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ARCHAEOMETRICAL STUDY OF THE USED MATERIALS IN QAJAR EASEL PAINTING USING XRD, XRF, PLM AND FTIR TECHNIQUES: A CASE STUDY OF "EGYPTIAN GIRL" TABLOUT

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ABSTRACT

This paper attempts to identify the materials used in Qajar easel paintings. For this purpose a Kamal-al-Molk easel painting named "Egyptian Girl" has been chosen as the case study.

Analytical techniques of polarized light microscopy (PLM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR) in conjunction with art historical study were the main tools used to identify used pigments including oil, varnish and canvas fibers in the painting.

According to the result of this research, the artist's palette is green earth, white lead, red lead, cerulean blue, raw amber, copper pigment, and white zinc was used as the white color for restoration purpose. plant-based glue, shellac and linseed oil were used as adhesive, varnish and drying oil in the painting. In addition, the fiber used in the canvas of the painting has been identified as cotton, while that used in restoration of the painting identified as wool.

KEYWORDS: Easel Paintings, "Egyptian Girl", Qajar Era, Kamal-al-Molk, Pigments, PLM, XRD, XRF, FTIR, Iran, Europe.

INTRODUCTION

The Qajar era is an important period in the history of Iranian art, because in this period, art and particularly painting is strongly influenced by the art and culture of Europe, and subsequently the combination of the European and Iranian traditions emerges as a hybrid art. According to Pakbaz, in this period, the royal portrait paintings and the influence of European Art reached their peak (Pakbaz, 2005). In Qajar school, the human body is of fundamental importance (Pakbaz, 2005). This shows European themes and compositions in Persian paintings of the 18th century (Canby,1999).

From the beginning of his artistic career, Kamal-al-Molk showed a clear and great interest in European naturalistic method. His travel to Europe began during the decline of Classical art. Impressionism was growing outrageously among the artistic circles and artists and gradually became known as a new style of painting. But the school never attracted Kamal-al-Molk (Dehbashi and Shabahang, 1987). The school of Kamal-al-Molk and his students', from its technical, formal and practical aspects was a definitely under influence of European art. As a result the influence of European painting in Iranian art became well established, and today's generation of Iranian painters is a logical continuation of Kamal-al-Molk's generation (Dehbashi and Shabahang, 1987).

"Egyptian Girl" is one of the paintings attributed to Kamal-al-Molk kept in the Museum of the Iranian Islamic Parliament. Its size is 98/5cm × 68/5cm and considering the surrounding frame it is calculated to be 119cm × 88/5cm, the technique used is oil painting, and according to its subscribed signature it dated as 1874 AD (1295 AH)(figure 1).

Figure 1. Egyptian girl, Kamal-al-Molk painting, 98/5cm × 68/5cm, 1874 AD)

There are no traces and signs of a narrative or story in this painting. It is also not created for any specific goal to convey or communicate any idea or belief; finally, this painting does not present any new definition of reality (Jansen, 1986).

Rezaee has identified pigments used in a late Qajar painting using the laboratory chemical tests and microscopy observation (Rezaee, 1995), but in his results he mentioned that laboratory study done on the varnish sample of the painting did not show any conclusive results. Rezaee expresses the results of his study on this painting as follows:

Red: vermillion, green: green earth (a mixture of celadonite and glauconite), blue: Prussian blue, brown: brown earth, black: iron compounds, varnishes: no certain results but probably shellac oils.

Nikbar studied a Qajar painting and noted that the pigments have been identified in the laboratory, but do not reflect the applied method (Nikbar, 2003). Nikbar expresses his findings as follows:

Dark blue: Prussian blue, light blue: indigo, white: white barium, chromium: sulfide arsenic, green: the combination of Prussian blue and ochre yellow, yellow: ochre yellow, iron oxide, brown: combination of iron and carbon dioxide, black: black iron oxide compound.

Naserabadi stated that he has used chemical tests to analyze a Qajar painting (Nasrabadi, 1997). The results of Nasrabadi's research have been reported as follows:

Red: tin sulfide, green: green Chromium, Brown: brown earth, white: white lead, gold pigment: tin sulfide.

In addition, Bayer Shams Muguyi has conducted research on two Qajar Paintings. In this research, the study of pigments is based on the use of ultraviolet light in the analysis and testing of physical and chemical saturation test, measurement and testing acidity (Bayer Shams Muguyi, 2003).

The result of the analysis of the first painting by Bayer Shams Muguyi Red: ochre; Yellow: ochre; Green: green copper; Dark Blue: azure blue synthetic; Brown: combination of black ochre; Golden Yellow: Copper; Black: carbon.

Results of the study done on the second painting were reported as follows:

Color: red lead, yellow: ochre, the green color combination of yellow ochre and blue indigo, light blue: Prussian blue, dark blue: synthetic ultramarine brown color combination of black ochre, Golden color: tin sulfide, White: Barium Sulfate.

It should be noted that the mentioned studies are done on public Qajar paintings known as Ghahveh khaneh (Coffee-House), but there has been no focus on the royal paintings which are the topics of this paper. Regarding the materials used by Qajar painters, there is a wide gap in research and study on this field, and this is because our knowledge of the materials used by Iranian artists is solely limited to the survived manuscripts and mural paintings, which generally belong to Timurid (1370-1506 AD) and Safavid (1501-1722 AD) periods.

According to Atarod's point of view, Qajar period can be considered as one of the most crucial periods in the history of Iran, since in that time Europe-in the 18th and 19th centuries- experienced a shift in its outlook and thinking styles, attempting to influence poor countries to establish its dominance in all economic, political and cultural aspects of these countries, and Iran was no exception (Atarod, 2002). In this period, Persian painting took a new form and some Iranian painters made their way to imitate European and Renaissance art. Dehbashi Sharif has introduced Kamal-al-Molk as the pioneer of classical Iranian and European painting in her thesis entitled "Study the paintings of Kamal-al-Molk's students and his influence on his students" (Dehbashi Sharif, 2004).

Now the question can be raised of whether the Qajar artists had changed the materials they used in their drawings and paintings and the themes of their artistic works under the influence of foreign determinants or have they followed their ancestors' art?, or whether the influence of European art on Iranian painting was only limited to the themes of the paintings or also on the used materials and pigments and methods and techniques as well? Mohammad Mehdi Marzbani has declared that during the periods in which the tendency for European art reached greater heights, the painters used to only apply techniques and thus no specific attention was paid to the themes and contents, and consequently Persian painting stopped growing and failed to hold the previous position as a result (Marzbani, 1993).

Thus, this article aims to analyze the materials used in the painting attributed to Kamal-al-Molk to determine what they are based on, and to what extent they were influenced by European art and whether there is any difference between the pigments used in royal and public paintings or not?

MATERIALS AND METHODS

A combination of methods, FTIR, PLM, XRD and XRF are required to complete the research.

Bruni pointed out that the blue samples of different works dating from the second century AD to before 1960 have been examined by the Fourier transform infrared micro-spectroscopy method. In this study, Fourier transform infrared micro-spectroscopy supported by micro-Raman spectroscopy and scanning electron microscopy methods coupled with energy dispersive X-ray, and spectrum for each pigment was determined (Bruni. 1999), it has also used by Liritzis and Polychroniadou (2007) for identification of mural paintings made by a a Greek artist of beginning of 20th century and identification of Theophrastus' pigments by Katasaros et al (2011)).

Identification based on the use of polarizing microscopy is presented as useful method, and a complementary technique along with additional techniques like energy dispersive X-ray spectroscopy and Fourier transform infrared micro are introduced to identify pigments. As an example, in an article titled "Identification of Black and Red Pasta used in Ornamentation of the Walls of Alashaq Mosque in Cairo, the 15th Century". Bakr in 2005, in order to identify the colored pasta, polarizing microscopy and scanning electron microscopy with energy dispersive x-ray were applied. The study on samples consists of identifying pigments, additives and organic materials (Bakr, 2005).

In one article Miliani indicated that the infrared radiation spectroscopy with Fourier transform in the middle and near region of infrared, have been shown to be powerful tools for analyzing the inorganic materials in the paintings (Miliani, 2009).

