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Analytical Study of the Blue Pigments in some Islamic Monumental Decorated Ceilings in Cairo, Egypt

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Summary. Pigments are derived from a wide variety of substances, organic and inorganic, natural and artificial. The decorated ceilings in the Islamic monuments in Cairo had been decorated with different kinds of pigments that are still under scientific investigation and analysis for determination of the unknown materials. The aim of the paper is to make a survey of the blue pigments for making accurate determination. X- Ray Diffraction (X.R.D.) Scanning electron microscope S.E.M (EDAX) Light Optical microscope (L.O.M.) and Fourier transform infrared spectroscopy (FTIR), were adapted for analysis and investigations. The results of the study and a brief conclusion are presented.

Introduction

A pigment is a finely divided, colored substance that imparts its color effect to another material either when mixed intimately with it or when applied over its surface in a thin layer (colored substances that dissolve in liquids and impart their color effects to materials by staining or being absorbed are classified as dyes). Pigments may be classified according to color, use, permanence, etc. It is customary, however, to classify them according to origin, as inorganic and organic**.** Blue pigments considered as a one of the most popular pigments in Islamic decorated ceilings, which, came from the mineral lapis lazuli, though *azurite* (a form of copper carbonate) was also used, together with *Prussian blue* (iron blue ferric-Ferrocyanide $Fe_4[Fe(CN)_6]_3$, as were *Smalt* and *indigo* (dye). Since *Lapis lazuli* and *Smalt* are the most common blue pigments, so it will be discuss in some details:-

- *Lapis lazuli" ultramarine blue,* sodium sulfosilicate" ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$ (*NATURAL*) and $Na_{8\text{-}10}Si_6O_{24}S_{2\text{-}4}$ (*ARTIFICIAL*). ultramarine blue pigment is from the semi-precious stone, lapis lazuli, which is a mixture of the blue mineral, lazurite, with calcspar, and iron pyrites. Its present name, ultramarine, derives from *azrrum ultramarinum* or *azurro oltramarino* that formerly served to distinguish it from azurite Since 1828, the ultramarine of commerce has been an artificial product made by heating clay, soda, sulfur, and coal in furnaces. Microscopically, natural ultramarine is characteristic in appearance, and one can quite easily distinguish it from the artificial. The particles are clear blue and translucent; their fracture is conchodial and, when are not too finely divided, certain ones with squared corners and others shaped like sharp splinters can be seen.(1 :4)

- *Smalt* (SiO_2, K_2O, As_2S_3, CoO, and Al_2O_3) was the earliest of the cobalt pigments. It is moderately finely to coarsely ground potassium glass of blue color; the blue is due to small but variable amounts of cobalt added as a cobalt oxide during manufacture. Since *Smalt* is a coarsely ground glass it can be easily recognized at low magnifications. The particles show conchodial fracture and thin sharp edges of glass splinters.(2, 5: 8)

Experimental

Samples of the blue pigments were collected for investigation and analyses. The samples taken from, eight Islamic monumental ceilings in Cairo, these are the following: the mosque of Moheb El- Dien Abo El-Tayb (934-935 AH and 1537-1538 AD Ottoman period.(9)),Madrasa of El-Zaher Brqoq (786-788 AH and 1384-1386 Mamluk Jarkasy period), Madrasa of El-Ashraf Bersbay (829 AH and 1425 AD Mamluk Jarkasy period), The palace of the prince Seif El-Dien Taz Ebn Qtghg (753AH and 1352 AD Mamluk Bahary period), Madrasa of El-Kady Abd El-Baset (822-823 AH and 1419-1420 AD Mamluk Jarkasy period)and the mosque of El-Kady Yehia Zein El-Dien (848 AH and 1444 AD Mamluk Jarkasy period). X-ray diffraction method (X.R.D), Scanning electron microscope S.E.M (EDAX) Light optical microscope (L.O.M), and Fourier transform infrared spectroscopy (FTIR) were used to investigate and analyze the collected samples that mentioned before.

Results and Discussion

X-ray diffraction method (X.R.D)

X-ray diffraction method (X.R.D) was adapted for analyzes of the studied samples, but unfortunately as a result of the samples were so small the pattern of XRD was not scientifically acceptable, so the Scanning electron microscope S.E.M (EDAX) was used to achieve this objective.

Scanning electron microscope (S.E.M. "EDAX")

The scanning electron microscope (SEM) photographs and microanalyses were carried out by utilizing S.E.M. Philips XL 30 attached with EDAX unit, with accelerating voltage 30 K.V., magnification 10X up to 400.000X and resolution for W. (3.5nm). These samples were coated with carbon for investigation and analyses the samples as follows, (fig. 1: 16).

