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A multi-analytical approach for the archaeometric identification of natural dyes in Coptic Textiles, Nubia museum at Aswan, Egypt

By

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Abstract

Various analysis methods were used to identify the dyes used in a historical samples of dyed wool from a rare Coptic fabric was collected from the Nubia Museum in Aswan and their state of deterioration to create a plan for the preservation and restoration of the textile collection in this museum. High-performance liquid chromatographic methods, with ultraviolet-visible spectrophotometry detection (HPLC-UV/Vis) , FTIR Fourier transform infrared spectrophotometers were used to identify dyes and SEM scanning to determine degradation Caused by changes in the surface morphology of the Coptic sample. The results indicated that mixtures of organic dyes were used in this object in order to produce different colours. Such as indigo and madder, etc, were identified. The analytical results revealed that the wool sample suffered from deterioration, Moreover, The most frequently identified dyes included, and the results indicate that mixtures of organic dyes are used in dyeing these samples to produce different colours. The most dominantly identified colourants in samples collected from the Museum are laccaic acid, kermesic acid, munjistin and indigotin. The most dominantly identified dyestuffs are lac dye (Kerria lacca, Kerr), kermes (Kermesvermilio), madder (Rubia) species and indigoid dye source, either indigo (Indigofera species)or woad (Isatis tinctoria L.) the results helped dating of the historical object which belong to Sixth century AD.

Keywords*:* Coptic, Textiles, Natural Dyes, HPLC, FTIR, SEM.

1. Introduction

The term Coptic textiles are a general meaning applicable to a large number of historical Egyptian textiles, which were produced in ancient Egypt from the Roman era to the Islamic era. It is noticeable that the ancient Egyptians were adept at using natural dyes to color their textiles in different shades. [1-3] Identifying the chemical composition of the natural dyes used in the coloring of historical textiles is an important step in the appropriate preservation treatment, and the selection of appropriate maintenance materials, as well as the methods and steps of treatment. [4].

Identification of natural dyes can be done by comparing unknown archaeological dyes with new known ones. Coptic textiles like wool were dyed with natural dyes from plant or animal origins. [5].It can also be said that identifying the colored dyes of historical textiles is very useful in the dating of textiles due to the type of dye and its manufacture [6-8].In other words, the identification

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of organic and natural colorants used to color cultural heritage and art objects is a difficult part of this investigation and definition, of analytical chemistry. [3, 9-11]**.**

The non-destructive (ND) methods are used to investigate the historical textile materials used in dyes used in historical and archaeological textiles and provide information as to where, when and how the textiles were dyed [12].in addition to preserve them not to destruct them [7].

High Performance Liquid Chromatography system with a Diode-Array-Detector (HPLC-DAD) is useful technique for the detection of a wide variety of dyes. [13- 17].This technique has proven to be useful for identifying by comparing unknown natural dyes with standard chemical dyes using different automated efficiencies [21].

The different tones that were discovered on Coptic textiles mainly come from nature. For example, the red color was produced from a vegetable source such as Rubia tintorum, and other source such as insect source (cochineal). The blue color has also been derived from a botanical source, the indigo plant. Compound colors such as green were obtained by dyeing with a mixture of indigo and saffron yellow. The purple color was created by dyeing in madder and indigo different type of mordents used such as Alum, ferric salt, and copper salt were used as a mordant to setting in the colors and dyes. Scanning electron microscopes (SEM) has been reported for understanding the deterioration of the textile materials [23]. The SEM allows greater detail, accuracy than the optical microscope [24].

This study provides important results on the types of natural dyes used in coloring Coptic textiles in Nubia artifacts in Aswan, as well as identifying the types of natural fibers and the degree of their damage. These data are important and will actually contribute to defining the different methods of maintenance and choosing the appropriate restoration materials, which is the next step for this research, which will be published scientifically. [25]

2. Materials and Methods

2.1Historical Samples:

The historical textiles that have been selected are considered Coptic textiles, dating back to the Roman era (6th century AD). The historical object is considered one of the rare textiles. They are displayed in the Nubia Museum in Aswan, Egypt with registration number 12381 image 1. The historical object is made of wool fibers, and it has been included in many shades such as blue, red, brown, black and green. The dimensions of the historical object are (length 44.5 cm, width 15. cm). It is also decorated with geometric motifs, which are longitudinal bands, where there is a wide band of red in the middle between two lines of blue.

