO_4.2H_2O$) attributed to the binder also; quartz (SiO_2) attributed to the aggregates and zinkite. Zinc compounds have been a well-known additive used for bleaching and brightening plaster and colors of the paintings admixed with animal glue [Van der 2002]. EDX revealed the presence of lead (main compound of red paint), in addition to halite (NaCl) which related to salt contamination; the presence of salts has degraded the rough plaster layer. Salts (as halite) are crystallizing not only on the surface of the wall, but in areas of detachment where interlayer separation is occurring in the plaster.

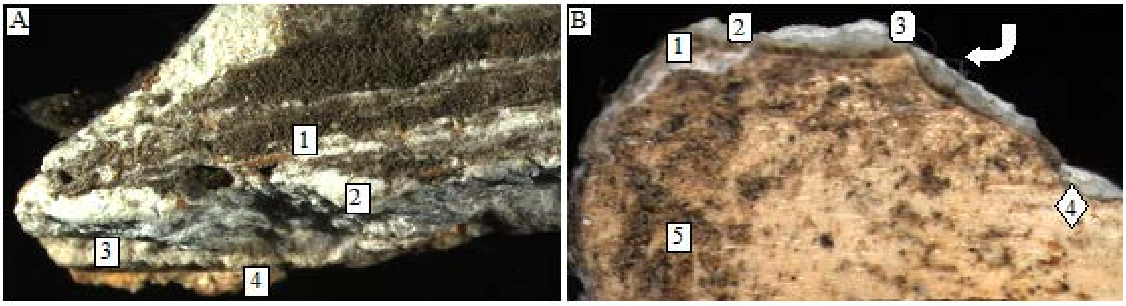

Figure: 5 Microscopic images of the painting layer of Kerabia School a: plaster of Kerabia school, 1 wooden support; 2 - coarse ground layer, 3- fine preparation layer, 4- paint layer b: photomicrographs of the paint layer and canvas fiber 1- coarse ground layer 2- canvas fiber 3- fine preparation layer 4- beige color 5- organic stains and the arrow refers to canvas fiber.

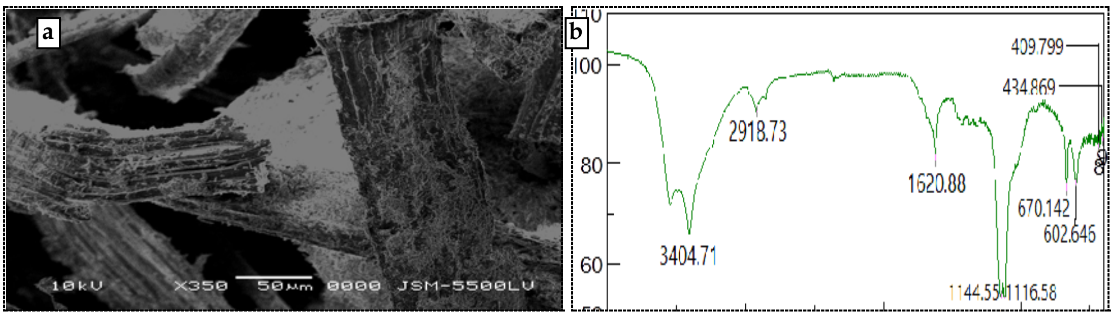

Figure 6 Investigation of the fiber of canvas, a: SEM image of canvas fiber (linen), b: FT- IR pattern of canvas

