International Journal of Engineering Research and General Science Volume 3, Issue 3, Part-2 , May-June, 2015
ISSN 2091-2730

Characterization of Painting Materials of Presage of Angel Gabriel to the Priest Zechariah Icon

Gomaa Abdel-Maksoud[a], Yousry M. Issa[b,*], Mina Magdy[c]

[a]Conservation Department, Faculty of Archeology, Cairo University, Giza, Egypt.

[b]Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt.

[c]National Museum of Egyptian Civilization, Cairo, Egypt.

E-mail: gomaaabdelmaksoud@yahoo.com (G. Abdel-Maksoud)

yousrymi@yahoo.com (Y. M. Issa)

minamagdy_2000@yahoo.com (M. Magdy)

Abstract- The aim of study is identification, determination, and assessment of the painting materials of Coptic icon, presage of angel Gabriel to the priest Zechariah. Different analytical techniques were applied for characterization of the icon materials. The results revealed that the rigid support was *Tamarix* hardwood, the flexible support was linen fibers, the ground materials was gypsum. The pigments were vermilion, kermes carmine red and ultramarine blue, the binder was egg yolk, and the varnish was mastic resin. The chemical analyses showed the stability of icon materials with surrounding environment, in addition to the impact of metal salts result in decreasing of the free amino acids of egg yolk binder and cracking the paint film.

Keywords: Icon; characterization; OM; ATR-FTIR; FESEM-EDX; AAA.

1. INTRODUCTION

Application of analytical chemistry in archaeology can refer to the term "archaeological chemistry" and has benefit aspects in conservation, restoration of the artworks. It provides valuable information about the materials used in artworks such as the nature of materials and the processes that used to make and change them [1].

The "Coptic" word refers to the Egyptian Christians artworks [2]. The "Icon" word describes a religious image and it is associated with the painting of the Orthodox Churches [3]. The painting of icon is composed of four layers (support layer, ground layer, paint layer "pigments and binder", and varnish layer) [4]. Characterization of the icon materials will give information about the state of icon and the effect of the aging and environmental conditions. There are many factors that make the process of identifying the icon layers is difficult such as the use of small quantity of the sample and the lack of sample purity.

The chemical compositions of icon materials are very complex so analytical methods with high spatial resolution will be used. Light microscope (OM) is used to identify the fibers. In addition to that, it can be used for identification of the fiber group.

Fibers have a characteristic appearance in the cross-sectional view. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) is used for determination the chemical structure of painting materials. Field emission scanning electron microscope (FESEM) is used to provide information about the surface texture such as fine cracking and the nature of relationship between the pigment and the binding medium at the surface. Energy dispersive spectroscopy (EDS) is used to characterize the elemental chemical composition. Amino acid analyzer (AAA) is used to detect the free amino acids of proteinaceous binder. The metal ions in the pigments can form complexes with some amino acids leading to change the amount of free amino acid measured [5].

Icon of presage of angel Gabriel to the priest Zechariah has been hold (Fig. 1) in *Church of* Saint Mercurius in south of Cairo. The church dates back to 6th century. The icon is believed to have been drawn by Yuhanna Al-Armani and dates back to 18th century.

Fig. 1. Icon of Presage of Angel Gabriel to the Priest Zechariah.

Angel Gabriel stands left to the altar. Angel Gabriel presages the priest Zechariah with birth of his son "John the Baptist". The priest Zechariah wears sticharion with red color at the upper part and white color at the lower part, blue-color tailasan with brown cap on his head. The priest Zechariah also holds thurible in his left hand and there is golden halo around his head. Angel Gabriel has two white wings, upper brown wear and lower green wear. The altar has white appearance and alternate tiles of blue-white color. The icon shows deterioration at the lower right part. Five samples were carefully extracted from deteriorated parts including: wood support, canvas fibers, light red color "deteriorated part of the outer frame", dark red color "deteriorated part of the inner frame", and violet Color "deteriorated part of the floor tiles".

2. EXPERIMENTAL

2.1. Samples

Five samples were taken from the damaged parts of the icon and analyzed by different techniques. The samples were wood specimen, canvas fibers, light red color, dark red color, and violet color.

Six reference materials were assembled and analyzed by ATR-FTIR method for comparison with the historical samples. The reference samples includes: ground (gypsum), chalk (filler), binder (egg yolk), pigments (vermilion, artificial ultramarine blue), and varnish (mastic resin) materials. Egg yolk sample also analyzed by amino acid analyzer to be compared with the historical sample.