On the other hand, Favaro in another article studied a group of 10 paintings by this famous Italian artist in the 19th century, between 1893 and 1908, using Fourier transform infrared micro-spectroscopy and scanning electron microscopy with energy dispersive X-ray analyses (Favaro, 2010). Therefore, to examine the pigments presented in the historical samples from the case study in this research ("Egyptian Girl" painting by Kamal-al-Molk), polarizing microscope, X-ray fluorescence and X-ray diffraction methods were used. Also, to determine the molecular structure of organic material (such as oils, adhesives, resins, fibers) and control the quality and purity of ingredients and identify some minerals (e.g. carbonates, sulfates, phosphates and silicates), the Fourier transform infrared spectroscopy technique was used. Furthermore, historical-analytical studies of the painting are brought into use for elaborating the issue.

Fourier transform infrared spectroscopy (FTIR) device, manufactured by Germany Bruker 'Tensor 27', with wavelengths ranging from 4000cm-1 to 400cm-1, was used to detect and analyze the pigments, adhesives and fasteners used in "Egyptian Girl". The polarizing microscope, manufactured by Jen company, model 'BK-POL', was used for identifying and analyzing the fibers and pigments used in the painting, the X-ray diffraction, manufactured by Philips Dutch company, 'model PW1800' was used to examine the compositions used in the existing pigments, and the X-ray fluorescence device, manufactured by the Dutch company, Philips,' model PW1480' was used for determining the percentage of some elements in the pigments used in the "Egyptian Girl" painting. The graph of the results of studies conducted on the samples has been comparatively studied by Fourier transform infrared spectrometry graph database of IRUG 2000. Moreover, the peaks of the graphs obtained from examining the samples have been studied based on Barbara Stuart's instructions in her book as well (Stuart, 2007).

In addition, for preparing the solid sample in FTIR examining method, about 5 to15 mg of the sample is mixed with approximately 400 mg of pure and dry potassium bromide, which is made into homogeneous powder, and then using the tablet making device, the powder is made into a transparent and thin sample by putting 10 tone of pressure on it. Potassium bromide (KBr) shows a neutral effect in the Fourier transform infrared spectrum and does not leave any trace in the consequent spectrum.

SAMPLING

The number of the whole extracted samples from the surface and back of the work is 20. It includes three samples of the fibers, thirteen samples of the colors used in this painting, and four samples of the pastes used in the work. Among the three samples of the fibers, two of them are extracted from the main fibers of the work, and one is extracted from the fibers used in its restoration. There are 4 samples extracted from green color, two of them from green, one from olive green and one from pale green. Only one sample from black, blue, red, gold, gray, ochre and skin colors has been extracted. Two samples of the white color have also been extracted from two separate spots of the work. The samples are coded according to the English alphabet and their priority in being extracted from each spot of the work. The points being sampled from the back and surface of the painting are shown in the Figure (2).

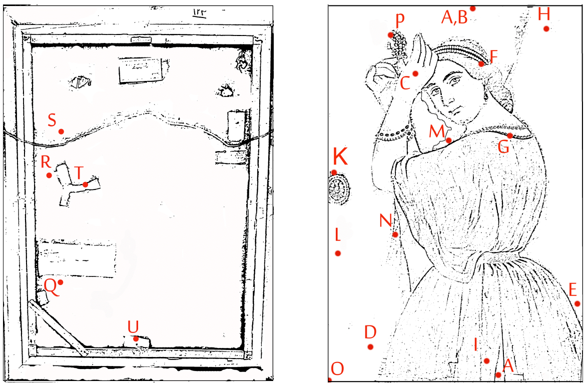


Figure 2: Points being sampled of the back and the surface of the painting

In Table1, samples' codes, locations, their types, the spots from which the samples have been extracted, and also the applied experiments on the samples are presented.

Table 1. Samples provided from "Egyptian Girl" painting

	Sample code	The location of the sample	Sample type	Region	Experiments
1	A1	Central vertical part on the top	Fiber	Damaged region	PLM
	A2	Central vertical part on the bottom	Fiber	Damaged region	PLM
2	B	Central vertical part on the top	Green color	Damaged region	FTIR, PLM, XRD, XRF
3	C	Top left side	Skin color	Damaged region	FTIR, PLM, XRD, XRF
4	D	Bottom left side	Green color	Restoring Region	FTIR, PLM, XRD, XRF
5	E	Bottom right side	Olive green color	Restoring region	FTIR, PLM, XRD
6	F	Top right side	White color	Damaged region	FTIR, PLM
7	G	Top right side	Red color	Damaged region	FTIR, PLM, XRD
8	H	Top right side	Blue color	Damaged region	FTIR, PLM, XRD
9	I	Central vertical part on the bottom	Gray color	Damaged region	FTIR, PLM, XRD
10	K	Top left side	Ochre color	Damaged region	FTIR, PLM, XRD
11	M	Central vertical part on the top	Black color	Damaged region	FTIR, PLM, XRD
12	N	Central horizontal part on the left	Pale green color	Damaged region	FTIR, PLM, XRD
13	O	Bottom left side	Golden color of the margin	Damaged region	FTIR, PLM, XRD, XRF
14	P	Top left side	White color	Damaged region	FTIR, PLM, XRD
15	Q	Bottom left side	Paste of the back of the painting	The layer of the back of the canvas	FTIR, XRD
16	R	Top left side	Paste of the back of the painting	The layer of the back of the canvas	FTIR
17	S	Top left side	Paste of the back of the painting	The layer of the back of the canvas	FTIR
18	T	Top left side	Paste of the back of the painting	Restoring region	FTIR
19	U	Bottom left side	Fiber	Restoring region	PLM

RESULTS AND DISCUSSION

Taking into account the FTIR spectra of the samples under study, it is observed that all the tested samples have at least one O-H bond. This bond has an absorption frequency range of wavelengths between 3600 cm^{-1} and 3200 cm^{-1}. From another standpoint, according to Barbara Stuart, oleic substrates, carbohydrates, and resins contain O-H hydrogen groups which vibrate in this interval. However, many pigments, specifically those with watery structures and having one molecule in their coordination sphere, exhibit absorption peak in this interval. For example, composition of Verdigris ($Cu_2(OAc)_4(H_2O)_2$) whose structure contains two water molecules exposes absorption peak at this frequency.

The second peak observed in the graphs of all samples is related to the vibration of alkane C-H stretching bond which occurs in the wavelength interval of 3000 cm^{-1} to 2800 cm^{-1}. Generally, this vibration emerges in the form of a strong and branched peak (two or several branches). On the other hand, oils, carbohydrates, and waxes vibrate in the wavelength range of 3000 cm^{-1} and 2800 cm^{-1} and expose absorption peak. Accordingly, such vibrations cannot be directly attributed to a specific group since nearly all organic compounds have elastic C-H bond vibrations.

According to the FTIR graph of linseed oil in Stuart's book, it is known that there is an elastic two-branch C-H bond peak in this oil. Hence, the linseed oil is likely to be present in all tested samples. Based on Barbara Stuart's statements and also the FTIR graph of linseed oil that she has presented, it is demonstrated that oils and resins have a sharp peak in the emergence interval of carbonyl groups. The vibration position of absorption frequency is different, depending on the type of carbonyl group in these structures (aldehyde, ketone, carboxyl acid, ester, amide, anhydride, and chloric acid). This interval varies from the frequency of 1810 cm^{-1} to 1650 cm^{-1}. Since no sharp peak is observed in this interval in the FTIR graphs of the tested samples, two arguments can be inferred:

First, these carbonyl groups are hydrolyzed as a result of moisture and variable acidic conditions and their abundance is reduced in the sample texture to the extent that just a weak peak remains. Second, sample matrices in general might be something other than oils and resins (such as waxes, carbohydrates, and proteins) which have common peaks with oils and resins in the intervals of similar O-H hydrogen bonds and elastic C-H bonds but do not expose absorbing vibrations in the emergence intervals of the carbonyl groups. Another interesting point in the FTIR graph acquired from the experimental samples is the absorption peak at the frequency of 1400 ± 15 cm^{-1} for the samples H, F, G, C, B, K, M, E, P, D, N, and I, which is not observed in the reference FTIR graph for linseed oil in Stuart's book. This intense, wide peak is probably due to the presence of carboxylate salts in the samples and/or is associated with the resin tissue (with insect source) in the sample as a fingerprint region. These salts indicate a strong asymmetric elastic vibration around the frequency of 1400 cm^{-1} caused by resonance of the carbonyl group with the adjacent C-O group.