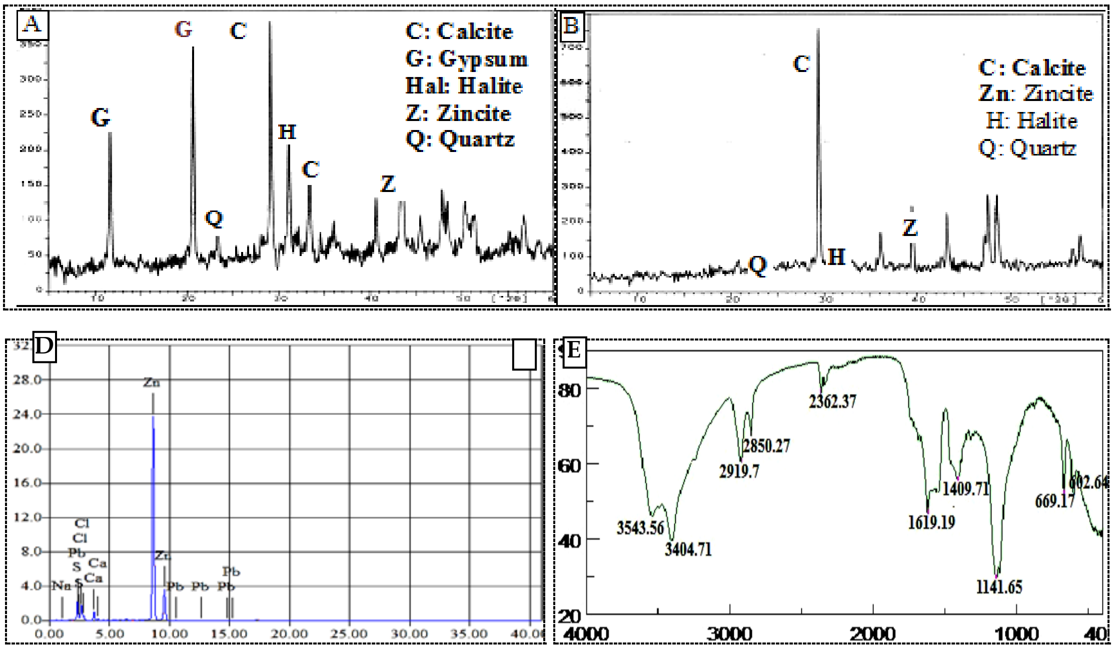

Figure: 7 a,b:, d: FT- IR pattern of preparation layer e: XRD pattern of coarse preparation layer, f: XRD pattern of fine preparation layer, g: SEM-EDX pattern of fine plaster.

Mineralogical & Chemical Composition

Mineralogical, chemical and micro structural properties of the pigments have been determined by XRD, Light Optical microscope and SEM-EDS analysis. The mineralogical composition of some pigments was not determined by XRD due to their low concentration in the thin films over priming layers. Hence, SEM-EDS analyses were carried out to find the elements which were present in the painting layers. Infra-red spectral was used of characterization of binder. The red, yellow, olive-green, white, brown, lemon yellow, pink and beige of color have been analyzed and the results are summarized at table 1, 2.

Red pigment

The optical investigation of red pigment sample shows, it was applied as a thick layer, the paint layer is applied directly on the underlying substrate which is rich in detachment part, black stains and fibers (Fig.8).

The SEM image shows indistinguishable crystal form of the brownish and red pigmented ochre is found. The elemental composition analysis of the red painting surfaces indicate that it is mainly composed of calcium (Ca), iron (Fe), silicone (Si), zinc (Zn), sulphure (S), lead (Pb), barium (Ba), titanium (Ti), magnesium (Mg),) and aluminum (Al) (Fig.9).

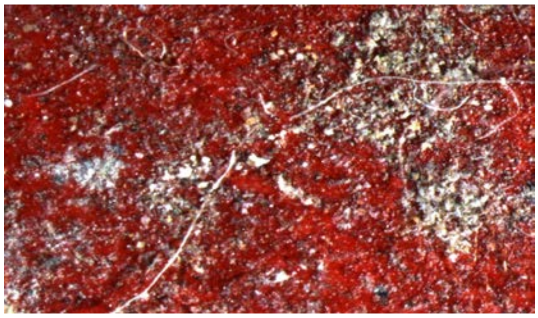

Figure 8 Photomicrographs of the red color at the ceiling of Krabia School

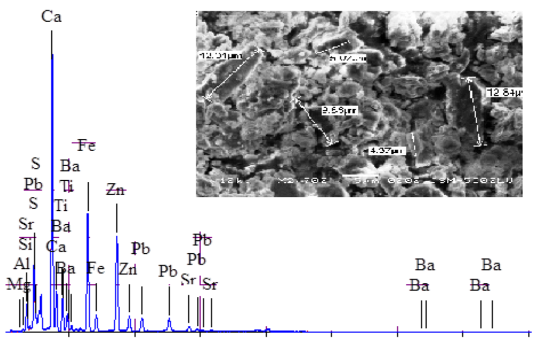

Figure 9 SEM-EDX Pattern of red pigments at the ceiling of Krabia School.

XRD patterns of the red sample (Fig.10) shows the presence of red lead (minium, Pb_3O_4), calcite, hematite, gypsum, zinkite and halite.

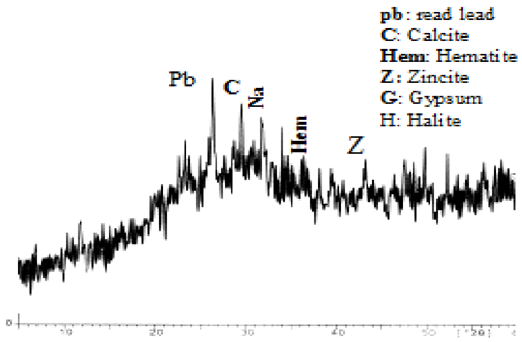

Figure 10 XRD pattern of of the red color at the ceiling of Krabia School

The FTIR spectrum of the red paint, gave the characteristic bands of red lead, it was detected in the areas and gave a weak band at 3540.67, 2922.59, 1620.88, 1421.28, 1116.58, 668.214, 527.436, 447.404 cm^{-1}. The above results suggesting that, this colored paint could be prepared by the use of mixture of red lead (minium Pb_3O_4) and iron oxide, calcite, gypsum and zinkite is originated from preparation layer and the presence of halite is due to salt contamination.