2.2. Instruments

Leica motorized optical microscope system attached with a digital Camera Leica ICC50 HD (Leica DM750, Wetzlar, Germany) was used for identification of the canvas fibers and wood specimen.

The samples were analyzed by Vertex 70 FTIR spectrometer (Bruker Optics, Billerica Inc., Massachusetts, USA) equipped with a diamond ATR and DLaTGS detector. The spectral range was from 400-4000 cm^{-1} and resolution was 4 cm^{-1}, with 16 scans.

Field emission scanning electron microscope (Quanta FEG-250, FEI company, Hillsboro, OR, USA) equipped with EDX unit (Energy Dispersive X-ray Spectrophotometer, EDAX Apollo SDD, Mahwah, New Jersey) was performed to study the samples. The samples were examined in low-vacuum mode at an accelerating voltage 20 kV, resolution of 1 nm, and magnification 14× up to1,000,000×.

LC 3000 amino acid analyzer (Eppendorf, Hamburg, Germany) was used for analysis of the proteinaceous binder. The chromatographic separation was performed on a cation exchange column BTC 2410-4 µm, 125×4 mm and lithium citrate buffer system. The device is controlled by WinLC combined with EZChrom data software.

3. RESULTS AND DISCUSSION

The study by OM, ATR-FTIR, FESEM, and EDS analyses reveals that the rigid support is hardwood and the flexible support is linen fibers and the ground material is a mixture of gypsum, lead white, the binder is egg yolk and the varnish is mastic resin.

Optical microscope demonstrates that cross-section of wood (Fig. 2) belongs to the hardwood, *Tamarix* species (*Tamarix aphylla*). It is characterized with diffuse-semi ring pores, cluster pores, thin-thickness fibers (¼ lumen), multi-seriate rays (5-20 cells), heterocellular rays, and abundant crystals in rays [6-8].

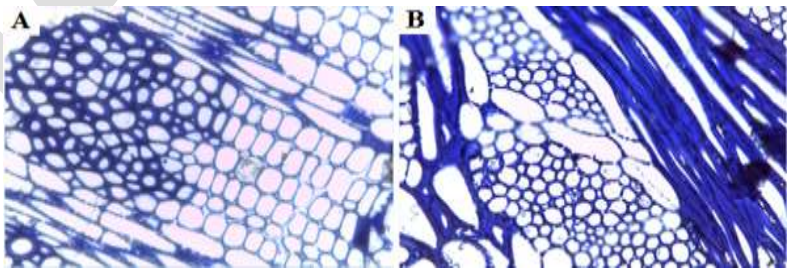

Fig. 2. Cross-section of Wood.

(A) Transverse Section (B) Longitudinal Section

Canvas fibers (Fig. 3) are examined by optical microscope. It is linen fibers characterized with nodes and cross cracks along the fibers [9].

Fig. 3. Fibers of Canvas.

ATR-FTIR spectra of the reference samples (Table 1) give characteristic bands that will be compared to the bands of historical samples (Table 2).

Gypsum is characterized with ATR-FTIR bands at 3536-3283 cm^{-1} υ(O-H), 1644-1620 cm^{-1} δ(O-H), 1140-1102 cm^{-1} υ(SO_4^{-2}), and 672-657 cm^{-1} δ(SO_4^{-2}) [10-12]. EDS microanalysis (Table 3) detects Ca, S, and O elements which are characteristic of gypsum [13].

Table 1. Characteristic Infrared Bands of the Reference Samples.

Material	Band (cm^{-1}), (Assignment)
Gypsum	3606, 3551 υ(O-H), 1110, 1087, 1007 υ(SO_4^{-2}), 658 δ(SO_4^{-2})
Chalk	1396 υ(CO_3^{-2}), 872, 712 δ(CO_3^{-2})
Vermilion	643 υ(Hg-S)
Artificial Ultramarine Blue	1120, 991, 948 υ(Si-O-Si)
Egg Yolk	3282 υ(N-H), 2923, 2853 υ(C-H), 1744, 1633 υ(C=O), 1541, 669 δ(N-H), 1541 υ(C-N), 1458, 1416, 1378 δ(C-H)
Mastic Resin	2930, 2868 υ(C-H), 1704 υ(C=O), 1453, 1377 δ(C-H), 1181, 1109, 1080, 1045, 1028, 1010, 987, 973, 945, 922 υ(C-O)

Table 2. Characteristic Infrared Bands of Paint Colors of Presage of Angel Gabriel to the Priest Zechariah.