Visual examination shows that the number of threads per square centimeter is (10 in the torsion direction and 25 in the weft direction). The historical object is characterized by a state of weakness; as it becomes clear to us some separate pieces and threads, the historical piece needs restoration and maintenance. Three different samples were collected from the historical object, which were carried out according to conservation standards. The three samples are small fibers that were separated from the historical textile and could not be incorporated back into the historical textile. Figure No (1) Shows the details of the historical object [25- 33].

Fig. 1: Show the historical object from Coptic textile object dating back to Romanic era from Nubia Museum in Aswan

3. Experimental

3.3.1. Dyeing Process

1. Extraction of color: drenching the dyestuff within the water for 12 hours. At that point warming for 1.5 hours at 70 ^{o}C and strainer and isolating the strong parts from the color solution.
2. Planning silk fabric: dousing the Silk fabric in water with common soap for 12 hours and after that bubble for 1 hour and wash to induce freed of wrapping up materials.
3. The coloring prepare put the silk fabric within the color arrangement with delicately string at temperature 70^{o}C for 1.5 hours.
4. Stringent shower: break up the mordant in the water at that point colored silk samples from the previous step will put within the mordant bath for 30 min at temperature 60^{o}C. After that, the colored textiles will flush water [16-20].

2.3 Preparation of dyed wool Samples as standard

Samples of new wool were dyed by commercial natural dyes combined with different mordant to be used as standard samples in the identification of the historical dyes under test. Munjistin [34] and Alizarin was obtained from Acros Organics (Belgium) employed as reference material and was used as received. Purpurin was purchased as 90% pure from Acros Organics (Belgium) and it was used as a reference material after was purified through multi recrystallization procedures with ethanol. Xanthopupurin.[35].6-bromoindigotin [36] and indigotin [37] were synthesized and

purified according to literature procedures from commercially available starting materials. This dyeing was carried out according to methods described by [38-39].In addition; new woollen textiles were dyed with natural dyes, which are likely to be present in the historical object. At first, the dye solution was extracted from natural dyes, and then the woolen textiles were dyed with it.

3.3 Dye extraction procedure

To perform analysis process for the historical sample was obtained about (3-5 mg) of the Coptic textile and it was dissolved in 0.5 mL of 2 M concentrated TFA. Temperature at 60 C, The liquids were kept in a water bath for 10 minutes and at room temperature, it was cooled and the liquid was evaporated using nitrogen gas at room temperature. The dry residue was dissolved in 0.5 ml di methyl sulfoxide (DMSO),at a temperature 60ºC ,the dissolved solution of the solid sample was heated in a water bath for 20 minute, after that, the dissolved samples were filtered using syringe filter 0.2 mm membranes. Then injected into the HPLC system [40-42]

3.4. Identification of dyestuff and Chromatographic system

To perform the chromatographic analysis, a device is used to perform this analysis HPLC Agilent 1100 integrated method equipped with a G1313A automated injector, a G1311A pump, and G1315B multi-wavelength diode-array detector (DAD). It was used to separate compounds chromatographic analysis was done with a ZORBAX Eclipse XDB-C18 (4.6 X 150 mm, 5 mm) olumn from Agilent (USA), all steps were done at room temperature (20 C). The gradient elution program utilized two solvents: solvent A: CH3 CN- 0.1% TFA and solvent B: H2O - 0.1% TFA was used as eluent. Gradient elution program: initial 90% B isocratic for 3 min, 3 - 60 min linear gradient to 5% B. The elution was performed at a 1 mL/min flow rate and 20 mL injection volume. Chromatographic peaks of compounds were monitored simultaneously at 254 nm, 275 nm, and 288 nm. The chromatographic data were analyzed using Agilent Chemstation Rev.B.02.01-SR1. After that, the identification of the natural dyes was done by their UV spectral characteristics [40 - 41, 44].

