



# THE UNPUBLISHED COPTIC TEXTILES OF THE MONASTERY OF ST. JOHN THE THEOLOGIAN: PRELIMINARY RESULTS OF PREVIOUS ALTERATIONS AND SCIENTIFIC ANALYSIS

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## ABSTRACT

The monastery of St. John the Theologian in Patmos, which dates back to the 11th century, is today a major spiritual and artistic entity in the Mediterranean archaeological, ecclesiastical and cultural history. Since 1999, the monastery has been included in the UNESCO World Heritage list, which demonstrates its historical significance. The monastery preserves and holds a significant number of works of great archaeological, ethnographical and historical value which have not been studied systematically. In particular, the archaeological textiles, which were recently donated by Mr. Albert- Jean Antonelli and kept in the monastery, have not attracted the interest and special attention of the scientific community (historians, archaeologists, conservators) and the literature is scarce. The monastery keeps 84 Coptic textiles: (82 Coptic textile fragments, one large tunic and one large tapestry fragment) which date between the 4<sup>th</sup> and 7<sup>th</sup> centuries A.D. This paper will briefly present the unpublished Coptic textile collection focusing on the paradoxical ways of display methods with incompatible materials and the application of scientific techniques to identify the fibre structure and the dyes used, via FTIR, SEM, OM and SEM methods.

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**KEYWORDS:** Coptic textiles, St. John the Theologian, UNESCO, fibres, Patmos, Raman, FTIR, SEM, OM, preventive conservation

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## 1. INTRODUCTION

Several Coptic textile fragments or tunics are stored and/or exhibited in Museums in Greece, Europe and beyond. Egyptian monasteries were established by the Christian inhabitants of the Nile Valley, who were named as Coptic by the Arabs after the 7th century (Thomas, 2007).

The special environmental conditions (constant dry) and the burial customs allowed the preservation of these fabrics with their admirable decoration and their multicolour palette.

A small number of Coptic textile fragments are exhibited or stored in museums or private collections, such as the Coptic Museum of Cairo, the Egyptian Museum of Cairo, the Metropolitan Museum of New York, the Victoria & Albert Museum, the British Museum, the Petrie Museum and others. There are few museum collections in Greece that include in their collections Coptic textiles such as the Byzantine & Christian Museum of Athens, the Archaeological Museum of Athens, the Benaki Museum, the Museum of Greek Folk Art in Athens, the Paul & Alexandra Kanellopoulou in Athens, the Byzantine Museum of Thessaloniki and the V. Papantoniou Peloponnesian Folklore Foundation in Nafplio.

The majority of them have been preserved for storage, while there are few which are exhibited in museum showcases. Most of these items were purchased or donated to museum collections, and the interventions followed had a rational approach and lacking the conservation methodology. However, there are cases that the textiles or tunics are in the possession of private owners or/and come from trading activities and therefore are not preserved properly. These textiles usually undergo various insufficient treatments so that they appear preserved making it easier for the antique dealer to achieve a higher selling price.

The main aim of this work is to identify the state of preservation of the archaeological Coptic textile collection held at the Monastery of St. John of the Theologian in Patmos (World Heritage Monument, UNESCO) and to detect any previous alterations. Coptic textiles have not been preserved so far in any Eastern Orthodox Monastery. These works, which survived due to the dry climate in Egypt, are a unique testimony to the shape of the fabrics that is now lost. The monastery of St. John in Patmos is the only Orthodox Monastery in the entire Eastern Church with such a large number of Coptic textiles. The collection is comprised of eighty-four (84) Coptic textiles from the 4th to the 7th centuries A.D, and is one of the most comprehensive collections in

the Eastern Orthodox Christian Church. This paper will present the paradoxical methods of display causing damages to the collection with incompatible materials and techniques. In the case of this collection, fifteen (15) different methods were documented which have been applied unorthodoxically to the Coptic fragments placing the textiles into new frames, causing further damage.

A secondary aim of this study is to apply a range of analytical techniques in order to identify the dyes used for the decoration of the textiles.

Physicochemical methods are widely used nowadays in order to give answers to crucial archaeological, conservation and art historical questions. These analytical techniques can be applied on several cultural heritage artefacts both organic and inorganic and has proven to be a significant tool in Conservation Science. Such techniques can be distinguished in broad categories depending on the information they provide e.g. material characterization and imaging techniques.