Color	Bands (cm^{-1}) in IR Spectra	Material
Light Red	3394, 3283, 1642, 1622, 1102, 672	Gypsum
	635	Vermilion
	3394, 3283, 2919, 2850, 1642, 1622, 1537, 1392, 672	Egg Yolk
	3394, 3283, 2919, 2850, 1642, 1622, 1392, 1102, 1051	Mastic Resin

Dark Red	3390, 3287, 1644, 1140, 657	Gypsum
	3390, 3287, 2981, 2951, 1727, 1537, 1445, 1235	Kermes Carmine Red
	3390, 3287, 2981, 2951, 2852, 1727, 1644, 1537, 1445, 1384, 657	Egg Yolk
	3390, 3287, 2981, 2951, 2852, 1727, 1644, 1445, 1384, 1235, 1140, 1096, 1031	Mastic Resin
Violet	3536, 3400, 1620, 1116	Gypsum
	1409, 872	Chalk
	3536, 3400, 1075, 872	Ultramarine Blue
	3536, 3400, 2921, 1737, 1243	Kermes Carmine Red
	3400, 2921, 1737, 1620, 1409	Egg Yolk
	3536, 3400, 2921, 1737, 1620, 1409, 1243, 1186, 1116, 1075, 984	Mastic Resin

Egg yolk shows characteristic bands at 3400-3283 cm^{-1} υ(N-H), 2981-2850 cm^{-1} υ(C-H), 1737-1620 cm^{-1} υ(C=O), 1537, (672-657) cm^{-1} δ(N-H), 1537 cm^{-1} υ(C-N), and 1445-1384 cm^{-1} δ(C-H) [14-17].

Mastic resin is proved by appearance of ATR-FTIR bands (Table 2) at 3536-3283 cm^{-1} υ(O-H), 2981-2850 cm^{-1} υ(C-H), 1737-1642 cm^{-1} υ(C=O), 1644-1622 cm^{-1} υ(C-C), 1445-1384 cm^{-1} δ(C-H), and 1392-984 cm^{-1} υ(C-O) [18-20].

FESEM micrographs (Fig. 4) show the topography of paint surface and state the paint film of historical samples.

All samples taken from different positions (colors) produce the same behavior regarding the support, ground, binder and varnish material.

Table 3. EDS Microanalysis and Elemental Composition (Atomic Percentage) of Each Color of Historical Sample.

Element	Light Red	Dark Red	Violet
C K	44.99	60.06	27.40
O K	20.01	26.94	39.10
Na K	1.19	0.83	-
Mg K	-	0.55	0.38
Al K	0.98	1.03	1.81
Ca K	1.29	1.14	2.35
Si K	1.79	1.29	0.51
S K	14.31	1.07	9.53
Cl K	0.13	0.23	1.09
K K	-	0.47	-
P K	0.76	0.80	-
Fe K	0.75	0.40	0.82
Hg L	13.79	-	-

Sn L	-	4.81	-
Mn K	-	0.10	0.14
Co K	-	0.11	0.23
Zn K	-	0.18	4.32
Ti K	-	-	5.76
Ba L	-	-	5.87
As K	-	-	0.70

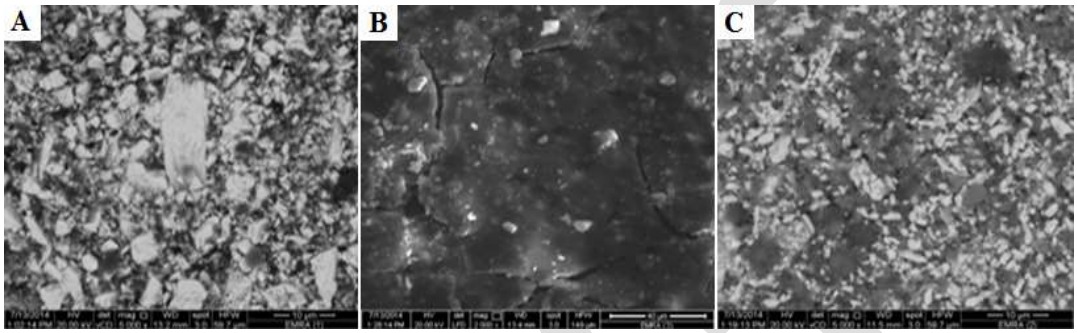

Fig. 4. FESEM Micrograph of Historical Samples: (A) Light Red Color; (B) Dark Red Color; (C) Violet Color.