4. RESULTS AND DISCUSSION

4.1 Morphological study:

The smallest sample of loose sutures was taken for examination with SEM that was available from different parts to examine the texture and condition of the fibres and their damage are shown in (Fig. 2A and B). The most common changes in fibre morphology were surface, dents, and large openings, holes, fractured by transverse fissure, longitudinal splitting, and brittle ends (Fig. 2 C and D).Textiles deteriorate naturally by heat, oxidation, moisture, radiation, microbiological attack.

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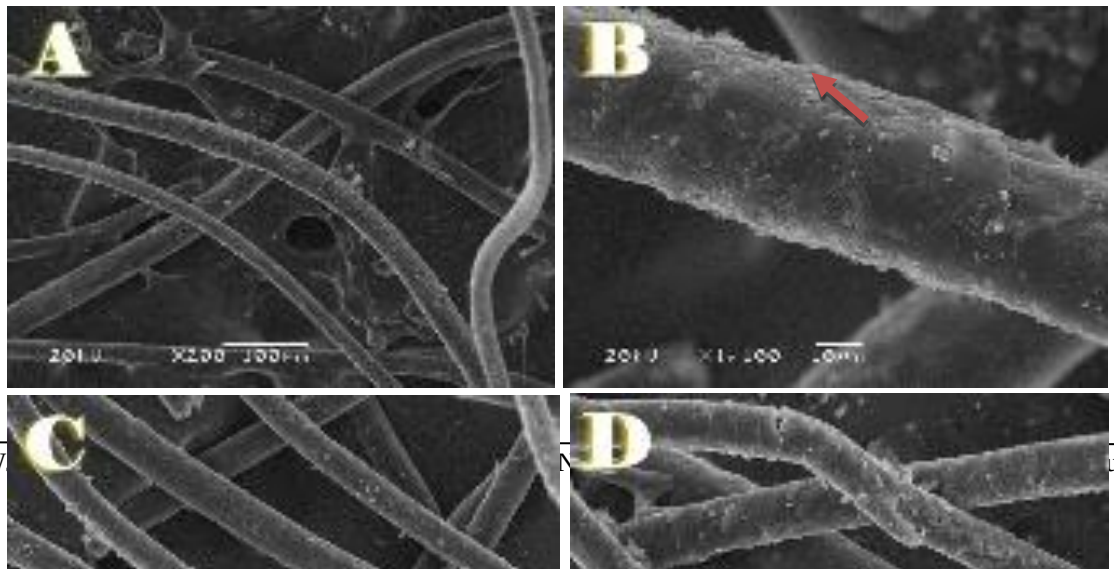

Fig. 2: shows the SEM images of the historical textile object, (A) shows the wool fibers of objects, While (B - D) shows deterioration of ancient wool fibers, with different magnifications (100X, 350X, and 500X). SEM shows different types of deterioration such as broken, fractures with longitudinal splitting, and fragile ends.

4.2 Identification of natural dyes according to UV spectral characteristics

It is clear from the visual examination that all the chromaticities are present on the fibers to a sufficient degree for conducting the analysis using (HPLC-DAD). Natural dyes compounds were indented based on the characteristic UV-Vis spectra of each compound. The extracted dyes were measured by HPLC-DAD and the absorption maxima were recorded for each extract. Table 1 and Figs. 3 and 4 show the obtained results. The obtained results were compared in different ways; first way by using the absorption maxima of the standards color compounds mentioned in the literature, and the second way, by using obtained data of the newly dyed woollen fabric with standard natural dyes from the Egyptian local market. [45- 46]

Table 1: Show classification of natural organic dyes according to Hofenkde Graaff (2004) [47]

Colour	Mordant dyes	Vat dyes	Direct dyes
Red	Madder		Henna
	Kermes		
	Cochineal		
	Lac dye		
	Brazilwood		
Yellow	Weld		Annatto
	Dyer's broom		Saffron
	Sawwort		Turmeric
	Young Fustic		
	Fustic		
	Persian berries		
Purple and Blue	Logwood	Woad	Indigo carmine
		Indigo	Orchil
		Tyrian purple	
Black	Gallnuts		
	Sumac		