Brown Pigment

The examination of brown color by LOM (Fig.11) shows, the color and the preparation layers are inhomogeneous in thickness, most probably due to inadequate preparation of the paint layers and shows brown spots and sand grains mixed with matrix.


Figure 11 photomicrograph of the brown color at the ceiling of Krabia School

The sample under SEM investigation shows cavities and degradation surface. The elemental composition of the brown color indicated that it is mainly composed of zinc (Zn), Sulphide (S), calcium (Ca), iron (Fe), and chloride (Cl)) (Fig.12).

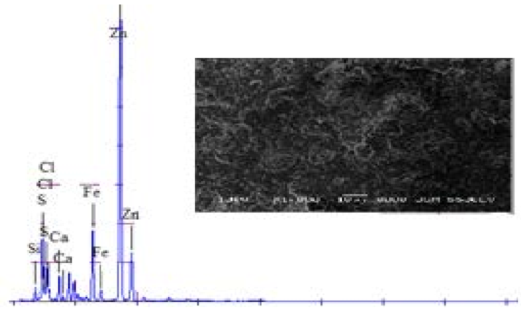

Figure 12 SEM-EDX Pattern of brown pigments at the ceiling of Krabia School

The mineralogical composition of the brown color sample by XRD (fig.13) shows, the sample composed of zinkite (ZnO), calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$) hematite (Fe_2O_3) and halite (NaCl).

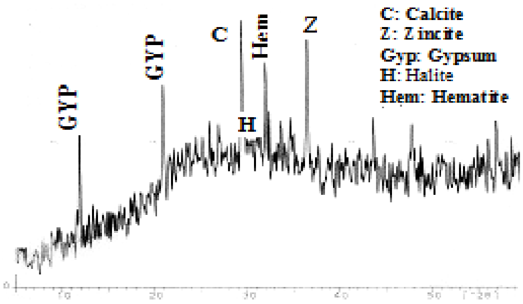

Figure 13 XRD pattern of of the brown color at the ceiling of Krabia School

The observation of elements found in the composition of the color sample and results of XRD may indicate, the brown color is hematite (Fe_2O_3), the presence of zinkite, calcite and gypsum is originated from preparation layer and the presence of halite is due to salt contamination.

Pale-Brown Pigment

The photograph of LOM (Fig.14) shows the pale brown layer tends to yellow and the paint layer is inhomogeneous in surface and rich in voids and coated with dirt. The paint granules of olive green color were undefined by SEM. The elemental composition analysis of the pale-brown color surfaces (Fig.15) indicate that it is mainly composed of calcium (Ca), Zinc (Zn), sulphide (S), barium (Ba), iron (Fe) and silicum (Si).

Figure 14 Photomicrograph of the pale-brown color at the ceiling of Krabia School

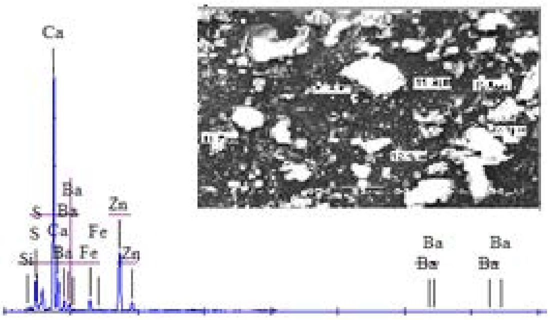

Figure 15 SEM-EDX pattern of pale-brown pigments at the ceiling of Krabia School

The mineralogical composition of the color was determined by XRD (Fig. 16) as calcite ($CaCO_3$), zinkite (ZnO), hematite (Fe_2O_3), Quartz (SiO_2) and halite ($NaCl$) (Fig.16). According to these results, the pale-brown color is prepared by mixing of yellow barium sulfate ($BaSO_4$) and hematite (Fe_2O_3). The calcite and zinkite can originate from preparation layer and quartz from aggregates.

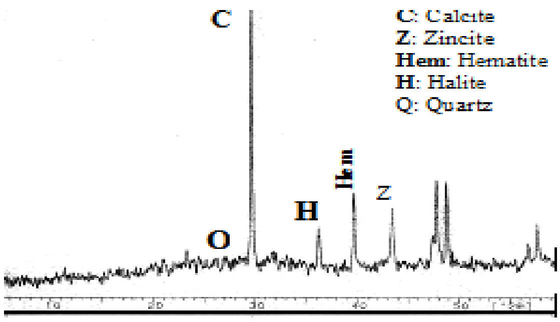

Figure 16 XRD pattern of the pale- brown color at the ceiling of Krabia School

Lemon yellow pigment

The optical investigation of the lemon yellow paint (Fig.17) shows that the paint layer is homogeneous in surface and has a brown spots. SEM observation show that, the paint comprised of fine prism grains characteristic lead oxide. EDX analysis confirmed the presences of Zinc (Zn), sulphide (S), lead (Pb), chloride (Cl), sodium (Na) and calcium (Ca) (Fig.18).