3.1. Light Red Color

EDS microanalysis (Table 4) detects Hg, S elements that are characteristic for vermilion pigment [21-23]. FESEM micrograph (Fig. 4) shows aggregation of particles of the pigment. ATR-FTIR spectra (Fig. 5) manifest bands at 635 cm^{-1} that refer to vermilion pigment [24,25]. Mercury ions can form complexes with egg yolk protein and this assumption is confirmed by amino acid analysis (Table 4). The results obtained show that content of some amino acids of light red color are reduced (aspartic acid, threonine, serine, valine, leucine, phenylalanine, histidine, lysine, and methionine) or zeroed (tyrosine) as a result of oxidation process in which the mercury cations can form complexes with egg yolk binder [17,26,27].

Table 4. Relative Concentration of Amino Acids of Light Red Color and Reference Sample.

Amino Acid	Light Red Color	Reference Sample
Aspartic Acid	4.60	5.06
Threonine	1.62	3.38
Serine	3.50	5.10
Glutamic Acid	40.69	39.44
Proline	4.79	2.05
Alanine	15.89	7.97
Valine	2.79	4.28
Leucine	3.47	7.57

Phenylalanine	5.55	6.43
Histidine	2.10	2.45
Arginine	10.19	7.65
Lysine	3.91	4.90
Methionine	0.27	0.98
Isoleucine	0.62	-
Tyrosine	-	2.74

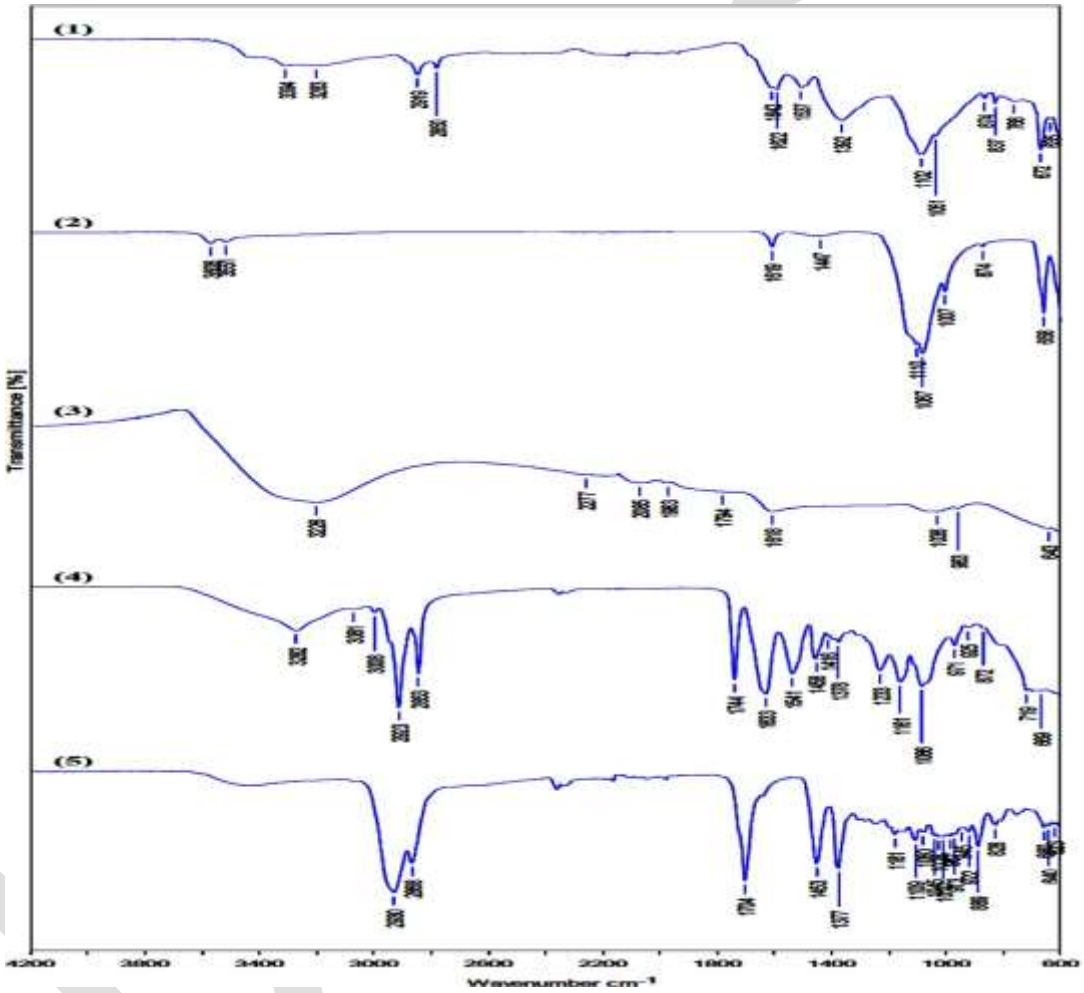

Fig. 5. ATR-FTIR Spectra of: (1) Historical Sample "Light Red Color"; (2) Gypsum; (3) Vermilion Red; (4) Egg Yolk; (5) Mastic Resin.