- Sample A-BLUE pigment with painting ground from the mosque of Moheb El-Dien Abo El-Tayb ceiling of Qebla Iowan. The result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *lapis lazuli" ultramarine blue,* ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$) is the main component. The oxides of CaO and SO_3 represent the painting ground plus some impurities.
- Sample B-BLUE pigment with painting ground from Madrasa of El-Zaher Brqoq ceiling of Qebla Iowan (the sample was covered with a thick layer from dirties). (The result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *Prussian blue* $Fe_4[Fe(CN)_6]_3$ is the component, (intervention by the committee). The oxides of ZnO, CaO, and SO_3 represent the painting ground and dirty.
- Sample C -BLUE pigment with painting ground from Madrasa of El-Ashraf Bersbay ceiling against Qebla Iowan (the result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *Smalt* (SiO_2, K_2O, As_2S_3, CoO and Al_2O_3) is the main component plus some impurities. the presence of Cu oxide, is an indication of mixing a small quantity of *azurite* ($2CuCO_3.Cu(OH)_2$)
- Sample D-BLUE pigment with painting ground from Madrasa of El-Ashraf Bersbay ceiling of Qebla Iowan the result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *lapis lazuli" ultramarine blue,"* ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$, is the main component plus some impurities. The oxides of CaO and SO_3 are so high, which represent the painting ground.

- Sample E-BLUE pigment with painting ground from the palace of the prince Seif El- Dien Taz Ebn Qtghg ceiling Hramlek 1. (The result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *lapis lazuli" ultramarine blue* ($3Na_2O_3$ 3 Al_2O_3 $6SiO_2$ $3Na_2S$), is the main component. The oxides of ZnO, BaO, and SO_3 represent the painting ground plus some impurities.
- Sample F-BLUE pigment with painting ground from the palace of the prince Seif El- Dien Taz Ebn Qtghg ceiling of Hramlek 2. (The result of SEM (EDAX) microanalyses and the attached Photomicrograph show that *Smalt* (SiO_2, K_2O, As_2S_3, CoO and Al_2O_3) is the main component plus some impurities.
- Sample G-BLUE pigment with painting ground from Madrasa of El-Kady Abd El-Baset against Qebla Iowan ceiling. (The result of SEM (EDAX) microanalyses and the attached Photomicrograph shows that *lapis lazuli" ultramarine blue* ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$, is the main component. The oxides of CaO and SO_3 represent the painting ground plus some impurities.
- Sample H-BLUE pigment with painting ground from the mosque of El-Kady Yehia Zein El-Dien Qebla Iowan ceiling. (The result of SEM (EDAX) microanalyses and the attached Photomicrograph shows *lapis lazuli" ultramarine blue* ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$), is the main component. The lead oxide PbO_2 represent red pigment and background. The presence of Cu oxide is an indication of mixing a small quantity of *azurite* ($2CuCO_3.Cu(OH)_2$) also.

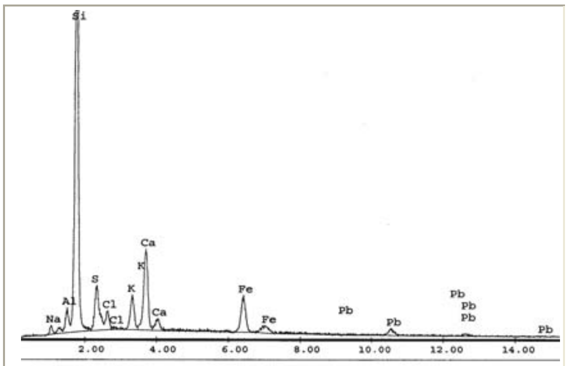


Fig.1 -SEM (EDAX) microanalyses, sample A.

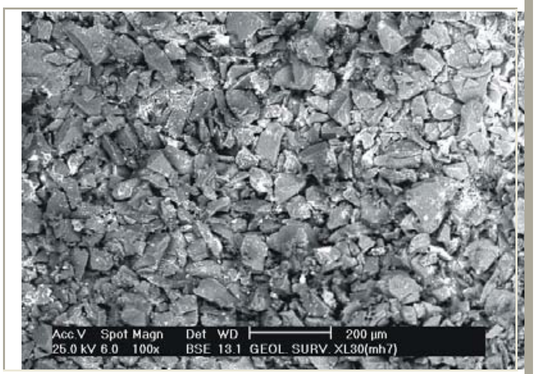


Fig.2- SEM Photomicrograph, sample. A

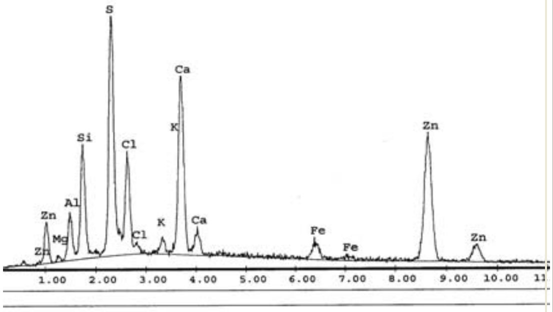


Fig.3 -SEM (EDAX) microanalyses, sample B.