Table 2: Examination results for historical wool samples dyed with natural dyes

Samples	Rt. Time (min)	Compound
	20.875	Laccaic acid

Sample 1	30. 387	Purpurin
	39. 072	Indirubin
	26 727	Alizarin
	22.552	munjistin
Sample 2	30.925	Indigotin
Sample 3	30.963	Indigotin
	47.459	Di bromoindigotin

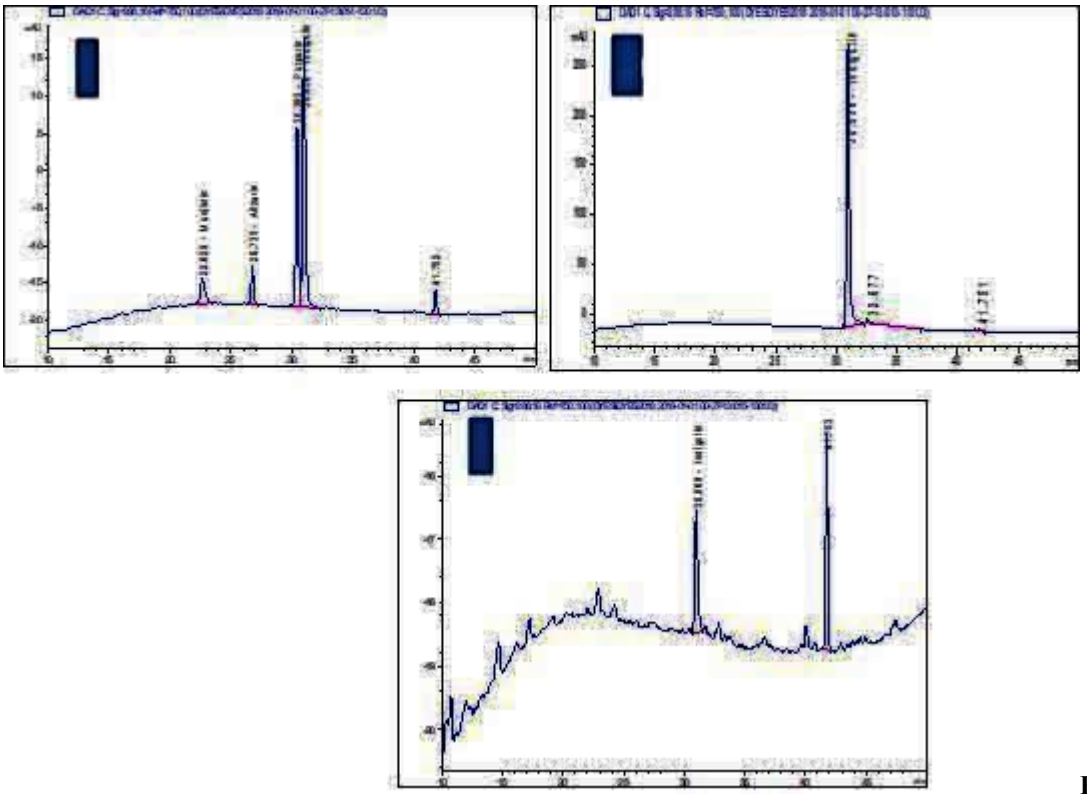

Fig. 3: Chromatograms of TFA extract of samples 1 (a) , samples 2(b) , and samples 3(c)