Archaeological textile is a material which due to its nature is very fragile and therefore is very scarce in the archaeological record, especially in Greece due to the Mediterranean climate (Margariti *et al.*, 2012). Researchers have applied several techniques mainly Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Computed Tomography (CT) and others (Alexiou *et al.*, 2017) in order to identify the manufacturing technique (weaving, fibres), shape, etc.

On the other hand, conservation of Coptic textiles is an area ill explored and the bibliography is limited to few publications (Landi and Hall, 1979; Marko and Dobbie, 1982; Hillyer, 1984; Enas Abo El Enen Amin, 2017, 2018). In addition, the scientific study of Coptic textiles found in Greece is limited and scarce in the literature while the published studies are fragmentary (Georga-Tsourinaki, 1989; Tsourinaki, 2002; Karapanagiotis *et al.*, 2011).

Recent advancements in state of the art physicochemical methods allow results of better quality in a non-destructive manner or by collecting extremely small size samples. Sampling in such studies is important to follow ethical conservation principles, and small samples preferably are taken from already damaged areas.

The application of the physicochemical techniques offers the basis for decision making on how to best preserve these rare and fragile objects. In addition, fills the gap in the history / archaeology of technology of Coptic textiles.

## 2. MATERIALS AND METHODS

In the present study a range of analytical techniques was used such as Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Raman spectroscopy and Fourier Transform Infra-Red Spectroscopy (FTIR) for the complete identification of the fibres and the dyes in five Coptic textiles. In particular, Optical Microscopy was used to identify the morphological characteristics of the fibres since it provides imaging of the specific fibres used in the textiles and therefore information regarding the weaving, embroidery etc. Scanning Electron Microscopy, operating with both secondary and backscattered electrons, provided high magnification of the fibres in cases where needed and assisted the Optical Microscopy study. Raman and FTIR Spectroscopy were used mainly to identify the chemical nature of the organic and inorganic dyes used. Additionally, in selected samples Surface Enchased Raman Spectroscopy (SERS) analysis was applied. It is worth noting that prior to the study of the historical samples, various standard reference dyes were analysed by FTIR and Raman techniques to facilitate the identification process. Also, the SERS technique proved to be effective in interpreting the spectra by reducing the luminescence phenomenon. A more invasive approach can be achieved in the future by using chromatographic techniques such as High-Performance Liquid Chromatography (HPLC) which offers full identification of the organic dyes used in textiles.

A total of fourteen (14) fibre samples were analysed. The samples are coming from four fragments of Coptic textiles and from the tunic of the collection from already damaged areas.

Optical Microscopy was performed using a stereomicroscope (Leica® MZ - 6) at the laboratories of the University Ecclesiastical Academy of Thessaloniki (U.E.A.TH.) with a digital image acquisition and analysis system. Furthermore, a Zeiss® Axioscope 40 polarized microscope equipped with a full white reflected light system and a 100 W ultraviolet mercury source was used. The microscope also includes a digital image capture and analysis system with a Canon® Power Shot A650IS camera.

A Jeol® JSM-6510 Scanning Electron Microscope coupled with an Oxford Energy Dispersive X-ray spectrometer (SEM-EDX) was used in this study. The SEM operated at 30 kV and the working distance was set at 10mm. The SEM images were obtained under electron beam power conditions at 10 kV and spot size at 5 nm. There was no sample preparation for the fibres under study.

A Renishaw® Raman device, equipped with a microscope and a CCD detector, was used in the labor-

atories of U.E.A.TH. As a source of excitation, a diode laser with a radiant emission wavelength of  $\lambda = 785\text{nm}$  was used. The beam size of the laser is of the order of  $\sim 2 \mu\text{m}$ . The power density on the surface of the sample was  $\sim 0.5\text{mW} / \mu\text{m}^2$  and the spectral resolution was  $\sim 4 \text{cm}^{-1}$ . Alignment and calibration of the spectrometer, before and after each measurement, was achieved by using a crystalline silica (Si) wafer.

In order to optimize the results and to avoid fluorescence during the measurements, SERS (Surface Enchased Raman Spectroscopy) technique and Renishaw solid state substrates (Klarite), were used.

Finally, the micro-FTIR spectroscopy analyses were conducted at the laboratories of the Univ. Eccl. Acad. Thessaloniki (UEATH) so as to provide enhanced information. In particular, a Perkin-Elmer® FT-IR spectrometer operating at the medium and near infrared range, was used. The spectra were collected with a spectral resolution of  $4\text{cm}^{-1}$  in the spectral range of  $4000\text{-}750\text{cm}^{-1}$  and 256 scans.