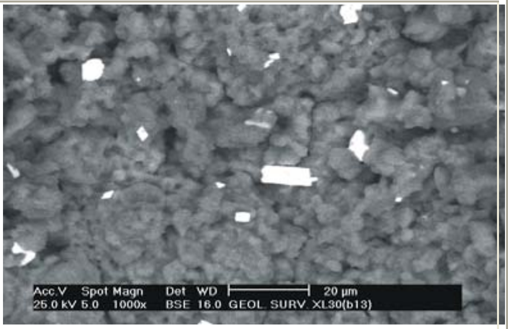


Fig.4- SEM Photomicrograph, sample B.

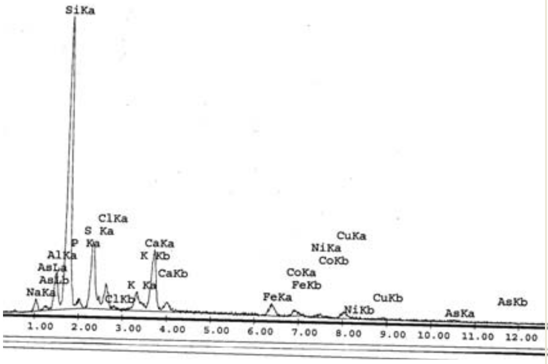


Fig.5-SEM (EDAX) microanalyses, sample C.

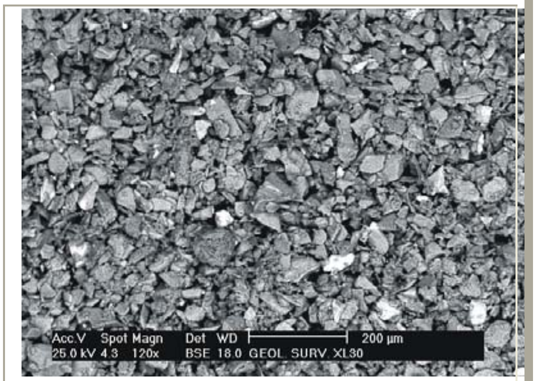


Fig.6- SEM Photomicrograph, sample C

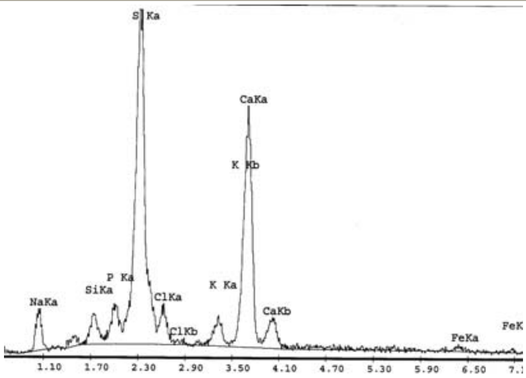


Fig.7 -SEM (EDAX) microanalyses, sample D.

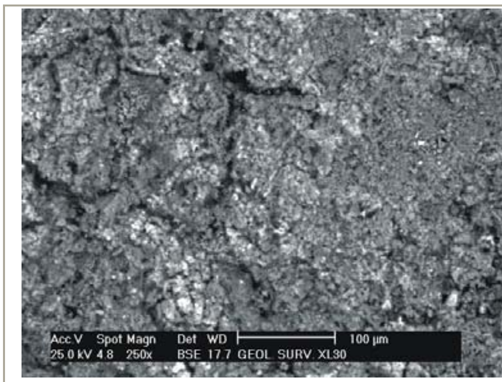


Fig.8- SEM Photomicrograph, sample D

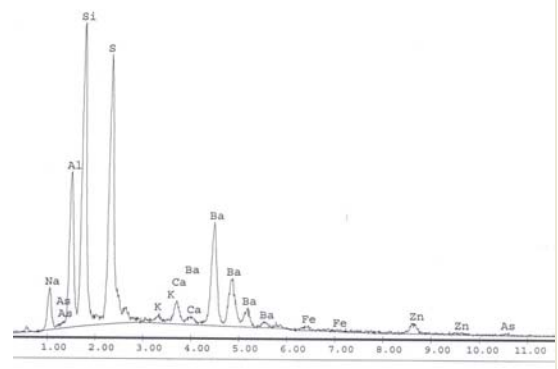


Fig.9 -SEM (EDAX) microanalyses, sample E.