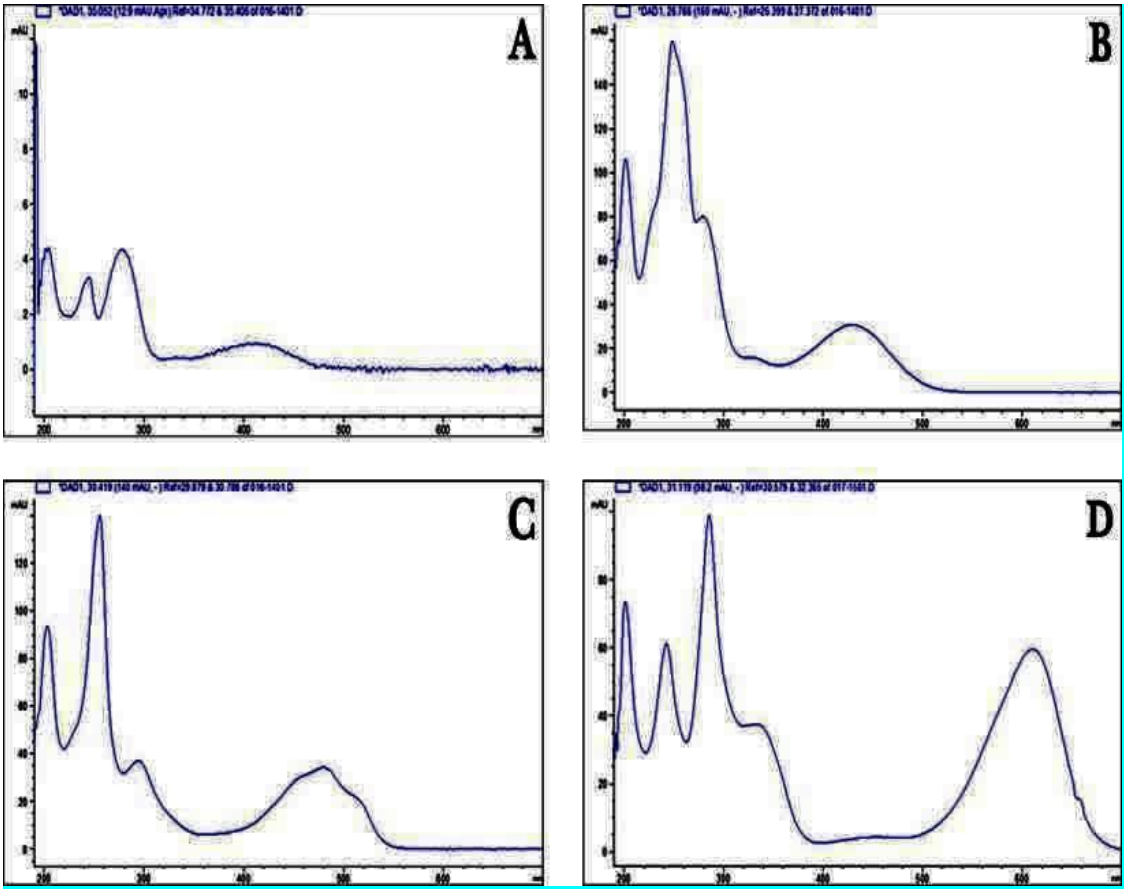

Fig. 4: UV-Vis absorption spectra for (A) Munjistin ,(B) Alizarin,(C)Puruprin ,(D) Indigotin

Table (3): The results of dyestuff analysis of investigated old samples

Sample Color	Detected compounds	Identified Dyes
Red	Alizarin –Purpurin - Munjistin	Madder dye
Green	Indigotin - Alizarin	(Indigo or woad) dye +Madder dye
Purple / blue	Indigotin – 6,6,Di bromo indigotin	Indigoid dye source + Tyrian purple

4.2.1 Sample 1 (Red Color)

It is evident from the results obtained from Figure No. 3 Figure No. 4, one can see the collected chromatogram maxima that appeared at 249, 279, and 429 nm, and this result shows that the compound is Alizarin. Looking at the other results, it is noticed that there are absorption maxima that appeared at 256, 295, and 480 that refer to Purpurin. The sample contains a mixture of madder dye. These results are in agreement with many other results, which indicate the use of madder as the main source for obtaining the red color. Madder was particularly famous for colouring historical textiles during the Coptic era, Where the weaver reached a great degree of sophistication and creativity in using local sources to produce

strong and comprehensive colours on the historical textiles at the time. [4, 23, 43- 44]

4.2.2 Sample 2 (Green Color)

These results from Fig 3 and 4 provide important information about the composite pigments that were used during the Coptic era to produce new hues. The results confirmed the presence of Alizarin, Puruprin, characteristic of madder dye, in addition to the presence of Indigotin, characteristic of blue indigo, as well as the presence of Lawsone, characteristic of henna dye. Where, the absorption maxima appear at 249, 280, and 430 nm which are characteristic of Alizarin. While absorption maxima appear at 255, 295, and 480 nm which are characteristic of Puruprin. On the other hand, absorption maxima that appear at 242, 285, 330, and 610 nm are characteristic of indigotin. Moreover, another peak found in sample 2 appeared at a retention time of 22.8 min, and maxima appeared at 251, 288, 440, and 487, which refers to the compound Lawsone compound of Henna dye. One can notice that this sample contains a mixture of madder, indigo, and Henna dye [45].