3.2. Dark Red Color

ATR-FTIR spectra (Fig. 6) exhibit characteristic bands at 3390, 3287 cm^{-1} υ(O-H), 2981, 2951 cm^{-1} υ(C-H), 1727 cm^{-1} $\upsilon(C=O)_{Carboxylic\ acid}$, 1537, 1445 cm^{-1} $\upsilon(C=C)_{Aromatic}$, 1235 cm^{-1} υ(C-O) that refer to kermes carmine red [12,28]. EDS microanalysis (Table 3) detects high amount of Sn element as tin oxide mordant for the organic dye. FESEM micrograph (Fig. 4) shows black

appearance indicating their organic composition and cracking of the paint film due to the presence of tin oxide can promote the oxidation process.

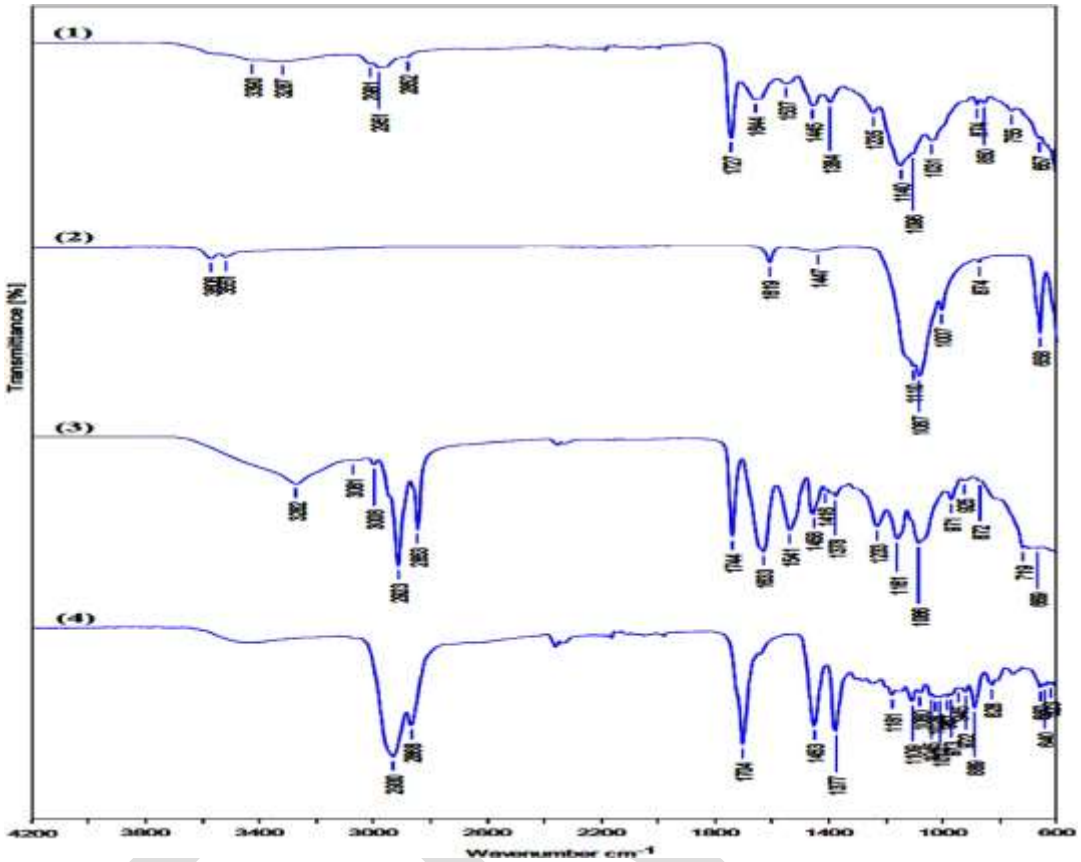

Fig. 6. FTIR Spectra of: (1) Historical Sample "Dark Red Color"; (2) Gypsum; (3) Egg Yolk; (4) Mastic Resin.