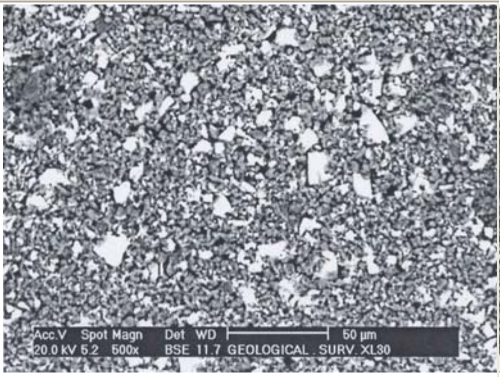


Fig.10- SEM Photomicrograph, sample E.

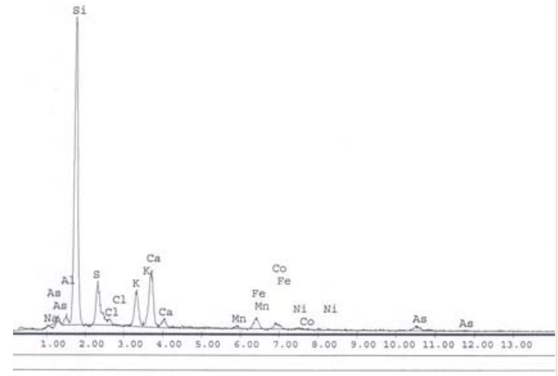


Fig.11 -SEM (EDAX) microanalyses, sample F.

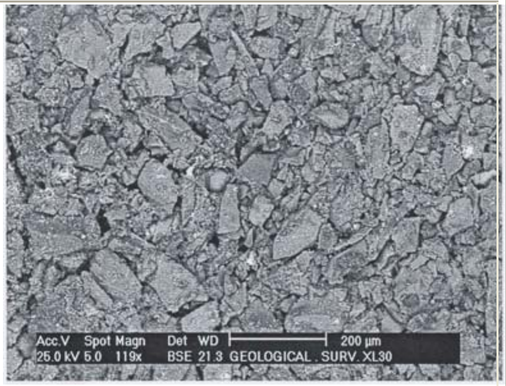


Fig.12- SEM Photomicrograph, sample F.

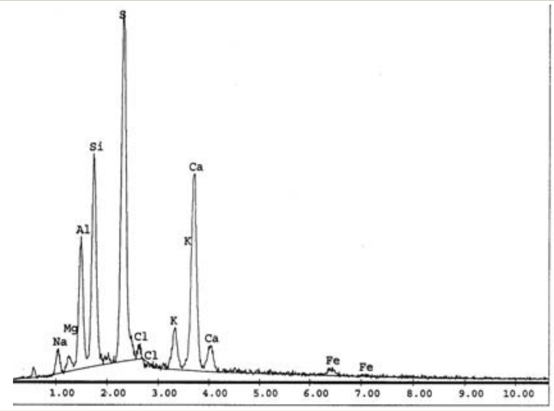


Fig.13 -SEM (EDAX) microanalyses, sample G.

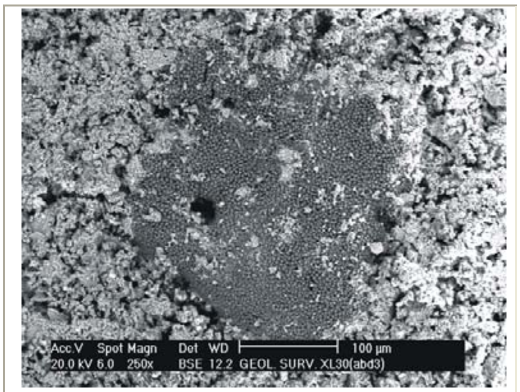


Fig.14- SEM Photomicrograph, sample G.

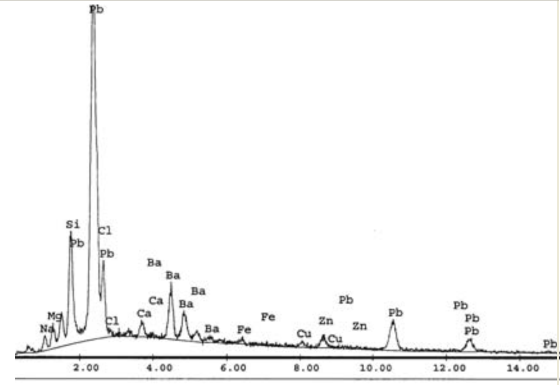


Fig.15 -SEM (EDAX) microanalyses, sample H.