4.2.3 Sample 3 (Purple-Blue Color)

Identified colorant in the extract of the Purple and Blue threads in the historical wool textile are Indigotin – 6,6-Di bromo-indigotin fig (3C) and This confirms that the dyes used in the purple and blue threads are Indigoid dye source and Tyrian purple. the blue sample is known from the literature that indigotin dye was commonly used in the t period on Coptic textiles (47), UV-vis has appeared that three absorption maxima appear at 242, 285, 330, and 610 nm which are characteristic for Indigotin in a visual dark blue historic sample appeared at retention time 31.49 min, as fig. (4D) by comparison with literature

4.3 FTIR Spectroscopy

The use of the FTIR technique is one of the important techniques in the field of historical organism examination, and identification of functional groups, chemical composition, and materials used in the manufacture of organic historical objects. In addition, it is considered one of the non-destructive techniques, and it is carried out with precision, and the natural dyes and colors in historical textiles are identified by comparing the examination of unknown historical samples with other modern known and standard samples. This research has used this technique to confirm the results obtained by analyzing using (HPLC), and in order to provide some information as it appears in Figure No. 5.

Figure 5a presents the examination of the infrared diffraction pattern, providing information indicating that the red color is Lac dye. One can see that appeared peaks are primarily assigned as O–H in the plane and C=C aromatic ring stretching peaks at 1234-1222 cm^{-1} of lac dye [49] were observed. In addition, it was noticed that the C–H stretching appears in the range 2920–28521 cm^{-1}, on the other hand, the vibration band of OH groups appears at around 3268 cm^{-1}. The characteristic C=C aromatic ring stretching peak appears at 1321 cm^{-1}. According to the literature, these results confirm that the dye is a Lac dye.

The analysis using (FITR) also provides information indicating the presence of madder dye as a source of red berries in the historical object. FTIR-ATR analysis of sample No 1 shows characteristic fingerprint spectral features of C=C bond stretching, conjugated C=O groups, carbonyl groups,-OH groups in the region of 1100 cm^{-1} to 1600 cm^{-1}, which, according to the spectral database of Fig 5 , (A) are characteristic functional groups found in madder root.

The analysis using (FTIR) also provides information indicating the presence of mixture of madder dye and indigo dye as a source of green berries in the historical textile object. As shown in Fig 5B,

the spectrum of indigo is shown with a specific peak at 2920 cm^{-1} due to the N–H stretching, the band attributed to rocking vibrations of N–H groups is observed at about1230 cm^{-1}. A peak at 1630 cm−1 that is because of C=O stretching, Vibrations involving C–H rocking are recognized at1455, 1438 and 1230 cm^{-1}.On the other hand, Fig (5C), show the vibrations of five- and six-membered rings are identified at 1318, 1031, 877 the purple color is a mixture between the indigo pigment and 6, 6· dibromindigotin. The spectrum of indigo is shown with a specific peak at 2921cm^{-1} ,2852 cm^{-1} , 1628, 1527 cm-1,1417 cm^{-1} ,1318, 1229 cm^{-1}, 1168 cm^{-1} .