Another analogous part in the FTIR graph of the experimental samples and the reference FTIR graph of linseed oil in Stuart's book, is the broad absorption peak (with moderate intensity) in wavelength interval of 1300 cm^{-1} to 900 cm^{-1}, which is seen in all the samples except from M, G, F, and P. These absorption peaks reveal the presence of strong elastic vibrations for C-O bond (single) and are observed in alcohols, ethers, esters, carboxylic acids, and anhydrides. According to Stuart, oil chains which contain one of the former radicals vibrate in this interval of absorption frequency. In her book, Barbara Stuart mentioned a long sequence of aliphatic chains with absorbing vibration in intervals of 750 cm^{-1} to 700 cm^{-1} (720 cm^{-1}) as another characteristic of oils. Many oils have this vibration, referred to as long chain absorbing vibration, because of their macromolecular structure. But, as observed in the FTIR graphs of the tested samples, none of them exhibited absorption peak or vibrated in the wavelength interval of 750 cm^{-1} to 700 cm^{-1}. Moreover, all samples except for Q, T, S, E, D, O, N, and M assume absorption spectrum in the interval of 1000 cm^{-1} to 650 cm^{-1}, which is associated with bending vibrations outside of the alkene plane. Such vibrations belong exclusively to the oleic groups whose structures contain unsaturated carbonic sequences. Furthermore, most colors, especially those with more intense chromic intensity, include large chains of unsaturated carbonic bonds (e.g. saffron). The FTIR graphs of some tested samples like F, I, E, D, Q, S, T, O, and G have absorbing vibrations at frequencies less than 607 cm^{-1}, which are attributed to carbon-halogen bonds in their chemical structures. Samples E and D are both extracted from green pigments, sample B has been extracted from the original and damaged part, and sample E extracted from the restored part of the painting. As can be seen, regarding the gained graphs from the FTIR of these two samples, sample B is quite similar to sample E (Figures 3 and 4). Both samples have the same peaks in 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, close to 1600 cm^{-1}, close to 1400 cm^{-1} and 1300 cm^{-1} to 900 cm^{-1} wavelength ranges. Since sample B of green has been extracted from the original part and sample E of the olive green extracted from the restored part of the work, the differences between their peaks could be from the additive materials for making tonality in one color in sample B, or the impurities in E sample for the restoration materials applied to it.

The graphs of these two samples have been studied, compared and analyzed with the existing graphs in the IRUG 2000 and FTIR graphs database (Figures 5 and 6).

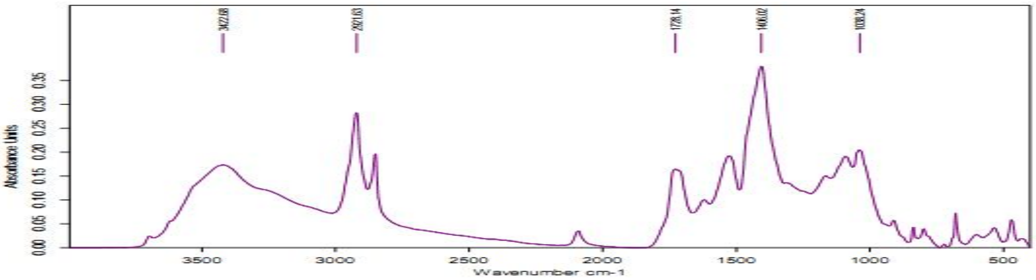


Figure 3. FTIR graph of B

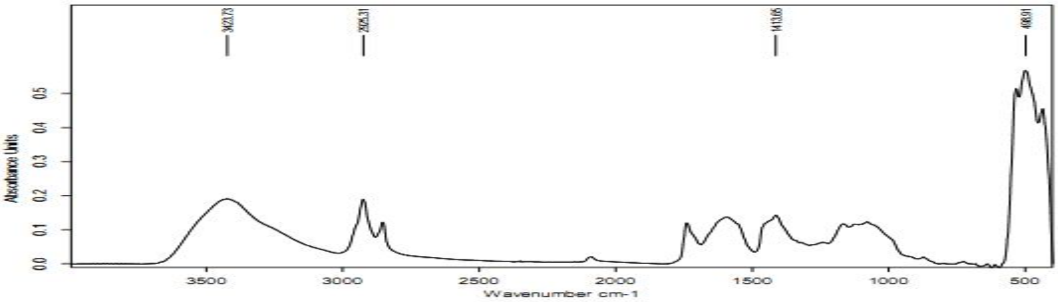


Figure 4. FTIR graph of E

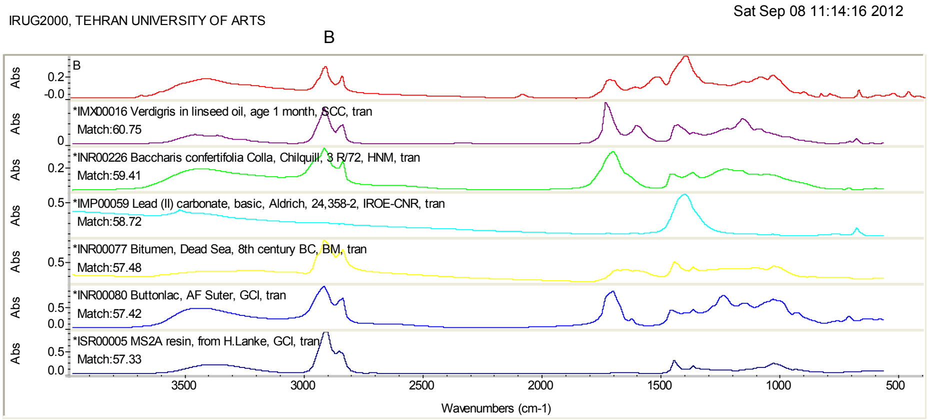


Figure 5. FTIR graph of the analysis of sample B with adaptive search database IRUG 2000

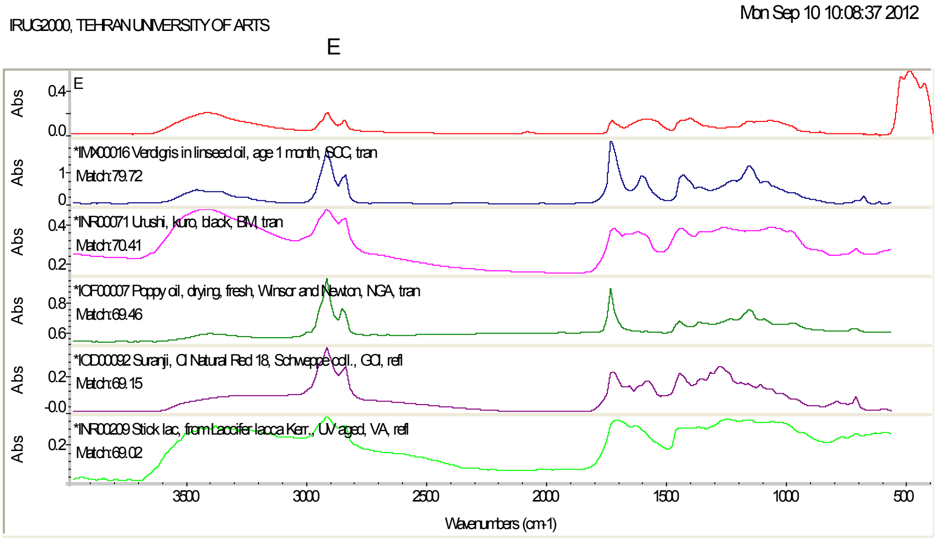


Figure 6. Comparative search for FTIR graph of the analysis of sample E by IRUG 2000 database