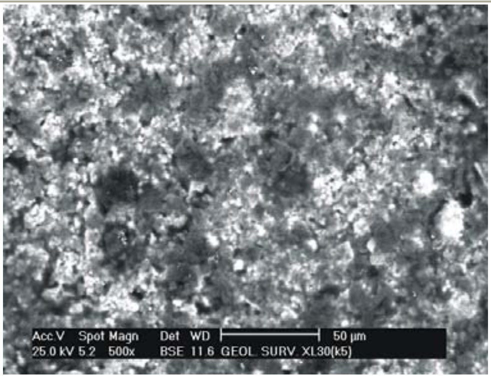


Fig.16- SEM Photomicrograph, sample H.

Light Optical Microscope (L.O.M.)

L.O.M was used to investigate surface samples of the different blue pigments from the monumental ceilings under studying. The samples were covered with Linseed oil to make it to be so clear to see the grain size distribution. The results are emphasize the EDAX results and shows the fading of the blue pigment and severe deterioration of the pigments as a result of different deterioration factors as follows (Fig.17: 24):-

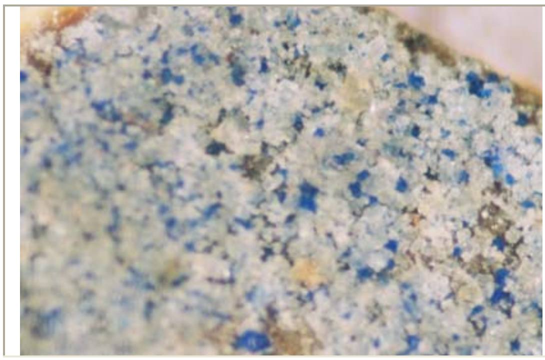


Fig.17- LOM Photomicrograph shows the Scattered grains of the blue pigment on silica background A X.63.

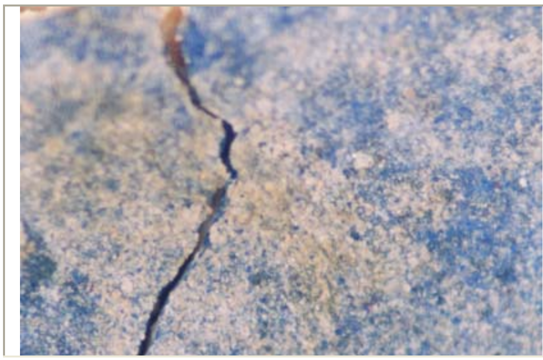
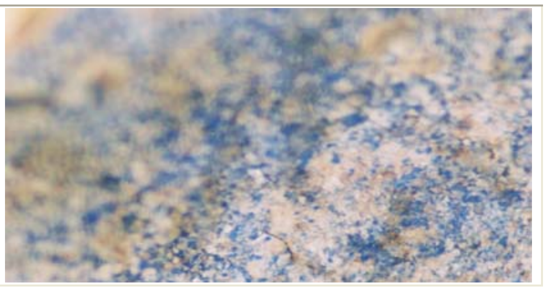


Fig.18- LOM Photomicrograph shows the blue pigment covered by a thick layer of dirt's B. X.16.



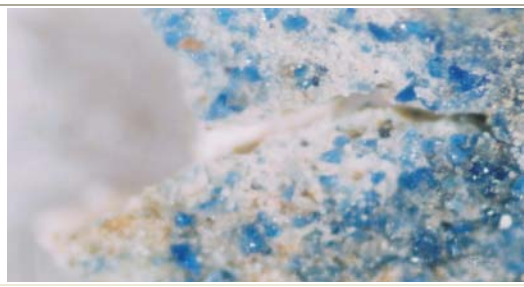
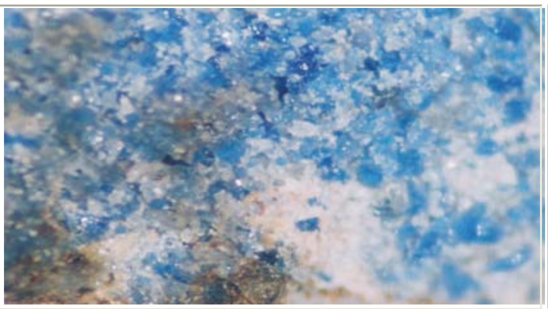


Fig.19- LOM Photomicrograph shows the Scattered grains of the blue pigment on the painting ground C. X.63.