Figure 17 Photomicrograph of the lemon yellow color at the ceiling of Krabia School

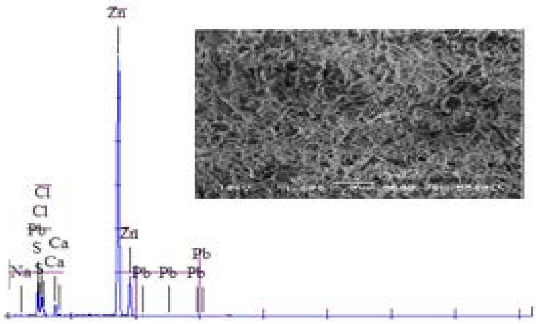

Figure 18 SEM-EDX Pattern of lemon yellow pigments at the ceiling of Krabia School

Mineralogical composition of the color composed of zinkite (ZnO), gypsum ($CaSO_4.2H_2O$), microcline ($KAlSi_3O_8$), lead oxide (Massicot, litharge PbO) and halite ($NaCl$) (Fig.19).

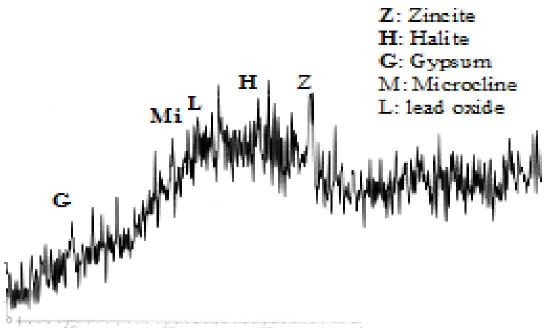

Figure 19 XRD pattern of lemon yellow color at the ceiling of Krabia School

Considering the elemental analysis, it can be claimed that a Massicot, litharge (PbO) is responsible of the lemon yellow color. Lemon yellow was first used as a color name by the early nineteenth century British colourman Field, although the composition was not given at the time (Eastaugh, et al., 2000).

White Pigment

Among the various pigments that were used in the decoration of the Krabia School, the white pigment. Optical microscopic investigation shows the pigment layer is slightly thick with different chromatic hues range from red to yellow, rich in voids and covered with dust (Fig.20).

Figure 20 Photomicrograph of the white color at the ceiling of Krabia School

SEM observation of the white sample shows the heterogeneity of titanium crystals dispersed within the preparation layer. In EDX analyses of the white color amounts of calcium (Ca), Titanium (Ti), aluminum (Al), sulphide (S), silicon (Si) and vanadium were determined (Fig.21).

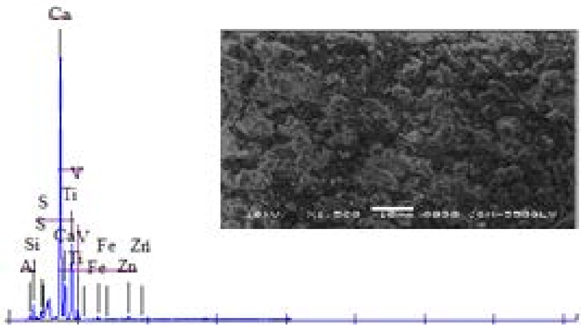

Figure 21 SEM-EDX Pattern of white pigments at the ceiling of Krabia School

In the mineralogical analyses of the sample by XRD (Fig.22) calcite, zinkite, halite, and microcline were observed. Considering elemental study, it can be claimed that white color was prepared from white titanium (titanium di oxide TiO_2). The calcite and zinkite can originate from preparation layer, microcline from aggregates and halite from salts. Vanadium affords a number of other colored compounds which might also conceivably have been tried as pigments (Eastaugh et al., 2000).

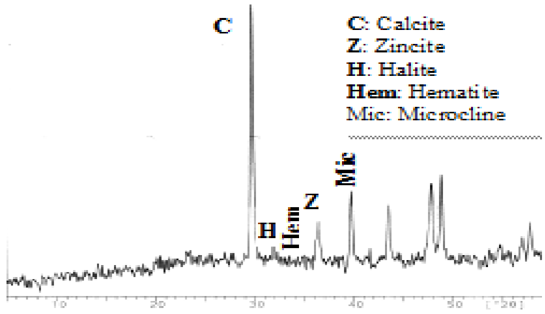

Figure 22 XRD pattern of white color at the ceiling of Krabia School

Titanium dioxide white is a collective term for various titanium dioxide pigments, notably the rutile and anatase forms of titanium (IV) oxide (Robin, 2002). Titanium dioxide white pigments in the common sense are the products of twentieth century technology and while titanium is abundant in nature, the element was not known until the late eighteenth century. Commercial production of titanium dioxide whites is carried out under several methods.