3.3. Violet Color

Violet color may result from mixing the natural ultramarine blue and kermes carmine red pigment. ATR-FTIR spectra (Fig. 7) show characteristic bands at 3536, 3400 cm^{-1} υ(O-H), and 1075, 872 cm^{-1} υ(Si-O-Si), υ(Si-O-Al) that refer to a*luminosilicate* of natural ultramarine pigment [29] and bands at 3536, 340 cm^{-1} υ(O-H), 2921 cm^{-1} υ(C-H), 1737 $\upsilon(C=O)_{Carboxylic\ acid}$, and 1243 cm^{-1} υ(C-O) refer to kermes carmine red [12,28]. Appearance of chalk (Fig. 7) with characteristic ATR-FTIR bands at 1409, 872, and 712 cm^{-1} as carrier for kermes carmine pigment [10,11,30]. FESEM micrograph (Fig. 4) shows distribution of large particles of ultramarine and black appearance of kermes pigment. EDS microanalysis (Table 3) detects of Ca, Al, S, Si and Mg elements of ultramarine pigment [29,30]. The cations (Ca, Al) can catalyze the oxidation process of proteinaceous binder and this appears obviously with bands of oxalate 1620 cm^{-1} with broad band at 1409 cm^{-1} [30,31].

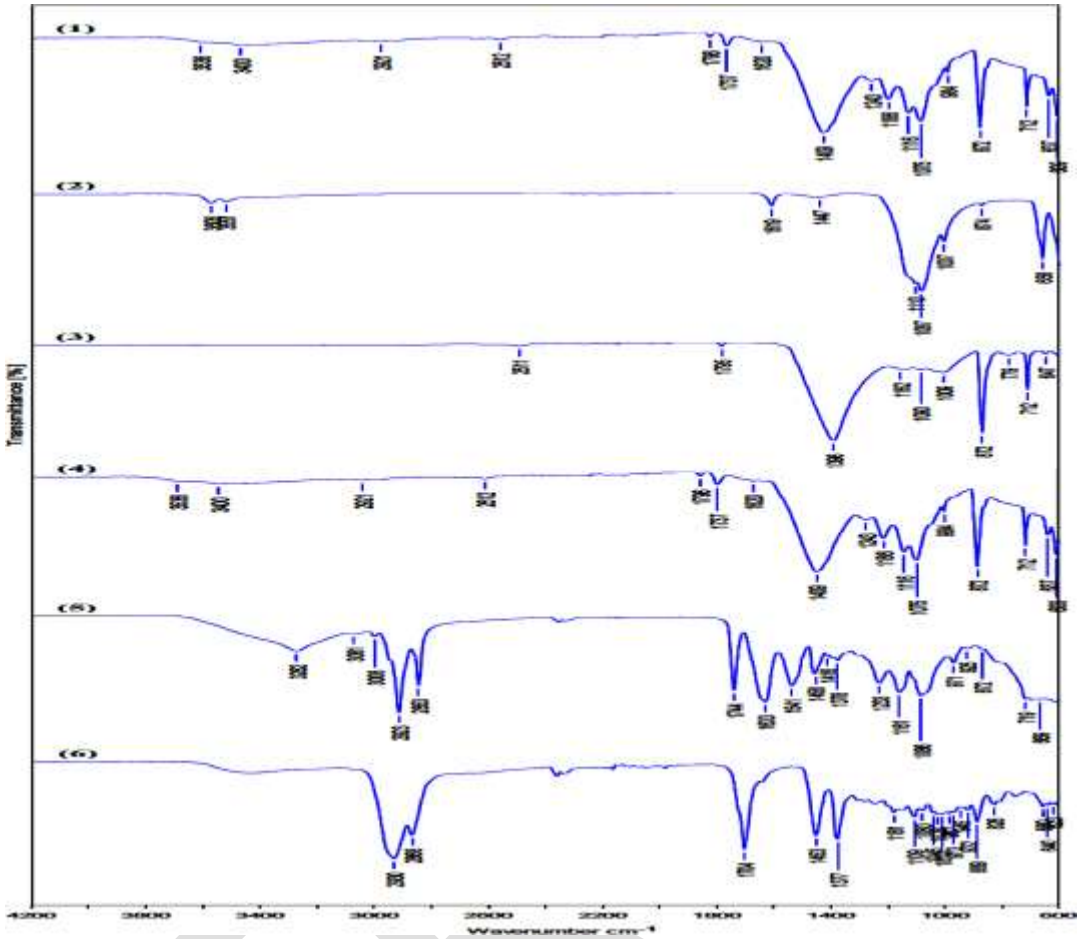

Fig. 7. ATR-FTIR Spectra of: (1) Historical Sample "Violet Color"; (2) Gypsum; (3) Chalk; (4) Artificial Ultramarine Blue; (5) Egg Yolk; (6) Mastic Resin.