As it can be seen in the FTIR graphs illustrations of E and B samples, both samples have the same peak with Verdigris in linseed oil in the wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, close to 1600 cm^{-1} and close to 1400 cm^{-1}. Verdigris in linseed oil, with 60/75 % similitude to the B sample and 79/72 % similitude to E sample, is identified as the first known material in the examined graphs in the IRUG 2000 database. Chemical composition of Verdigris is ($Cu_2(OAc)_4(H_2O)_2$) and both samples E and B have a wide peak with moderate intensity associated with O-H hydrogen bond in the 3600 cm^{-1} to 3200 cm^{-1} interval. Also, both samples have a two-branch peak with moderate intensity associated with the elastic C-H bond in the interval of 3000 cm^{-1} to 2800 cm^{-1}. Furthermore, the peaks around 1600 cm^{-1} (nearly 1592 cm^{-1}) are related to carboxylate salts and belong to asymmetric elastic vibration of acetate radical. The peak that emerged around frequency l400 cm^{-1} (± 15) is again probably associated with carboxylate salts causing an asymmetric elastic vibration. The remarkable event in the FTIR spectrum in this sample is the emergence of a wide peak in the interval of 1300 cm^{-1} to 900 cm^{-1}, indicating the presence of C-O groups. Concerning the weak peak that emerged in the 700 cm^{-1} to 600 cm^{-1} interval, it can be stated that this peak is linked to long carbonic chain and probably belongs to the oils. According to IRUG database, the green pigment of patina in linseed oil was found to be present in the sampled tissue, and considering the structure of this substance, it can be concluded that: firstly, there exists an elastic C-H peak that belongs to CH_3 group in the obtained FTIR graph, and secondly, O-H hydrogen peak is observed in the FTIR graph of the sample; this peak is associated with the O-H bond of water molecule (moisture) in the coordination sphere of the respective compound. The peaks observed at frequencies of 1400 cm^{-1} and 1600 cm^{-1} are linked to asymmetric vibrations of patina acetate in linseed oil and indicate presence of acetate radical. On the other hand, emergence of peaks at frequencies of 1038 cm^{-1} and 1728 cm^{-1} might be attributed to oleic connections of the sample because the oils tend to peak in the 1300 cm^{-1} to 900 cm^{-1} interval. As it is mentioned, there is linseed oil in both samples, and regarding Barbara Stuarts' instruction, existence of the same peaks in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, 1750 cm^{-1} to 1730 cm^{-1}, 1480 cm^{-1} to 1300 cm^{-1}, 1300 cm^{-1} to 900 cm^{-1}, demonstrates the fact that there is oil in samples B and E (Stuart, 2007). In comparative FTIR graphs of sample E in IRUG 2000 database, the third material with 58/72 % of similitude is shown to be the white Lead ($Pb_3(CO_3)_2(OH)_2$). Since white lead (lead carbonate) is an anion radical (CO_3^{-2}) and this carbonate radical, like the acetate radical in patina of linseed oil, is able to weaken the carbonyl absorption peak, it can be asserted that the similarity between white lead and sample B reported in the correlation graph of this sample in IRUG database might result from the analogy of carbonate group in white lead and acetate group of patina in linseed oil. The reason is that both of the aforementioned groups cause a moderate absorption peak near frequencies of 1400 cm^{-1} and 1600 cm^{-1}. Nevertheless, assuming the presence of white lead in this sample, since sample B has been extracted from the original and damaged part of the work, it could be concluded that the artist had used the white lead pigments for creating different color tonalities in the painting.

In the comparative FTIR graph of sample E, as previously mentioned, copper oxide (verdigris) in linseed oil, having 79/72 % similitude with sample E, is shown as the first examined material in the IRUG 2000 database. Urushi black is also shown to be the second material, with 70/41% similitude. According to chemical composition of Urushi ($R\text{-}C_6H_5O_2$), the wide peak of O-H absorbing vibrations in 3600 cm^{-1} to 3200 cm^{-1} interval can be attributed to the O-H group of Urushi pigment. Since sample E has been extracted from the restored part of the work, it is likely that this color was added to the work during the restoration process. It is also incredulous that this kind of color belongs to the far East, thus if this color had been used by the artist himself, it could be said that the traces of the influence of Eastern materials can be seen in this work, considering that other samples of this kind of color such as the red Urushi with 68/33 % accordance, and raw Urushi with 66/85 % similitude, can be observed below the FTIR graph of sample E. Nevertheless, the definite influence of Eastern materials on this painting is not a forgone conclusion, and therefore, studying this issue requires more research.

Sample N, like sample B, is a green color extracted from the original and damaged part of the work. The first material compared with N sample is shown to be varnish paste with 74/91 % similitude. The second identified sample in the comparative FTIR graph of sample N is presented as the amber pigment, with 74/43 % similitude. The third identified material in the comparative FTIR graph of sample N is presented as the red Urushi color, with 74/43% similitude. Regarding the fact that amber pigment is a yellowish brown, and since sample N is green, it could be said that the artist had not used a pure green color for creating the color of sample N, instead he had used a combination of yellow, red and black colors in order to create his desired color.

Sample K has been extracted from the ochre pigment of the original and damaged part of the work. According to the FTIR graph of sample K, and compared to the graphs in IRUG 2000 database, the first distinguished material is reported to be amber color, with the similitude percentage of 73/68. As mentioned before, amber is a yellowish brown, which is a combination of iron oxide, manganese oxide, and clay. The fourth compared material with sample K is reported to be Japanese Urushi red with 67/69 similitude percentage. In the graph of sample K, according to Barbara Stuart's instruction, the peak in the wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, 1750 cm^{-1} to 1730 cm^{-1}, 1480 cm^{-1} to 1300 cm^{-1}, 1300 cm^{-1} to 900 cm^{-1}, demonstrates the presence of oil in this sample. Sample M has been extracted from the black pigments of the original and damaged part of the work. According to the FTIR graph of sample M, and compared to the graphs in the IRUG 2000 database, the first identified material is shown to be amber, with the similitude percentage of 85/09. Since sample M is the black sample of the work, an amber color could have been used for creating color tonality by the artist. The third compared material with sample M is reported to be Japanese Urushi black with 76/51 similitude percentage. Below the FTIR graph of sample M, the sixth identified material is reported to be shellac resin, with 76/01 similitude percentage.

As IRUG data confirm the presence of amber color ($C_{11}H_{14}C_1NO$) in samples N, K, and M, the elastic O-H bond in the FTIR graph of these samples is proved to be unrelated to amber because amber pigment contains no O-H bond. This could result from water molecules (moisture) and/or oleic, resin and carbohydrate connections. On the other hand, the elastic C-H bond of amber color vibrates in the 3000 cm-1 to 2800 cm^{-1} interval. It can be accordingly inferred that C-H absorption peak is related to C-H bonds of aliphatic chains of oils, resins, and carbohydrates, and also to the elastic C-H bond in amber color. Additionally, a weakened carbonyl group of amide type is present in samples N, K, and M, which vibrates in the frequency range of 1670 cm^{-1} to 1640 cm^{-1}. This vibration is associated with the amide carbonyl group in amber color. Some sort of elastic C-N vibration is observed in the FTIR graph of N, K, and M samples, which exhibits a moderate absorption peak in the 1350 - 1000 cm^{-1} interval. According to the analysis of the chemical structure of amber color, it is manifested that the respective absorption peak is associated with N-C bond in amber color. The FTIR graph of the same sample illustrates a moderate absorption peak in the 800 cm^{-1} to 600 cm^{-1} interval, which is caused by C-Cl bond in amber color. Note that CH_2Cl group generates a weak absorption peak in the 1300 cm^{-1} to 1230 cm^{-1} interval, which can be explained by the bending vibration of CH_2Cl group in this compound. Also, the aromatic C-H absorption peak is not observed in samples N, K, and M due to the large width of O-H peak, which can cover absorption peaks above 3000 cm^{-1} (3150 cm^{-1} to 3050 cm^{-1}). This is due to the induction of intense electronegative property of chlorine as well as carbonyl group which prevents bending oscillations of the CH_2 group. In addition, amber compound exhibits two absorption peaks at frequencies of 1475 cm^{-1} and 1600 cm^{-1}, which are associated with aromatic C=C bond. Besides, as implied before, Urushi color is also observed in correlation graph of IRUG for samples N, K, and M. Taking into account the chemical composition of Urushi ($R\text{-}C_6H_5O_2$), the wide peak of O-H absorbing vibrations in the interval of 3600 cm^{-1} to 3200 cm^{-1} can be attributed to O-H group in Urushi pigment. Also, the presence of a weak vibration in the 750 cm^{-1} to 700 cm^{-1} interval might be related to the R group positioned in Meta state of Urushi color, which is a carbonic chain with more than four carbons.