Fig.20- LOM Photomicrograph shows sharp edges of glass splinters of the blue pigment E. X.63.



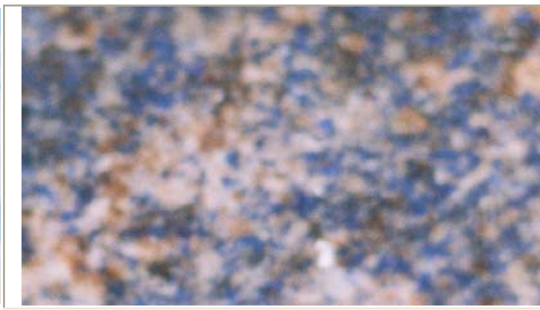
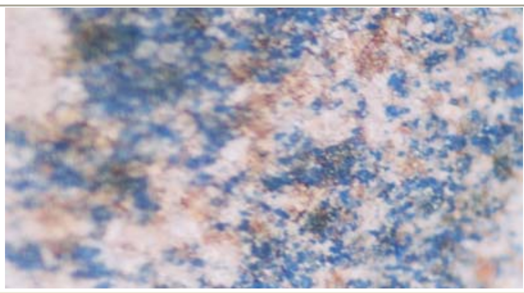


Fig.21- LOM Photomicrograph shows the fractures of the blue pigment F. X.63.

Fig.22- the Scattered grains of the blue pigment on the painting ground G. X.16.



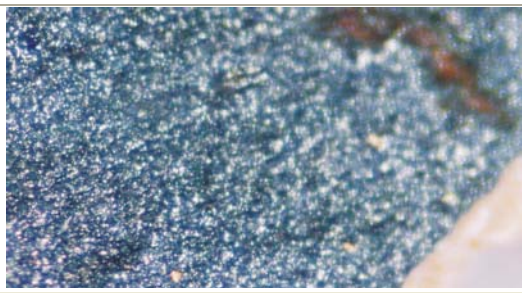
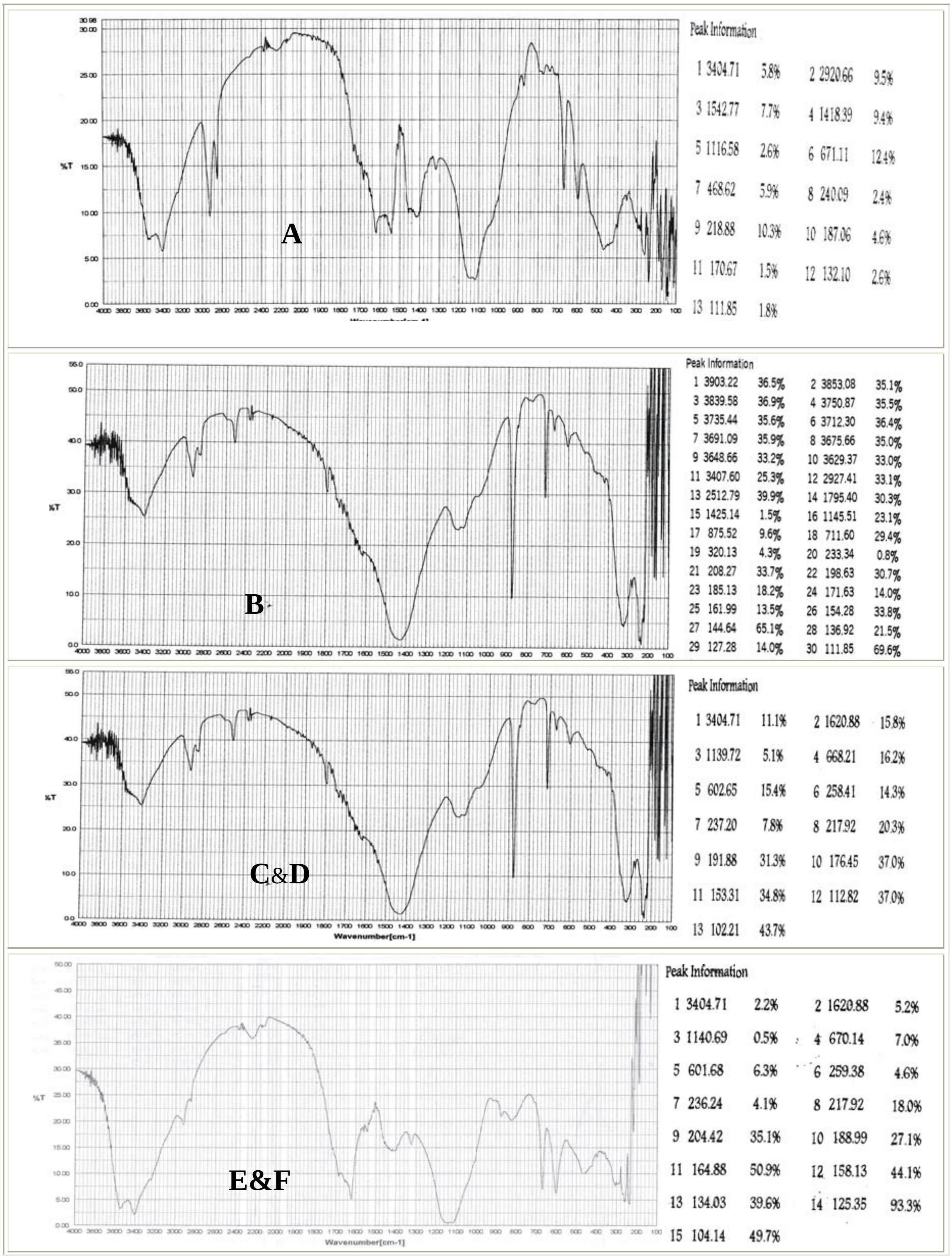