ACKNOWLEDGMENT

The authors would like to thank Dr. Wadea Malek (Ministry of Antiquities, Egypt) for his help during collection of the samples. The authors also are grateful to Dr. Rim Hamdy (Botany Department, Faculty of Science, Cairo University, Egypt) for identification of the wood specimen.

CONCLUSION

Combination of OM, FTIR, FESEM-EDX, and AAA was used to give information about the identity of icon materials. The obtained results show that *Tamarix* hardwood was used as rigid support and linen fibers as flexible support and gypsum as ground and vermilion, kermes carmine red, and ultramarine blue as pigments and egg yolk as binder and mastic resin as varnish materials. The good state of icon layers attributes to stability of the pigments with environment conditions and permanence of the colors. Taking into consideration the impact of metal salts toward the organic compounds, it may lead to degradation of the organic molecules and decreasing the content of amino acids, and cracking of the paint film.

REFERENCES:

[1] Z. Goffer, "*Archaeological Chemistry", 2nd Edn.*, John Wiley, England, 2007.

[2] Z. Skalova and G. Gabra, "Icons of the Nile Valley Egyptian", 1st Edn., International Publishing Company-Longman, Cairo, Egypt, 2003.

[3] V. Losskey and L. Ouspensky, "The Meaning of Icons", 2nd Edn., St Vladimir's Seminary Press, New York, 1983.

[4] W. S. Taft and J. W. Mayer, "The Science of Paintings", 1st Edn., Springer-Verlag, New York, USA, 2000.

[5] B. H. Stuart, "Analytical Techniques in Materials Conservation", 1st Edn., John Wiley, England, 2007.

[6] V. Dorge and F. C. Howlett, "*Painted Wood: History and Conservation", 1st Edn., J. Paul Getty Trust, Los Angeles, USA, 1998.*

[7] M. Van der Veen, "The Exploitation of Plant Resources in Ancient Africa", 1st Edn., Springer, New York, USA, 1996.

[8] N.M. Waly, Wood Anatomical Characters of the Egyptian *Tamarix* L. Species and Its Taxonomic Significance, Taeckholmia, 1999, 19, 115-125.

[9] M. Humphries, "Fabric Reference", 4th Edn., Prentice Hall, New Jersey, USA, 2008.

[10] M.T. D. Carbó, V. P. Martínez, J.V. G. Adelantado, F. B. Reig, and M.C.M. M. Moreno, Fourier Transform Infrared Spectroscopy and the Analytical Study of Sculptures and Wall Decoration, J. Mol. Struct., 1997, 410-411, 559-563.

[11] C. Genestar and C. Pons, Earth Pigments in Painting: Characterisation and Differentiation by Means of FTIR Spectroscopy and SEM-EDS Microanalysis, Anal. Bioanal. Chem., 2005, 382, 269-274.

[12] D. Kovala-Demertzi, L. Papathanasis, R. Mazzeo, M. A. Demertzis, E. A. Varellac, and S. Prati, Pigment Identification in A Greek Icon by Optical Microscopy and Infrared Microspectroscopy, J. Cult. Herit., 2012, 13, 107-113.

[13] J. A. Stratis, C. Makarona, D. Lazidou, E. G. Sánchez, A. Koutsoudis, M. Pamplona, R. Pauswein, G. Pavlidis, S. Simon, and N. Tsirliganis, Enhancing the Examination Workflow for Byzantine Icons: Implementation of Information Technology Tools in A traditional Context, J. Cult. Herit., 2012, 15, 85-91.

[14] R. Mazzeo, S. Prati, M. Quaranta, E. Joseph, E. Kendix, and M. Galeotti, Attenuated Total Reflection Micro FTIR Characterisation of Pigment–binder Interaction in Reconstructed Paint Films, Anal. Bioanal. Chem., 2008, 392, 65-76.

[15] R. J. Meilunas, J. G. Bentsen, and A. Steinberg, Analysis of Aged Paint Binders by FTIR Spectroscopy, IIC-Int. Inst. Conserv., 1990, 35, 33-51.

[16] V. Ganitis, E. Pavlidou, F. Zorba, K.M. Paraskevopoulos, and D. Bikiaris, A post-Byzantine Icon of St. Nicholas Painted on A leather Support. Microanalysis and Characterisation of Technique, J. Cult. Herit., 2004, 5, 349-360.