## 3. DOCUMENTATION OF PREVIOUS ALTERATIONS

Detailed documentation and recording at a micro/ macro-scale has been undertaken in a primary stage, using optical and USB microscopy. In particular, various information regarding the decoration, condition (stains, tears) and past conservation treatments on the textiles were obtained. The weaving patterns, the embroidery technique and any additions to the materials under study from past conservation efforts were identified and documented using micro-photography.

According to the observations fifteen (15) previous alterations have been documented causing further damage to the archaeological textiles such as:

1. The fabric surface glued on an acidic paper surface to four or five different points with synthetic glue and the perimeter of the fabric surface is further secured by the use of metal elements (staples), (Fig. 1a, b).
2. The fabric structure is secured with adhesives at four on an acidic paper surface with no use of metal elements.
3. The fabric surface is secured on an acidic paper surface only with the use of metal elements (staples), (Fig. 2a).
4. The fabric structure is secured on a fabric with oxidized metal elements (pins), (Fig. 2b).
5. Large areas of losses and loose fibres have been secured with sewing machine on a new fabric (Fig. 3a).
6. The fabric was stitched on a new textile support that had been laboratory aged (Fig. 3b).

7. The fabric structure is secured with sewing machine on an acidic paper board (Fig. 4a).

8. The fabric structure is secured with sewing machine on an acidic paper board combined with adhesives (Fig. 4b).

9. The textiles are glued with synthetic adhesive to a newer fabric.

10. Splinters are joined together with quick seam and glued with adhesive on cardboard.

11. The textile fragments are glued with double sided adhesive tape (Fig.5a)

12. Combination of double-sided tape and adhesive.

13. Loss of material restored on cardboard.

14. Fabrics which, during their placement on the frames, are attached on other fabrics which do not belong together.

15. The main face of the fabric is glued upside down on cardboard with adhesives (Fig. 5b).

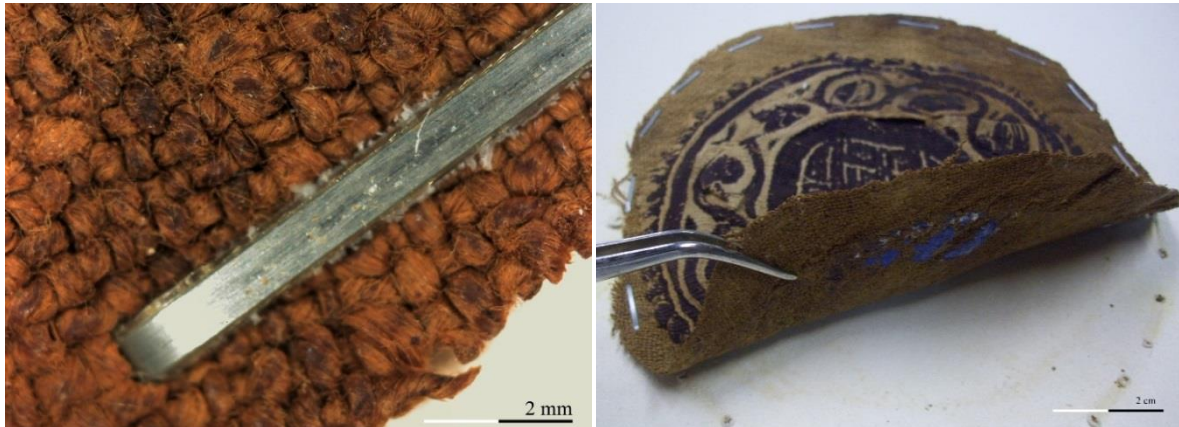


Figure 1. a. Detail of the metal stapler; b. Detail during the removal from the paper board.



Figure 2. a. Detail from the oxidized metal stapler, perimetrical on the fabric structure; b. Detail of the oxidized nail, causing further splits and losses.



Figure 3. a. Detail from the previous treatments using sewing machine to stabilize the fragment on new fabrics; b. The fabric is stitched on a new textile support that had been laboratory aged.



Figure 4. a. The fabric structure is secured with sewing machine on an acidic paper board. b. The fabric structure is secured with sewing machine on an acidic paper board combined with adhesives.