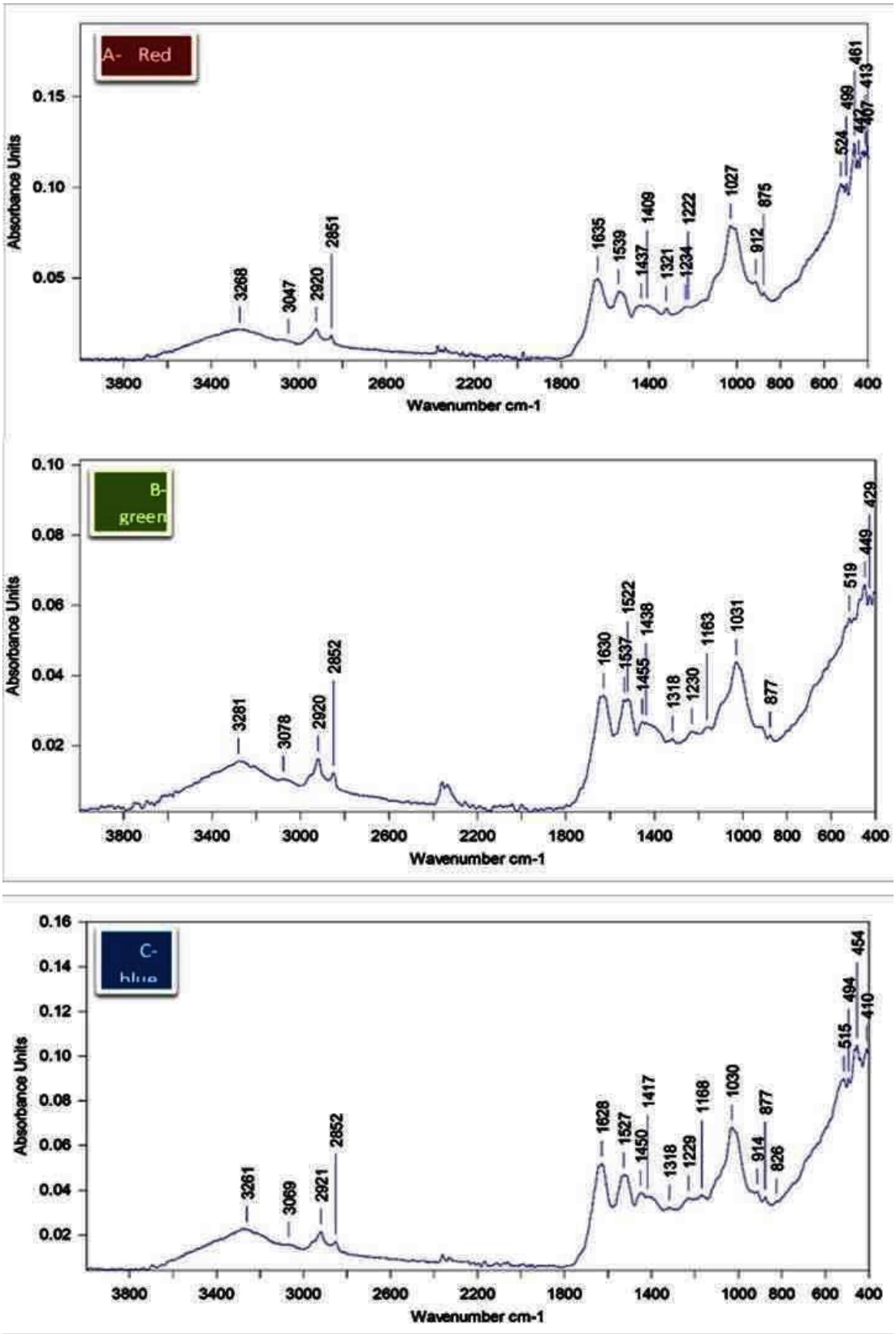

Fig 5: FTIR of Coptic madde dye of red wool historical textile (A), FTIR of Coptic madde dye of green wool historical textile (B), FTIR of Coptic Tyrian purple dye of purple wool historical textile (C},

Conclusion

Examinations and analyses are a very important stage in the preservation of cultural heritage. It is useful to identify the chemical composition of the historical object in the dating of historical objects, as well as to develop an appropriate treatment and restoration plan, in addition to choosing the appropriate restoration materials. The study indicated the possibility of combining different methods of examination to obtain information on historical objects. The results indicated that mixtures of organic dyes are used in dyeing these samples to produce different colours.

The results indicate that mixtures of organic dyes are used in dyeing these samples to produce different colours. The most dominantly identified colourants in samples collected from the Museum are laccaic acid, kermesic acid, munjistin and indigotin. The most dominantly identified dyestuffs are Lac dye (Kerria lacca, Kerr), Madder (Rubia) species, either Indigo dye (Indigofera species)or woad (Isatis tinctoria L.).

These results confirm the historical information in the Museum of in that the tested textile objects date back to the end of the 6th century. This conclusion is in agreement with the initial dating of samples according to the style of the decorations.

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