Fig.23- LOM Photomicrograph, Details from G.X. 63.

Fig.24- LOM Photomicrograph shows the blue pigment with red H. X.63.

Fourier transform infrared spectroscopy (FTIR)

In the analysis of painting materials, infrared spectrometry can be used for analyses of many pigments (both organic and inorganic), binders and varnishes. Many organic compounds with similar chemical composition and structures have similar pattern in the IR range. This is true, fore example, of protein containing binders, such as glue, egg white (glair) and yolk. Thus, this instrumental technique is useful for the identification of the general class of a binder, but not usually for specific binder identification.(10) The most modern generation of infrared spectrometers, called "Fourier transform". FTIR was adapted here, for analyses of the pigments binders from the monumental ceiling's, under studying, which revealed from studying the spectrum, the functional groups and the comparative study with standard organic binders that, the binders in the samples are protein compounds (glue). The samples, B and H, are rich in carbonate groups" Painting ground (Fig.25A: 25H).


%T
Wavenumber[cm-1]
A
Peak Information
1 3404.71 5.8% 2 2920.66 9.5%
3 1542.77 7.7% 4 1418.39 9.4%
5 1116.58 2.6% 6 671.11 12.4%
7 468.62 5.9% 8 240.09 2.4%
9 218.88 10.3% 10 187.06 4.6%
11 170.67 1.5% 12 132.10 2.6%
13 111.85 1.8%
B
Peak Information
1 3903.22 36.5% 2 3853.08 35.1%
3 3839.58 36.9% 4 3750.87 35.5%
5 3735.44 35.6% 6 3712.30 36.4%
7 3691.09 35.9% 8 3675.66 35.0%
9 3648.66 33.2% 10 3629.37 33.0%
11 3407.60 25.3% 12 2927.41 33.1%
13 2512.79 39.9% 14 1795.40 30.3%
15 1425.14 1.5% 16 1145.51 23.1%
17 875.52 9.6% 18 711.60 29.4%
19 320.13 4.3% 20 233.34 0.8%
21 208.27 33.7% 22 198.63 30.7%
23 185.13 18.2% 24 171.63 14.0%
25 161.99 13.5% 26 154.28 33.8%
27 144.64 65.1% 28 136.92 21.5%
29 127.28 14.0% 30 111.85 69.6%
C&D
Peak Information
1 3404.71 11.1% 2 1620.88 15.8%
3 1139.72 5.1% 4 668.21 16.2%
5 602.65 15.4% 6 258.41 14.3%
7 237.20 7.8% 8 217.92 20.3%
9 191.88 31.3% 10 176.45 37.0%
11 153.31 34.8% 12 112.82 37.0%
13 102.21 43.7%
E&F
Peak Information
1 3404.71 2.2% 2 1620.88 5.2%
3 1140.69 0.5% 4 670.14 7.0%
5 601.68 6.3% 6 259.38 4.6%
7 236.24 4.1% 8 217.92 18.0%
9 204.42 35.1% 10 188.99 27.1%
11 164.88 50.9% 12 158.13 44.1%
13 134.03 39.6% 14 125.35 93.3%
15 104.14 49.7%