Orange Pigment

The optical investigation of the orange pigment sample (Fig.23) shows that the paint layer is inhomogeneous in surface and rich in voids.

Figure 23 Photomicrograph of the orange color at the ceiling of Krabia School

The SEM observation shows the grains of ochre. The elemental composition analysis of the orange painting surfaces indicate that they are mainly composed of zinc (Zn), sulfide (S), lead (Pb), (Cl) calcium, iron (Fe), sodium (Na) and chloride (Cl) (Fig.24).

In the mineralogical analyses of the brown color by XRD, zinkite (ZnO), hematite (Fe_2O_3), lead oxide (massicot PbO), anhydrate ($CaSO_4.2H_2O$) and halite were mainly observed in XRD spectrum (Fig.25).

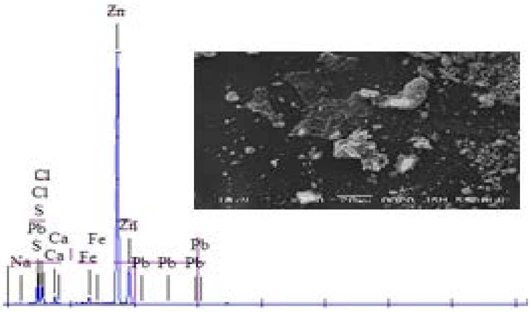

Figure 24 SEM-EDX Pattern of orange pigments at the ceiling of Krabia School

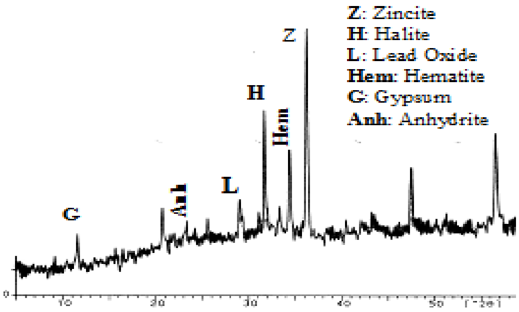

Figure 25 XRD pattern of orange color at the ceiling of Krabia School

According these results it can claim that, the orange pigment prepared from mixing of massicot (PbO) and hematite (Fe_2O_3). The observation of sodium (Na) and chloride in the paint layer can be explained as salts. The presence of anhydrite is due to the result of the transformation of gypsum ($CaSO_4.2H_2O$) by thermal weathering.

Pink Pigment

There is no explanation of the derivation of the word pink which came into use in the early sixteenth century. Pink was rarely used as a term standing alone by the second half of the eighteenth century and was generally qualified with an adjective; brown pink, Dutch pink, French pink and Italian pink (Eastaugh et al 2000). The use of this term as applied to a light red appears to occur in the middle of the seventeenth century (Harley et al 1982). LOM photograph (Fig.26) shows homogeneous in color surface; the color tends to yellow and rich of micro-cracks. The surface shows brown spots, perhaps it can organic stains or insects remains.

Figure 26 Photomicrograph of the pink color at the ceiling of Krabia School

SEM shows the grains of the color components. EDX analysis confirmed the presences of zink (Zn), sulphide (S), barium (Ba), iron (Fe), calcium (Ca), silicone (Si), lead (Pb), sodium (Na) and chloride (Cl) (Fig27).

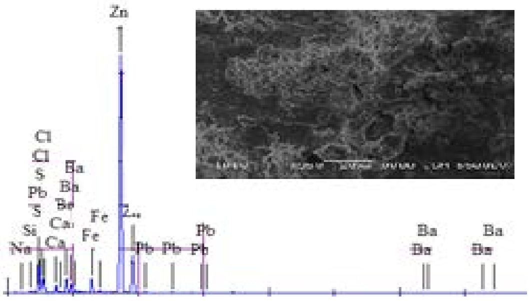

Figure 27 SEM-EDX Pattern of pink pigments at the ceiling of Krabia School

The mineralogical analyses of the pink color revealed the presence of zinkite, gypsum, quartz, lead oxide (massicote PbO) and halite (Fig.28).

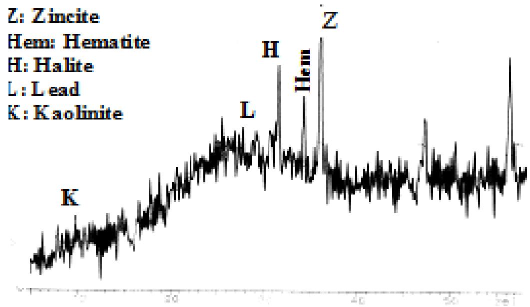

Figure 28 XRD pattern of pink color at the ceiling of Krabia School

According the elemental analysis, the pink pigment appears as a mixing of yellow barium sulfate ($BaSO_4$) mixed with lead oxide (massicote PbO) and iron oxide. The presence of zinc related to ground layer, quartz from aggregates, halite from salt contamination and kaolinite from dust layer which covered the paint layer.