Sample D, like sample E, is from green pigments which are extracted from the restored parts of the work. In the comparative graph of sample D, the first identified material is identified as Storax, a kind of gum provided by the amber tree, with the similarity percentage of 69/51. The peak in wavelength ranges from 3600 cm^{-1} to 3200 cm^{-1}, 3100 cm^{-1} to 2800 cm^{-1}, 1650 cm^{-1} to 1600 cm^{-1} and 1480 cm^{-1} to 1300 cm^{-1}, and could be because of the existence of resin in this sample. In this sample, like the case for samples E and N, Urushi color can be distinguished. In the comparative FTIR graph of sample D, the third identified material is known to be red Urushi with 66/96 % similitude. Regarding the fact that sample D has been extracted from green and restored parts of the painting, it could be concluded that for creating the green color of this spot of the work, instead of using a pure green, a mixture of colors were used as well. Since a weak absorption peak is observed in the 1670 cm^{-1} to 1600 cm^{-1} (1629 cm^{-1}) interval, according to the FTIR graph of sample D, one can reach the conclusion that a long coupling of C=C bonds exist in this sample. And, through analyzing the results acquired from IRUG database, it can be proved that the nearest substance in the tested sample is saffron ($C_2OH_{24}O_4$) with a probability of 67.67% because this compound contains a long unsaturated carbonic chain. As stated earlier, the extensive vibration in the interval of 1300 cm^{-1} to 900 cm^{-1} can be attributed to the oleic and carbohydrate constituents, since the presence of these vibrations in the saffron sample is impossible. On the other hand, in correlation to the graph of sample D, the Urushi color is also detected like in samples N, K, and M. According to the chemical composition of Urushi ($R\text{-}C_6H_5O_2$), the wide peak of O-H hydrogen absorbing vibrations in the 3600 cm^{-1} to 3200 cm^{-1} interval might be associated with the O-H group in Urushi pigment. Also, another possibility is that the observed O-H hydrogen peak is associated with the O-H bond of water molecules (moisture) in the respective sample. In examining the comparative FTIR graph of sample D, there is no evidence of a pure green color being used. Regarding the existence of Japanese Urushi color in all three E, N and D samples, and also regarding the fact that all three samples are green and have been extracted from the restored and original parts of the work, it could be said that it is likely that the artist has used this kind of color; however, as mentioned before, proving this possibility requires more research and study.

Samples F and P have both been extracted from white pigments belonging to the original and damaged parts of the work, and sample C was also extracted from damaged area in the hand of the model and as the sample of skin color that contains many white pigments, a great similitude between the FTIR graphs of samples F, P, and C can be seen. All three samples have the same peak in the range of wavelengths from 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, 1480 cm^{-1} to 1300 cm^{-1}, close to 680 cm^{-1}.

Considering the FTIR graphs of samples F, P and C, and compared with graphs in the IRUG 2000 database, in all three samples, the first adapted material is shown to be white lead, having the highest similitude percentage. The similitude percentage of 66/971 in sample F, 78/ 53 in sample P, and 78/78 in sample C, is distinguished as white lead. In FTIR graphs of all three samples there is a strong absorption peak near the wavelength interval of 1400 cm^{-1}, which is related to the anion radical of carbonate in lead composition. This absorption peak in this wavelength interval is present due to formation of resonance forms for the carbonate compound. In addition, it is noteworthy to point out that the white lead compound is capable of generating absorption peak only at this frequency, and hence, other absorption peaks observed in FTIR graph of these samples belong to oleic, resin and carbohydrate connections. According to Barbara Stuart's instruction, the existence of common peaks in the graphs of samples F, P and C in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3100 cm^{-1} to 2800 cm^{-1}, 1600 cm^{-1} to 1650 cm^{-1}, 1480 cm^{-1} to 1300 cm^{-1}, also show the existence of resin in these samples. Regarding the presented table for determining the kind of natural resin by Barbara Stuart, and with regards to FTIR graphs of samples F, P and C, the existence of peaks in wavelength ranges from 1730 cm^{-1} to 1738 cm^{-1} and 2930 cm^{-1}, the presence of carbonyl bands and stretching bonds of C-H is confirmed. Stretching vinyl bonds in the graphs of these samples might have been weakened or even diminished for various reasons. According to Barbara Stuart's instruction in distinguishing these types of bonds and comparing the present peaks in the graphs of samples C, P and F based on this instruction, the possibility of the presence of insect based resin in these samples is raised.

Sample I, has been extracted from the gray color of the work. According to the FTIR graph of sample I and comparing it to graphs in IRUG 2000 database, white lead is reported to be the first distinguished material, with the similitude percentage of 73/23. Considering the fact that samples P, F and C are also reported to be white lead, it could be said that white pigment was the artist's main color in creating the work. In the FTIR graph of this sample, a strong absorption peak is detected in the vicinity of 1400 cm^{-1} wavelength; this peak is generated by anion radical in the composition of white lead.

In addition to the white lead, the second identified material is shown to be Whiting with the similitude percentage of 58/77 and the fourth identified one is reported to be calcite white color with the same percentage of 54/23 similitude. Since sample I has been extracted from the damaged original part of the work, the presence of Whiting and calcite could be due to the proper background preparation for the painting in this work, since the results of distinguishing samples C, F and P, and also the high percentage of the similitude of white lead in this sample, the use of white lead as the main white color in this work is more likely.

Sample H has been extracted from the blue pigments from the damaged original part of the work. Regarding the FTIR graphs of sample H, and compared with graphs in the IRUG 2000 database, the first identified material is reported to be white lead with 68/06 similitude percentage. In this sample, like the case for samples I, C, F and P, white lead has the highest similitude percentage. In the FTIR graph of this sample, a strong absorption peak is detected in the vicinity of 1400 cm^{-1} wavelength; this peak is generated by anion radical in the composition of white lead.

Sample G has been extracted from the red pigment of the original and damaged part of the work. Regarding the FTIR graph of sample G and comparing it to the graphs in IRUG 2000 database, the first determined material is reported to be oxide green with linseed oil, with the similitude of 76/52%. For better ripening their color, artists usually add a complimentary color to it. Considering this fact, it might be said that the reason for the presence of oxide green in red color sample could have been the artist's desire to ripen the red color. According to Barbara Stuart's instruction, the existence of the same peaks in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3000 cm^{-1} to 2800 cm^{-1}, 1480 cm^{-1} to 1200 cm^{-1}, demonstrates the presence of carbohydrate; the same peaks in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3100 cm^{-1} to 2800 cm^{-1}, 1740 cm^{-1} to 1640 cm^{-1}, and 1480 cm^{-1} to 1300 cm^{-1} demonstrates the presence of resin; the same peaks in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 3100 cm^{-1} to 2800 cm^{-1}, 1750 cm^{-1} to 1730 cm^{-1}, and 1480 cm^{-1} to 1300 cm^{-1} demonstrates the presence of oils; and the same peak in wavelength range of 1480 cm^{-1} to 1300 cm^{-1} demonstrates the presence of proteins in these samples. In this sample shellac varnish has been distinguished with 75/09% similitude. The gathered data from the FTIR graph of sample G is mostly related to the materials accompanying pigments, such as varnish oil used in this painting. We will discuss the kind of red pigment in sample G in XRF, XRD and PLM tests.

Sample O has been extracted from the golden pigments of the margin of the work. Considering the FTIR graph of sample O, and compared to the graphs in IRUG 2000 database, the first distinguished material is reported to be cellulose nitrate ($C_{12}H_{17}(ONO_2)_3O_7$), having 70/78 similitude percentage. Since sample O is extracted from the wooden frame in the margin of the work, the existence of nitro cellulose in the comparative FTIR graph of this sample could be because a small portion of wood might have entered into the sampling capsule, and in examining the FTIR graph, the cellulose in the texture of the wood is similar to the graph of nitro cellulose. Peaks at frequencies between 1300 cm^{-1} and 900 cm^{-1} in sample O are associated with elastic C-O vibrations in cellulose molecule. Also, the vibration in frequency interval of 1550 cm^{-1} to 1350 cm^{-1} in sample O emerged as a strong peak, and is related to vibration of NO_2 group in cellulose nitrate. The fourth identified material is reported to be Chrysocolla blue (CuH_2O_2) (an inorganic material hydrated copper silicate), with the similitude percentage of 49/81. The XRD and XRF tests reports have confirmed the presence of copper in this sample. The reason for the existence of this kind of blue in the comparative FTIR graph of this sample could be the presence of copper in the O sample and Chrysocolla blue.