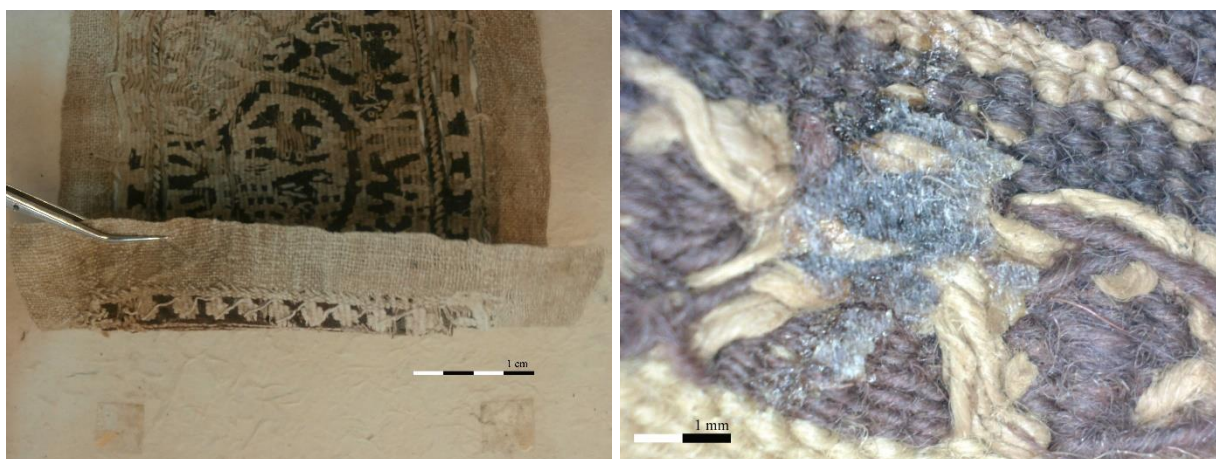


Figure 5. a. The textile fragments are glued with double sided adhesive tape; b. Detail using USB microscope showing the adhesive stain on the fabric structure.

#### 4. RESULTS - PHYSICO-CHEMICAL ANALYSIS

According to the detailed Optical Microscopy study (Fig. 6) and especially with the help of Scanning Electron Microscopy (Fig. 7) two different fibre categories were identified in the total of fourteen (14) fibre samples: two (2) were identified as linen (Ferreiro F. et al., 2002) while the remaining twelve (12) were made from wool (Odlyha et al., 2007).

Additionally, the  $\mu$ FTIR spectra of the samples S1a, S1b, S1c, S1d, S5b, S5c, S6a, S6b, S7a, S7b, S10a and S10b indicated that the fibres have a protein origin since the  $1650\text{ cm}^{-1}$  peak represents amide I and the  $1545\text{ cm}^{-1}$  amide II of the wool fibre. Furthermore, the peaks of cysteine, basic amino acid of the woollen fibre, can be distinguished which show absorption in the  $1121\text{ cm}^{-1}$ ,  $1071\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$  (Odlyha et al., 2007). Finally, the broad peak at  $3400\text{ cm}^{-1}$  is due to the absorption of water molecules in particular hydroxyls (Zhang and Wyeth, 2010).

The  $\mu$ FTIR spectra of the samples S5a and 10c revealed that the fibres have a cellulite origin since the vibration modes at  $4000\text{-}2995\text{ cm}^{-1}$ ,  $2900\text{ cm}^{-1}$ ,  $1430\text{ cm}^{-1}$ ,  $1375\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  are characteristic for the kind of the form of cellulose (crystalline or amorphous). More specifically, the vibration at  $1430\text{ cm}^{-1}$  corresponds to the crystalline phase, while the vibration at  $900\text{ cm}^{-1}$  corresponds to the amorphous phase. The broad peak at  $900\text{ cm}^{-1}$  represents the higher percentage in the distorted structure of cellulose and the shift of the  $1430\text{ cm}^{-1}$  peak in lower frequencies expresses the degradation of cellulose (Kavkler et al., 2011).

The  $\mu$ Raman spectra of samples S1b, S5b and S5c showed characteristic peaks which correspond to fibres of protein nature and in particular to wool fibres (Carter et al., 1994; Pozzi, 2011). The peak at  $1100\text{ cm}^{-1}$  of the Raman spectra of the S10c fibre sample expresses the asymmetrical vibration of the glycoside bond of linen (Jahn et al., 2001). Wool and linen fibres is common used in the history of Coptic

textiles taking into consideration the literature (Hofenk de Graaff, 2004).