Olive-green Pigment

The photograph of LOM (Fig.29) shows the olive-green layer tends to black and the paint layer is inhomogeneous in surface and rich in cracks, voids and coat of dirt and salts grains. The SEM photograph shows disintegration and rich in voids and cracks. The elemental composition analysis of the color surfaces indicate that it is mainly composed of zinc (Zn), calcium (Ca), Barium (Ba), sulphite (S), iron (Fe), sodium (Na) and silicone (Si) (Fig30).

Figure 29 Photomicrograph of the olive-green color at the ceiling of Krabia School

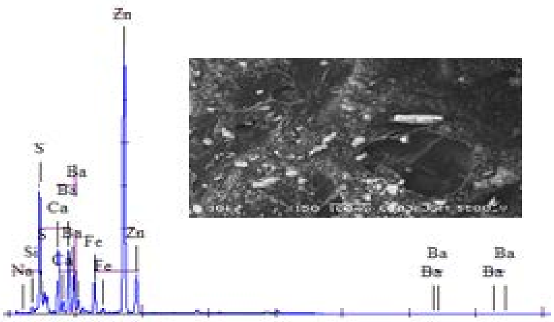

Figure 30 SEM-EDX Pattern of olive-green pigments at the ceiling of Krabia School

The mineralogical composition of the color was determined by XRD as Barite ($BaSO_4$), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$) and Quartz (Fig.31). According to the above results, the olive-green color is prepared by mixing of yellow barium sulfate ($BaSO_4$), Magnetite (Fe_3O_4) and Hematite (Fe_2O_3). The calcite and gypsum can originate from preparation layer, quartz from aggregates and anhydrite is the result of the transformation of gypsum ($CaSO_4.2H_2O$) by thermal weathering.

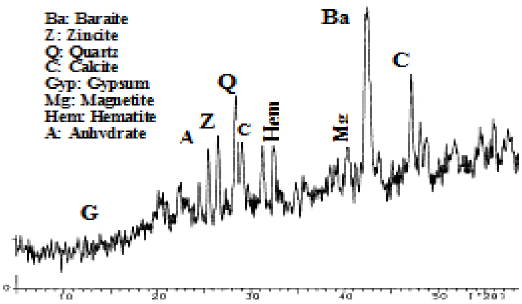

Figure 31 XRD pattern of the olive-green color at the ceiling of Krabia School

Beige Pigment

The color was observed in the back ground of the painting. The morphological observation of the Beige color sample (Fig.32) shows that the paint flakes from the under painting, fall of cracks, crumbing and dropping off in small particles, also it is covered with organic spots which resemble organic binder, the presence of these spots may be related to organic varnish.

Figure 32 Photomicrograph of the beige color at the ceiling of Krabia School

SEM observation shows the crystals are anhedral with inclusions and fringed rims. The result of EDX analysis for the beige color microanalysis revealed the presence of calcium (Ca), sulphide (S), silicon (Si), strontium (Sr), zinc (Zn) and Iron (Fe) (Fig.33).

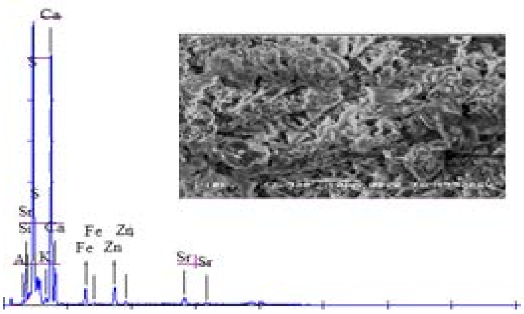

Figure 33 SEM-EDX pattern of beige pigments at the ceiling of Krabia School

XRD patterns of the beige color (Fig.34) indicated that they were mainly consists of calcite, hematite, zinkite and halite.

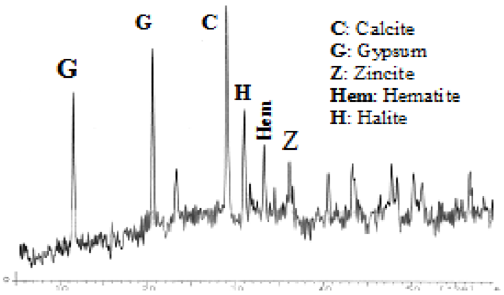

Figure 34 XRD pattern of beige color at the ceiling of Krabia School

According to the elemental analysis of the color, it can claimed that, the beige color came from Celestite ($SrSO_4$) and iron oxide. Celestite ($SrSO_4$) (or celestine) is a naturally occurring strontium sulfate mineral with chemical composition $SrSO_4$. Pure Celestite is white or colorless, but it may vary in color from red to green or brown due to the presence of impurities such as iron (Deer et al., 1992) implies that Celestite and its synthetic analogue, strontium sulfate, have been used as a white pigment commonly known as strontium white.