Samples Q, R, S and T are all samples extracted from the applied paste on the back of the work, and are extracted from the damaged original parts of the painting and the restored parts as well. Considering the FTIR graphs of these four samples, Q, R, S and T, the samples are similar to one another. All four samples have the same peak in wavelength ranges of 3600 cm^{-1} to 3200 cm^{-1}, 1680 cm^{-1} to 1600 cm^{-1}, and 1300 cm^{-1} to 900 cm^{-1}. Considering the resulted FTIR graphs of samples Q, R, S, and T, and compared to the graphs in IRUG 2000 database, the first identified material in all four samples is known to be the gum of the Myrrh tree which has the highest similitude percentage. The second identified material in all four samples is Mandrake paste, and the third identified material is reported to be Tragacanth. Since IRUG has identified plant resin as the most plausible substance for these samples, based on the chemical structure of plant resin ($C_{21}H_{28}O_2$), it is inferred that the vibrations in the frequency interval of 1680 cm^{-1} to 1600 cm^{-1} are associated with C=C double bond in the plant resin sample. Furthermore, the presence of C-H bonds in the structure of plant resin could represent C-H stretching vibrations in these samples. Since all these materials have the same basis, the above alternatives are demonstrated, and we can finally point to the gum plant structure as the additive material in these samples.

Table 2. Samples analysis by FTIR

	Sample code	Sample type	Peaks in the wave length range	vibration of peaks	FTIR
1	B,E	Green	3200cm^{-1}-3600cm^{-1}	Stretching vibration of hydric O-H bonding	Verdigris in linseed oil
			2800cm^{-1}-3000cm^{-1}	Stretching vibration of C-H	
			1600±15cm^{-1} & 1400±15cm^{-1}	Asymmetric stretching vibration of the acetate base	
			900cm^{-1}- 1300cm^{-1}	Stretching vibration of C-O	
			650cm^{-1}- 700cm^{-1}	Long-chain carbon band	
2	N,K,M	Paled Green, Ochre, Black	3200cm^{-1}-3600cm^{-1}	Stretching vibration of hydric O-H bonding	Amber ‘ Urushi black &Urushi red
			2800cm^{-1}-3000cm^{-1}	Stretching vibration of C-H	
			1640cm^{-1}-1670cm^{-1}	Stretching vibration of C=O band in Amide group	
			1475±15cm^{-1} & 1600±15cm^{-1}	Stretching vibration of C=C band in Aromatic ring	
			1000cm^{-1}-1350cm^{-1}	Stretching vibration of C-N	
			1230cm^{-1}-1300cm^{-1}	Bending vibration of CH_2-Cl	
			600cm^{-1}-800cm^{-1}	Stretching vibration of C-Cl	
			700cm^{-1}-750cm^{-1}	Long-chain carbon in metha position	
3	D	Green	3200cm^{-1}-3600cm^{-1}	Stretching vibration of hydric O-H bonding	Sofflower yellow, Urushi black &Urushi red
			1600cm^{-1}- 1680cm^{-1}	Stretching vibration of C=C in conjugated chain	
			900cm^{-1}- 1300cm^{-1}	Stretching vibration of C-O	

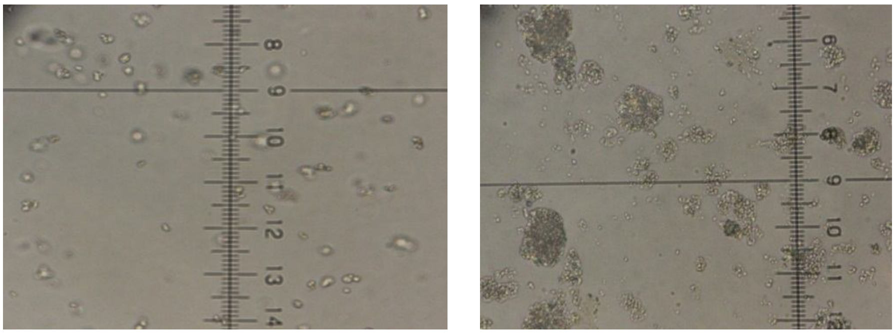
4	C,F,P	White	1400±15cm^{-1}	Asymmetric stretching vibration of the carbonate base	White lead
5	I	Gray	1400±15cm^{-1}	Asymmetric stretching vibration of the carbonate base	White lead
6	H	Blue	-	-	?
7	G	Red	-	-	?
8	O	Golden	1530cm^{-1}- 1600cm^{-1} (1550cm^{-1}) & 1300cm^{-1}- 1390cm^{-1} (1350cm^{-1})	Stretching vibration of Aliphatic R-NO_2	Cellulose nitrate
			900cm^{-1}- 1300cm^{-1}	Stretching vibration of C-O	
9	Q,R,S,T	Glue	2800cm^{-1}-3000cm^{-1}	Stretching vibration of C-H	plant gum

ANALYSIS USING POLARIZED MICROSCOPE

For preparing the samples, first of all the sample color is ground with Carnelian stone so that the particles are completely changed into powder. Then, by adding the liquid (Acetone+ alcohol+esther), binding and the paste that is contained in the sample, dissolve it; then to keep the sample fixed, a material called Cargille that has a gum and thermoplastic characteristic is used on the lam. For fiber samples a small piece is selected, untwisted, and then is fixed on the lam by using Cargille.

As it can be seen in illustration Figure 7a, the particles of sample P have fine and round particles that can be seen in a scattered or coherent form.

In illustration Figure 7b, the control sample particles of white lead are seen under the polarized microscope, which, as well as the particles of sample P have fine and round aggregations and are seen in a scattered pattern (Figure 7).



(a): Particles of P sample **(b): Particles of lead white sample**

Figure 7. Particles of P sample and Particles of lead white sample under the microscope, with analyzer, 600X

Sample P features are very similar to the control sample white lead according to the presented illustration. As it can be seen in illustration A, there can be no changes in the appearance of sample E particles under the microscope after placing the analyzer, and the same feature can be seen in the case of white lead particles on the one hand, and the physical appearance of the particles of both samples are also very similar on the other hand. White lead particles seem somehow greenish under the microscope. The particles are very tiny and disorganized and the reliefness of particles is comparatively well. Some bigger particles are sometimes observed among white lead particles. White lead has a high refraction index and is also considered as an isotropic material. Samples F and C, like sample P, are identified as white lead particles. Samples F and C particles also have a fine and round aggregation and are seen in a scattered form. After placing analyzer completely, there is no change in the brightness of the particles.

Samples C and F are also considered as isotropic materials and have a high refraction index .

In examining the samples, using a polarized microscope, samples B and N are also identified as terre verte1, as the control sample. The particles of these samples, like the case for control sample particles are terre verte, fine aggregation, circular and little reliefness. After using analyzer, these particles are viewed as tiny, bright and dark points. Samples B and N and terre verte are considered as non-isotropic materials which have a low refraction index. Samples D and E are identified, like control sample, as white copper. The particles of these samples, as the case for particles of control sample, are identified as white lead, with average aggregation, circular and coherent. After placing the analyzer completely, the brightness of the particles is not changed. White lead is considered as an isotropic material and has a high refraction index. White lead is pale blue with analyzer, and without it, is dark gray (like the smoke of a cigarette), and seems green as a mass . Sample G, as well as reference sample, is identified as red lead. The particles of this sample, as the case for particles of red lead sample, are considered as non-isotropic. The size of the particles of red lead ranges from average to large, and they have the shape of circular particles with rough surface. Some of these particles are polished and some are not. Some of the polished ones seem blue or green. The reliefness of particles is very high. After placing the analyzer completely, their brightness changes.

Sample H is distinguished as similar to the reference sample of cerulean blue. The particles of this sample do have, as the particles of the reference sample of cerulean blue, fine and round aggregation, the roughness of the particles is good, and the particles are like a ginger-root. After placing the analyzer completely their brightness does not change. Sample H and cerulean blue are considered as isotropic materials, and also have a high refraction index. In examining the samples by means of a polarized microscope, samples I and O were not distinguishable. The final identification of these samples is done in tests section, considering the results of other tests. Sample K is also distinguished similar to the reference sample of amber color. The particles of this sample, as the ones of the reference sample of amber color, have an aggregation from average to large. Red and orange pigments are sometimes found amongst them. The roughness of particles is good and they have a high refraction index. After placing the analyzer completely, their brightness does not change. Samples K and amber color reference sample are considered to be non-isotropic materials. In PLM test of sample M, firstly the similarity of this sample to amber reference sample was questionable and the FTIR test of sample M was thus examined again in order to gain confidence. In the result of the FTIR test of sample M, the existence of amber color, with 85/09 of similitude percentage has been confirmed. Regarding these data, sample M could be reported as amber color, and also in PLM test, the particles of sample M, similar to the reference sample of amber color, do have aggregation of average to large. Red and orange pigments are found among them from time to time. The reliefness of the particles is good and they have a high refraction index. After placing the analyzer completely their brightness is not changed. Sample M and the reference sample of amber color are considered as non-isotropic materials and have a high refraction index.