[17] K. A. Dooley, S. Lomax, J. G. Zeibel, C. Miliani, P. Ricciardi, A. Hoenigswald, M. Loewb, and J. K. Delaney, Mapping of Egg Yolk and Animal Skin Glue Paint Binders in Early Renaissance Paintings Using Near Infrared Reflectance Imaging Spectroscopy, Analyst, 2013, 138, 4838-4848.

[18] M. R. Derrick, D. Stulik, and J. M. Landry, "Infrared Spectroscopy in Conservation Science", *1st Edn.*, J. Paul Getty Trust, Los Angeles, USA, 1999.

[19] C. *Azémard*, C. Vieillescazes, and M. *Ménager*, Effect of Photodegradation on the Identification of Natural Varnishes by FT-IR Spectroscopy, Microchem. J., 2014, 112, 137-149.

[20] S. Prati, G. Sciutto, R. Mazzeo, C. Torri, and D. Fabbri, Application of ATR-far-infrared Spectroscopy to the Analysis of Natural Resins, Anal. Bioanal. Chem., 2011, 399, 3081-3091.

[21] M.L. Franquelo, A. Duran, L.K. Herrera, M.C. Jimenez de Haro, and J.L. Perez-Rodriguez, Comparison Between Micro-Raman and Micro-FTIR Spectroscopy Techniques for the Characterization of Pigments from Southern Spain Cultural Heritage, J. Mol. Struct., 2009, 924-926, 404-412.

[22] M.L. Franquelo, A. Duran, J. Castaing, D. Arquillo, and J.L. Perez-Rodriguez, XRF, μ-XRD and μ-Spectroscopic Techniques for Revealing the Composition and Structure of Paint Layers on Polychrome Sculptures After Multiple Restorations, Talanta, 2012, 89, 462-469.

[23] T. D. Chaplin, R. J.H. Clark, and M. *Martinón-Torres*, A combined Raman Microscopy, XRF and SEM–EDX Study of Three Valuable Objects – A large Painted Leather Screen and Two Illuminated Title Pages in 17th Century Books of Ordinances of the Worshipful Company of Barbers, London, J. Mol. Struct., 2010, 976, 350-359.

[24] S. Vahur, A. Teearu, and I. Leito, ATR-FT-IR Spectroscopy in the Region of 550–230 cm^{-1} for Identification of Inorganic Pigments, Spectrochim. Acta, Part A, 2010, 75, 1061-1072.

[25] S. Vahur, U. Knuutinen, and I. Leito, ATR-FT-IR Spectroscopy in the Region of 500–230 cm^{-1} for Identification of Inorganic Red Pigments, Spectrochim. Acta, Part A, 2009, 73, 764-771.

[26] L. Valianou, S. Wei, M. S. Mubarak, H. Farmakalidis, E. Rosenberg, S. Stassinopoulos, and I. Karapanagiotis, Identification of Organic Materials in Icons of the Cretan School of Iconography, J. Archaeol. Sci., 2011, 38, 246-254.

[27] C. Duce, L. Ghezzi, M. Onor, I. Bonaduce, M. P. Colombini, M. R. *Tiné*, and E. Bramanti, Physico-chemical Characterization of Protein–pigment Interactions in Tempera Paint Reconstructions: Casein/Cinnabar and Albumin/Cinnabar, Anal. Bioanal. Chem., 2012, 402, 2183–2193.

[28] P. L. Lang, C. D. Keefer, J. C. Juenemann, K. V. Tran, S. M. Peters, N. M. Huth, and A. G. Joyaux, The Infrared Microspectroscopic and Energy Dispersive X-ray Analysis of Paints Removed from A painted, Medieval Sculpture of Saint Wolfgang, Microchem. J., 2003, 74, 33-46.

[29] S. Bruni, F. Cariati, F. Casadio, and L. Toniolo, Spectrochemical Characterization by Micro-FTIR Spectroscopy of Blue Pigments in Different Polychrome Works of Art, Vib. Spectro., 1999, 20, 15-25.

[30] D. Ajò, U. Casellato, E. Fiorin, and P.A.Vigato, Ciro Ferri's frescoes: a Study of Painting Materials and Technique by SEM-EDS Microscopy, X-ray Diffraction, Micro FT-IR and Photoluminescence Spectroscopy, J. Cult. Herit., 2004, 5, 333-348.

[31] C. Miliani, B. Doherty, A. Daveri, A. Loesch, H. Ulbricht, B.G. Brunetti, and A. Sgamellotti, In Situ Non-invasive Investigation on the Painting Techniques of Early Meissen Stoneware, Spectrochim. Acta A, 2009, 73, 587-592