Table 1 EDX analysis results of pigments samples from Krabia School.

Elements	Red	Brown	Pale-brown	Lemon yellow	white	Orange	pink	Olive green	beige
Mg	2.04	-------	-------	-------	-------	-------	-------	-------	-------
Al	1.38			-------	3.6	-------	……..	-------	2.1
Si	10.00	10.87	1.83	-------	5.67	-------	2.77	3.69	8.05
S	2.31	17.95	5.3	13.8	1.04	10.9	14.74	25.45	28.18
Ca	51.92	9.78	76.37	7.82	60.95	5.22	4.51	17.68	54.62
Ti	2.39	-------	-------	-------	27.02	-------	-------	-------	-------
Fe	13.26	7.8	2.51		7.89	1.1	3.18	4.63	1.77
Zn	7.99	41.69	9.15	51.24	0.45	55.31	59.38	31.65	1.2
Sr	0.31	-------	-------		-------	-------	-------		2.3
Ba	4.99	-------	4.8	-------	-------	-------	5.5	12.84	-------
Pb	4.88	-------	-------	10.2	-------	7.14	0.22	-------	-------
V	-------	-------	-------	-------	0.66	-------	-------	-------	-------
Cl	-------	11.81	-------	12.32	-------	11.71	7.61	-------	-------
Na	-------	-------	-------	4.59	-------	9.10	2.06	4.02	-------

Table 2 XRD results of pigments samples from Krabia School.

Mineral	Red	Brown	Pale-brown	Lemon yellow	white	Orange	pink	Olive green	beige
Zinkite	7.16	26.38	11.2	30.45	9.64	48.89	43.14		10.84
Calcite	20.80	26,38	82.44	-------	62.61	-------	……..	-------	38.95
Gypsum	10.00	20.36	-------	20.15	-------	8.11	-------	2.45	28.25
Quartz	-------	-------	-------	-------	-------	-------	-------	19.66	-------
Hematite	17.66	10.97	2.88	-------	4.18	6.65	17.51	12.33	14.85
Halite	17.61	15.88	3.54	17.72	4.19	22.59	24.94		7.44
Barite	-------	-------	-------		-------	-------	-------	41.63	-------
Anhydrate	-------	-------	-------	-------	-------	4.79	-------	14.77	-------
Magnetite	-------	-------	-------		-------	-------	-------	3.95	-------
Microcline	-------	-------	-------	16.16	19.34	-------	-------	5.20	-------
Kaolinite	-------	-------	-------		-------	-------	7.84	-------	-------
Read Lead	27.34	-------	-------	-------	-------	-------	-------	-------	-------
Lead Oxide	-------	-------	-------	15.73	-------	8.49	6.25	-------	-------

CHEMICAL COMPOSITIONS OF BINDING MEDIA

Chemical composition of the binder was determined by FT-IR analyses. The results of FTIR analysis of the samples listed in (Tab.3, Fig.35), are remarkable consistent, showing that; the composition of the inclusion is very similar in all the samples studied. In the IR spectrum of the binding media, vibrations bands due to the hydroxyl (O-H) at 3400-3540 cm^{-1}, fatty acids (CH_2) at 2923-2 930cm^{-1}, esters (C=O) 2850-2864cm^{-1}, oxalate ($C_2O_4^{-2}$) at 1620 cm^{-1}, carbonate (CO_3^{-2}) at 1419 and 875 cm^{-1} and sulphate (SO_4^{-2}) at 1115 cm^{-1} were observed. The FT-IR spectrum of the binding media was similar with the ones of made with linseed oil (Dongye 2000). Hence, the observed fatty acids and esters bands in FT-IR spectrum may be explained due to the use of drying oils in the preparation of the binder.

Carbonate and sulfate bands may show the existence of calcium carbonate (calcite) and calcium sulfate hydrate (gypsum) in the samples as impurity originated from fine plaster layer. As a result of FT-IR of the binding media, it is concluded that wall paintings of Krabia School could be prepared by using drying oils such as linseed.

Table 3 FTIR results of paint layers in Krabia School.