Regarding Table 3, it is obvious that some samples could not be distinguished by using a polarized microscope. To do this, elemental analyses are needed along with PLM technique; and, in addition, the combination of several different colors by the artist makes the examination process more complicated. When only one pigment is being examined, the results are gained much easier, and since the pigment particles overlap in such cases, identification of these samples is a difficult task and could result in ambiguity. For example, a sample such as gray color (I) that may include several colors and even an amount of carbon could not be identified by a polarized microscope. Applying carbon used to be very common in black compositions, and if carbon existed in the sample, this will make the identification difficult since the polarized microscope is commonly used for identifying inorganic material. In this part, green samples, and samples B and N, in contrast to the results from Fourier transform infrared spectroscopy, are identified to be terre verte. The result of samples C, F and P were identified as being white lead, the same result as in Fourier transform infrared spectroscopy. Samples K and M were identified as being amber color, as confirmed in Fourier. Distinguishing the blue color proved cerulean blue pigment, but as it is mentioned previously, blue pigment (H) was been identified in Fourier test. Due to the shortage in the amount of blue pigment sample, XRD and XRF could not be done. Sample G, being examined by polarized microscope, was identified as red copper, while FTIR test of this sample had better identified the oil and varnish associated with pigment. Ochre sample being identified by polarized microscope was also identified as ochre yellow, while Fourier had distinguished it as being amber color. Samples O and I were not identifiable using polarized microscope.

Table 3. Analyses of samples by PLM

	Sample code	Sample type	**Sample appearance**	Result of PLM
1	A1	Fiber	Transparent tubes and a dark tube in the middle	Cotton
	A2	Fiber	Transparent tubes and a dark tube in the middle	Cotton
2	B N	Green	Fine and round aggregation and low reliefness. The particles are seen as tiny, bright and dark spots; after using the analyzer it is considered as a non-isotropic material that has a refractive index	Green earth
3	C F P	White	Particles of lead white, under the microscope tend to green. Particles are very small and irregular and their reliefness is comparatively good. Sometimes large particles are seen among the lead white particles. White lead has a high refractive index and is isotropic.	White lead
4	D E	Green	Average, organized and coherent aggregation. After placing the analyzer completely, particle brightness does not change. The material is isotropic and has a high refractive index.	White zinc
5	G	Red	Like the control sample of red lead, these particles are considered non-isotropic. Their aggregation is average to large and they are seen as round particles with hard and rough surface. Some particles are transparent and others are not. Some transparent particles appear to be blue or green. They have a high reliefness .After placing the analyzer completely the brightness of particles is changed.	Red lead
6	H	Blue	Fine and round aggregation with good reliefness. The particles are similar to ginger roots. After placing the analyzer completely, particle's brightness does not change. Samples of H& Blue Cerulean are considered as isotropic materials and also have a high refractive index.	Cerulean blue
7	I	Gray	-	?
8	K M	Ochre	Their aggregation is average to large. Red and orange pigments can sometimes be seen among them. They have a good reliefness and high refractive index. After placing the analyzer completely, particle brightness does not change. Control samples of Amber color & M sample are considered non-isotropic and also have a high refractive index.	Amber
9	O	Golden	Fine, round and inherent aggregation	?
10	U	Fiber	Scaly tubes	Wool

According to the physical appearance of A1 and A2 fiber samples, since there are twisted strips through the fibers, they are identified as being cotton fibers, and also according to the physical appearance of U leaf sample, because of the existence of the fiber's linear cross section of shell or scaly cells, this sample was distinguished as cotton leaf.

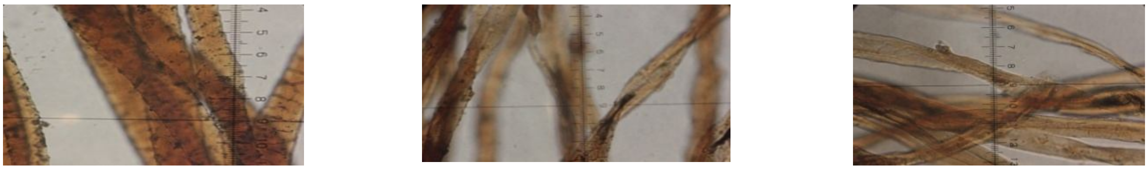

(A): A1 sample **(B): A2 sample** **(C): U sample**

Figure 8. Fiber samples under the polarized microscope,with 600X magnification

ANALYZING SAMPLES USING X-RAY DIFFRACTION

In this experiment, the compositions used in the samples were identified. In XRD experiment results, green pigments of the restored parts of samples E and D, using identification cards of ASTM by XRD were identified as white lead, while through FTIR, sample E they had been identified as being green oxide plus linseed oil, and sample D as a mixture of red, Urushi black and safflower yellow. But as mentioned before, the PLM result of these two samples confirms the existence of white lead. Regarding the fact that among all three FTIR, PLM and XRD experiments were done on these samples, the results of both PLM and XRD are the same, thus the result of examining samples D and E could be white lead. Though the samples were extracted from the green part of the painting and thus the pigments seem to be green, due to the existence of plenty of white lead, the results of the experiments done on D and E samples confirm the prevalent presence of white lead pigments in these samples.

As can be seen in the Table 4, samples M and K were not identifiable by this method. The result of FTIR experiment on samples M and K showed the presence of amber color as the material with the highest similitude with this sample, and results of PLM experiment also showed the similitude between these samples and the amber reference sample. Hence, the final identification of samples M and K could be reported to be amber color. The result of XRD experiment on sample H (blue pigment) demonstrates the presence of white lead compositions, cobalt compositions, tin and copper. The presence of white lead in this sample could be caused by the frequent use of white lead pigment in the blue pigment mixture by the artist. In the FTIR result of this sample, white lead was identified as having the greatest similitude percentage, having 68/06 percent similitude. As seen in the PLM experiment result, the similarity of this sample to the reference sample of cerulean blue was confirmed. Cerulean blue is a color resulted from the combination of cobalt and tin. According to these data, it can be said that the result achieved from the XRD experiment of sample H confirms the PLM result of this sample. XRD experiment of skin color pigment (sample C) also shows plenty of white lead sample, as confirmed in the PLM and FTIR experiments results. According to the results, the artist frequently used white lead in combination with other colors. XRD experiment results of sample P, like those of FTIR and PLM of this sample, also confirmed the presence of white lead. XRD experiment results indicate red pigment is a combination of red lead or red copper. As mentioned, in the FTIR results of sample G, some additive materials were distinguished along with the pigment in this sample, but the pigment itself was not identifiable. However, in PLM results of sample G, the presence of red copper was confirmed. According to PLM and XRD results, the final identification of sample G could be reported to be red lead. The results of experiments done on samples B and N show green samples that have been gathered from damaged parts of the painting were found to be terre verte pigments. Regarding the fact that among all three FTIR, PLM and XRD experiments done on these samples, the results of both PLM and XRD of these two samples are the same, thus the result of examining samples B and N could be reported as terre verte. The golden parts of the margin of the work were also identified as copper compositions. As it was mentioned previously, the artist in some cases applied copper compositions in order to create a golden color. In FTIR results of sample O, blue pigment, chrysocolla color that contains copper compositions, were distinguished as having 49/81 of similitude percentage. This could be due to the copper compositions in this sample, as XRD confirms. Finally, the paste on the back of the work was identified as being quartz compositions in XRD experiment results. As seen in the FTIR results of Q, R, S and T (paste samples on the back of the work), plant glue was identified as being the paste on the back of the work. Presence of quartz in the results of XRD experiment could be due to the dust on the work or the presence of quartz in paste compositions. The results of XRD experiment on samples are presented in Table 4.