Furthermore, using the spectroscopic analytical techniques ( $\mu$ FTIR,  $\mu$ Raman and SERS) four different dyes were identified and were used in the majority of the textiles (Table 1): madder (2/14) (Fig. 8a), indigo (4/14) (Fig. 8b), granule (kermes) (2/14) (Fig. 8c) and weld (1/14) (Fig. 8d). The remaining five samples (5/14) were undyed and therefore did not exhibit any particular peaks in the corresponding spectra. The identification of the fibres was made by comparing the spectra of the samples under study with reference spectra of the specific dyes. As it can be seen at the corresponding figures (Fig. 8a-d) there is good agreement between the respective spectra.

The identified natural dyestuffs have been used since antiquity and are common for this type of textiles taking into consideration other published studies (Storey, 1978; Hofenk de Graaff, 2004; Abdel-Kareem *et al.*, 2010, 2011; Degani *et al.*, 2015; Mantzouris *et al.*, 2016). The dyestuffs found in these textiles are the madder, kermes, indigo and weld. Madder (*Rubia tinctorum L.*) is considered one of the oldest and most important natural dyes, described by Herodotus (5<sup>th</sup> c. B.C), Dioskouridis (1st c. A.D.) and

other philosophers and doctors in antiquity. It has also been used in Asia Minor and in Greece since the prehistoric age (Christophoridou *et al.*, 2006). Also in the 2<sup>nd</sup> and 3<sup>rd</sup> c. A.D madder and indigo was found in Roman graves, replacing the imperial purple (*purpura*), (Abrahart, 1977; Storey, 1978; Hofenk de Graaff, 2004). Madder has also been used to dye mainly wool fibres, and has been identified on archaeological textiles in Egypt (Hofenk de Graaff, 2004). Furthermore, kermes (*Kermes vermilio Planchon*) is one of the oldest red dyestuff in the world, mentioned also in the Old Testament, but also by the Greeks and Romans (Hofenk de Graaff, 2004). It is reported that kermes, as well as the purple and other luxurious materials, were used to dye textiles used by the royal families (Karapanagiotis *et al.*, 2012). Indigo dye (*Indigofera tinctoria L.*) belongs also to the oldest and most appreciated dyestuffs in the world (Storey, 1978; Balfour-Paul, 1998; Hofenk de Graaff, 2004). Finally, weld dyestuff (*Reseda luteola L.*) is well known for its usage during the Apostolic Age (Forbes, 1964; Hofenk de Graaff, 2004) and it has been extensively used in the tapestry workshops.