Wave number (cm^{-1})										Function group
1	2	3	4	5	6	7	8	9	10	
3540, 3403	3404	3410	3552	3404	3543, 3404	3401	3548, 3405	3545, 3404	3407	O-H stretching band 3600-3200
2922	2923	2930	2923	2921	2919	2922	…….	…….	…….	C-H stretching bands of fatty acids of oil.
…….	2852	2864	2850	…….	2850	2850	…….	…….	…….	C=O Esters band of oil
…….	1712	1797	…….	1798	…….	1739	…….	…….	…….	Very weak band due to C=O group of calcite
…….	…...	…….	…….	…….	…….	…….	1685	1685	1685	C=O stretching band of amides groups
1620			1620		1619		1620	1620	1620	N-H bend of amines group and O-H bending of Gypsum
1589	…...	…….	1550	…….	…….	1550	…….	…….	…….	N-H bending band of amide (I°) of animal glue.
1421	1416	1433	1408	1422	1409	…….	1409	…….	…….	C-H bending band of animal glue (alkenes) and CO_3^{2-} stretching band of calcite.
1116	1115	…….	1141	1115	1141	1115	1112	1140	1164	Stretching band SO_4^{2-} (Gypsum and Barite)
874	873	874	…….	875	…….	…….	875	…….	…….	O-C-O bending band of carbonate group of calcite.
711	797	781 712	…….	711	…...	…….	…….	…….	…….	C-H torsion band of oil
668 606	669 606	669 601	669 602	605	669 602	…….	669 602	.669 602	.669 603	SO_4^{2-} bending band of gypsum.

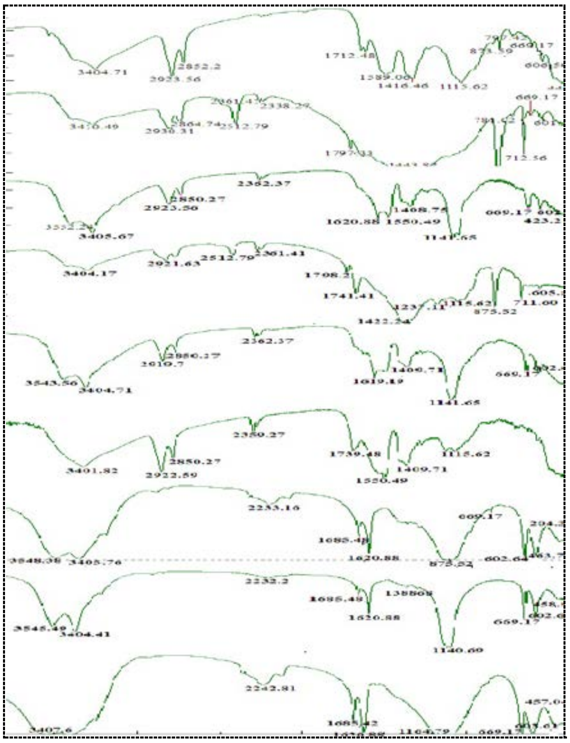

Figure 35 FT-IR patterns of the studied samples from Kerapia School.

CONCLUSIONS

This study was carried out in order to form a database of the application technique, material properties and deterioration problems of the wall paintings of the Krabia School with the purpose of conservation.

The wall paintings of the Krabia School are composed of two layers. The 1st starting from the bottom layer was as follows, wooden support, coarse layer, fine layer and paint layer. The coarse layer is composed of calcite ($CaCO_3$) mixed gypsum ($CaSO_4.2H_2O$), quartz (SiO_2), small amount of zinc and halite (NaCl) from salt contamination. The fine plaster layers composed of calcite ($CaCO_3$), quartz (SiO_2) and little quantities of zinc admixed with animal glue.

The analytical investigation of paint layers applied on Krabia School indicated tow red pigment, the first is red lead (minium Pb_3O_4) and the 2nd is iron oxides. Yellow pigment was identified as massicot (lead oxide PbO). The olive-green color is prepared by mixing of yellow barium sulfate ($BaSO_4$), Magnetite (Fe_3O_4) and Hematite (Fe_2O_3). Considering elemental study, it can be claimed that white color was prepared from white titanium (titanium di oxide TiO_2). According the analysis results it can claimed that, the brown pigment prepared from hematite. Pale-brown is mixing of barium sulfite ($BaSO_4$) and hematite. Strontium sulfite ($SrSO_4$) and hematite is responsible of the beige color. The pink color appears to be barium sulfate ($BaSO_4$) and hematite.

As a result of FT-IR of the binding media, it was concluded that wall paintings of Krabia School could be prepared by using drying oils such as linseed.The wall paintings in Krabia School, exhibit problems in preservation as a result of the salt (sodium chloride) that has formed on the painted surface. This whitish layer of salt, covering many areas of the wall paintings, affects significantly the aesthetic impact of the wall painting of Krabia School. Under the influence of environmental conditions (temperature, humidity, light, atmospheric pollutants, micro-organisms, etc.) these salts are subjected to cycles of crystallization–dissolution, leading to mechanical stresses and chemical alterations [Arnold et al 1985]. Also, the serious deterioration phenomenon of the paint layer is due to transformation of gypsum to anhydrite, the problem is more complicated by the existence of halite.

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