Table 4. The results of XRD analysis on samples

	Sample code	Sampling region	Sample type	The identified components
1	B	damaged area	Green	Green earth (Mg. Mn .Fe)$_6$SiO$_2$
2	C	damaged area	Skin's color	White lead Pb$_3$(CO$_3$)$_2$ (OH)$_2$
3	D	Restoration area	Green	White zinc ZnO
4	E	Restoration area	Green	White zinc ZnO
5	G	damaged area	Red	Red lead Minium(Pb$_3$O$_4$)
6	H	Damaged area	Blue	White lead & copper compounds&Cu$_5$.6Sn-CoO- Pb$_3$(CO$_3$)$_2$ (OH)
7	K	Damaged area	Ochre	?
8	M	Damaged area	Black	?
9	N	Damaged area	Paled Green	Green earth (Mg.Mn.Fe)$_6$SiO$_2$
10	O	Damaged area	Golden	Alloy Cu. SN
11	P	Damaged area	White	White lead Pb$_3$(CO$_3$)$_2$ (OH)$_2$
12	Q	Behind the Canvas layer	Glue	Quartz SiO$_2$

ANALYZING SAMPLES BY X-RAY FLUORESCENCE

Sample O, which was extracted from the golden parts of the margins of the work, was not identified in the FTIR experiment, it was also not identifiable in PLM experiment, but was distinguished to be of copper compositions in the XRD experiment. So, in order to find the final identification and also gain confidence over XRD experiment results, XRF experiment was also conducted on this sample. In XRF experiment, as can be seen in the table, the percentage of all existing elements in sample O is distinguished. Based on the fact that the amount of copper in this sample is more than other samples, the final result could be mentioned as being copper. The XRF experiment result of sample C, the skin sample color from damaged area of the work, in this experiment, as in FTIR, PLM and XRD, is distinguished as being white lead. Results of samples B and D also confirm the results of PLM and XRD experiments. As mentioned before, the FTIR experiment result of sample B was distinguished as green oxide plus linseed oil as a material with a high similitude percentage, while XRF, XRD and PLM experiment results show terre verte as the material present in sample B. According to these data the final result of sample B green could be reported as being terre verte. The FTIR result of sample D green was distinguished as a color mixture of saffron, Urushi red and Urushi black, while XRD and PLM experiment results had distinguished it as white lead in sample D. So, to gain confidence over the achieved results, XRF experiment was conducted over these samples. Finally, XRF experiment, as XRD and PLM experiments, also confirmed the presence of white lead. Sample I (gray color), which had been perceived as white lead in FTIR experiment, was distinguished to be gypsum. It must be mentioned that in comparative FTIR graphs of sample I, chalk powder, with 58/77 similitude percentage, follows white lead with 73/23 similitude percentage. As all the white pigments extracted from the original parts of the work and also the white color that was used in its restoration had been distinguished as white lead, the chalk powder could possibly be related to the background infrastructure layer of the work. The presence of calcium oxide in sample D with 36% and in sample B with 34% makes this possibility even stronger.

Table 5. Results of XRF analyzes on samples

	CuO	Fe_2O_3	Al_2O_3	ZnO	PbO	As_2O_3	CaO	SiO_2
B	-	-	-	-	-	%44	%34	%41
C	-	-	-	-	%100	-	-	-
D	-	-	-	%66	-	-	%36	-
I	-	-	-	-	-	-	%100	-
O	%35	%05	%10	-	-	-	%04	%26

In the end, the final results of comparing FTIR, PLM, XRD and XRF experiments are presented in Table 6. Final results of examining the samples are as follows: A1 and A2 fiber samples and U leaf sample are distinguished to be wool, N and B samples as terre verte, samples C, F and P as white copper, samples D and E white lead, sample G red copper, sample I chalk powder, sample H cerulean blue, samples M and K amber color, sample O copper compositions, and samples Q, R, S and T plant gum.

Table 6. Comparative analysis of FTIR, PLM, XRD and XRF t on the final extracted samples

	Sample code	Sample type	XRD	FTIR	PLM	XRF	Final result
1	A1	Fiber	-	-	Cotton	-	Cotton
	A2	Fiber	-	-	Cotton	-	
2	B	Green	Green earth $(Mg.Mn.Fe)_6SiO_2$	Verdigris in linseed oil	Green earth	Green earth	Green earth
3	C	Skin's color	White lead $Pb_3(CO_3)_2 (OH)_2$	White lead	White lead	White lead	White lead
4	D	Green	White zinc ZnO	Safflower yellow, Urushi black &Urushi red	White zinc	White zinc	White zinc
5	E	Green	White zincZnO	Verdigris in linseed oil	White zinc	-	White zinc
6	F	White	-	White lead	White lead	-	White lead
7	G	Red	Red lead Minium(Pb_3O_4)	?	Red lead	-	Red lead
8	H	Blue	White lead & copper compounds & $Cu5.6Sn$- CoO- $Pb_3(CO_3)_2 (OH)$	White lead	Cerulean blue	-	Cerulean blue
9	I	Gray	-	White lead	؟	Calcite	White lead
10	K	Ochre	؟	Amber	Amber	-	Amber

11	M	Black	؟	Amber	Amber؟	-	Amber
12	N	Pallid Green	Green earth $(Mg.Mn.Fe)_6SiO_2$	Amber ، Urushi black &Urushi red	Green earth	-	Green earth
13	O	Golden	Alloy Cu. SN	؟	؟	Copper	Copper
14	P	White	White lead $Pb_3(CO_3)_2(OH)_2$	White lead	White lead	-	White lead
15	Q	Glue	Quartz SiO_2	plant gum	-	-	plant gum
16	R-S-T	Glue	-	plant gum	-	-	plant gum
17	U	Fiber	-	-	Wool	-	Wool

The additive materials to "Egyptian Girl" painting are shown in Table 7. The applied varnishes in the work are distinguished to be shellac varnishes, the applied paste to be plant gum and the oil used in this painting is distinguished to be linseed oil.

Table 7.The additive materials to "Egyptian Girl"

Resin	Glue	Oil
Shellac	Plant resin	Linseed oil

CONCLUSION

According to the conducted experiments, the green pigment in the “Egyptian Girl” painting was found to be terre verte. Terre verte pigment has been recorded as a commonly used pigment in European wall paintings and foreign contemporary easel paintings during the Qajar period (Marras, 2010; Favaro, 2010). Although terre verte pigment is a mineral which is found in great amounts, apparently it was not commonly used in Iranian paintings. Among the reported green pigments used by Iranian artists, terre verte pigment was never used in wall paintings, manuscripts, and easel paintings. Thus it could be concluded that Kamal-al-Molk was influenced by foreign artists in his usage of terre verte pigment.

The result gained from experiments conducted over the "Egyptian Girl" painting showed three pigments of white lead, white tin and chalk powder. However, based on the results of identifying white samples extracted from damaged areas of the work, and also by conducting some experiments on the white sample and finding a great deal of chalk powder along with white lead in this sample as a result, it is concluded that the artist used white lead as the white color in "Egyptian Girl" painting, and white lead has been widely used in its restoration. The Iranian artist had used white lead, a common pigment in Iranian painting. So it could be said that the white pigment used in this painting was influenced by previous Iranian artistic periods to Qajar.

Distinguished black and yellow pigments in "Egyptian Girl" are amber color, which is a composition of iron oxide, manganese oxide and clay. It must be mentioned that it is considered as an earthen pigment that was not a new pigment during the Qajar period and had also been used in painting during the Safavid period, previous to Qajar.

During this project, the blue pigment used in "Egyptian Girl" painting was found to be cerulean blue. Artist's use of this pigment reflects his knowledge of new synthetic materials.

The red pigment used in this work was found to be red copper, red copper pigment was also used in Iranian manuscripts (Bruni, 2001). The artist’s use of red copper pigment was due to his influence from previous Iranian artistic periods to that time.

The golden pigments used in the"Egyptian Girl" painting were found to be alloys of copper. The use of this kind of pigment in this painting could be considered as a extension to its use during the Safavid period in Iran.

In the end, the color pallet of the "Egyptian Girl" painting attributed to Kamal-al-Molk is reported to be as follows:

Green: terre verte, white: white lead, red: red lead, blue: cerulean blue, yellow and brown: amber color, golden: copper compositions;

and the white color used in its restoration: white lead.

The paste sample applied on the back of the work: plant glue, the material used for ground layer: chalk powder, the applied varnishes in the painting: shellac varnishes, and the oil used in this work: linseed oil.

The fibers used to make the canvas were distinguished to be cotton, and those used in its restoration to be wool.

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