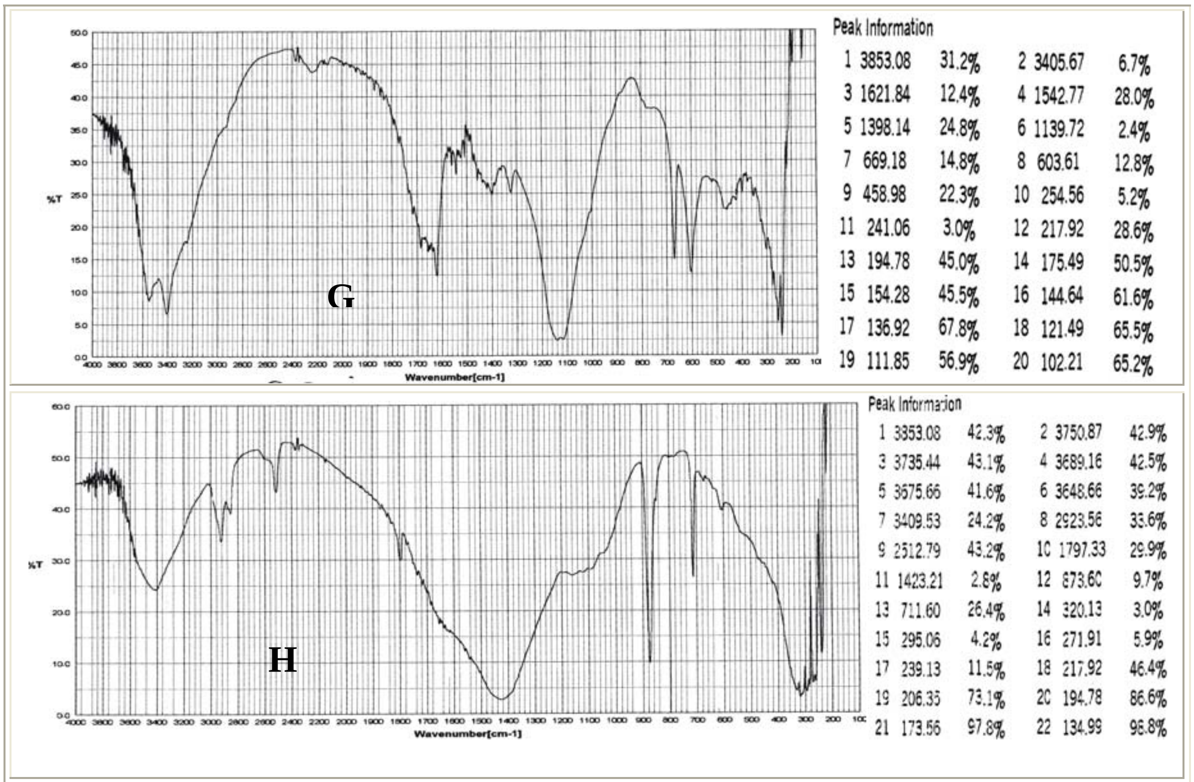


Fig.25-FTIR spectra for the blue pigments (A-H).

Conclusion

The results of the study have proved that:-

- BLUE pigments from the mosque of Moheb El-Dien Abo El-Tayb, ceiling of Qebla Iowan, Madrasa of El-Ashraf Bersbay ceiling of Qebla Iowan, the palace of the prince Seif El- Dien Taz Ebn Qtghg, ceiling Hramlek 1, Madrasa of El-Kady Abd El-Baset ceiling and El-Kady Yehia Zein El-Dien Qebla Iowan ceiling, results showed that *lapis lazuli" ultramarine blue, sodium sulfosilicate"* ($3Na_2O_3$ $3Al_2O_3$ $6SiO_2$ $3Na_2S$) is the main component. A small quantity of azurite ($2CuCO_3.Cu(OH)_2$) was added in the mosque of El-Kady Yehia Zein El-Dien ceiling.
- BLUE pigments from Madrasa of El-Ashraf Bersbay ceiling against Qebla Iowan and The palace of the prince Seif El- Dien Taz Ebn Qtghg ceiling of Hramlek 2. The results showed that *Smalt* (SiO_2, K_2O, AS_2S_3, CoO, and Al_2O_3) is the main

component plus some impurities. A small quantity of azurite ($2CuCO_3.Cu(OH)_2$) was added also in El-Ashraf Bersbay ceiling.

- BLUE pigments from Madrasa of El-Zaher Brqoq ceiling of Qebla Iowan, The results showed that *Prussian blue* (iron blue ferric- Ferrocyanide $Fe_4[Fe(CN)_6]_3$ is the component, (intervention by the committee).
- Glue is the binder of the studied pigments.

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