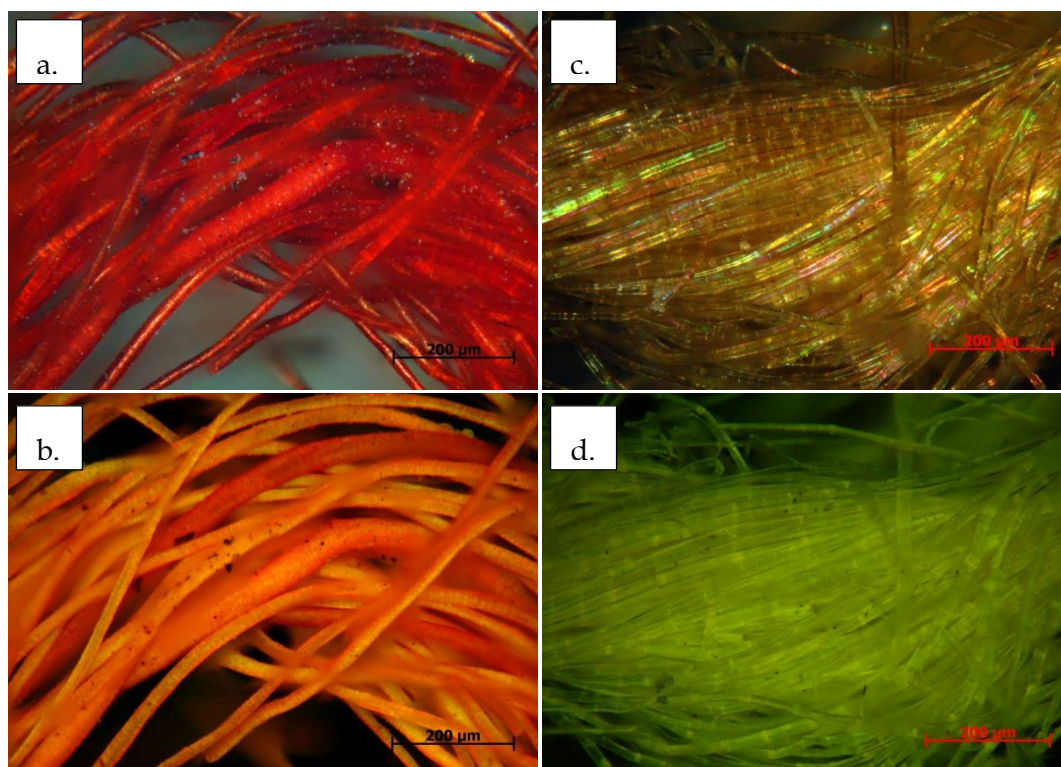


Figure 6. Sample S1a under the polarized optical microscope in a. visible and b. ultraviolet light. Magnification 100x. Sample S5a under the polarized optical microscope in c. visible and d. ultraviolet light. Magnification 100x. The main characteristics of the undyed linen fibre can be distinguished (Goodway, 1987).

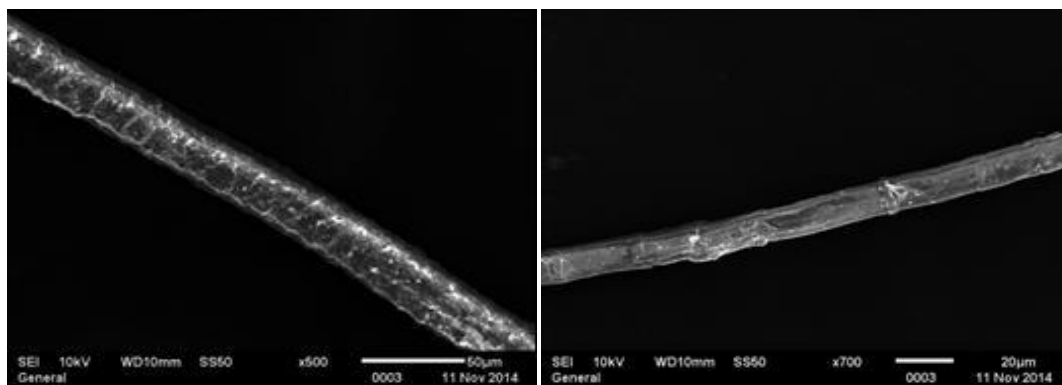
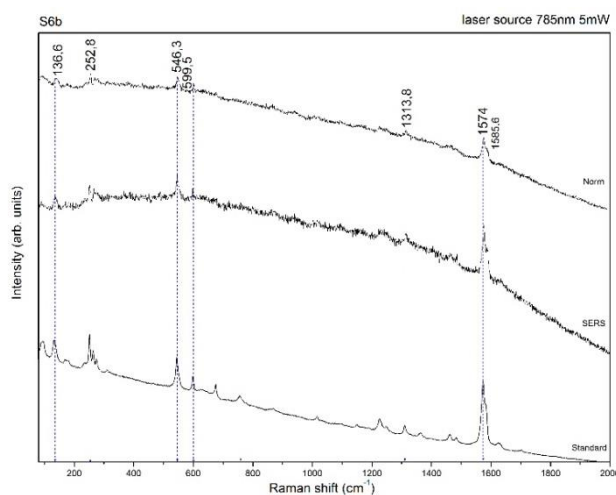
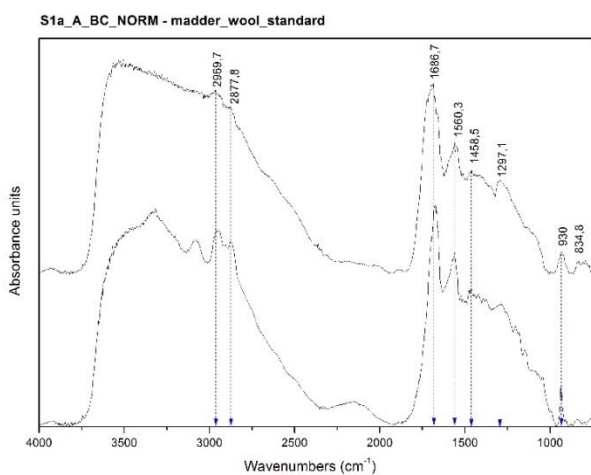
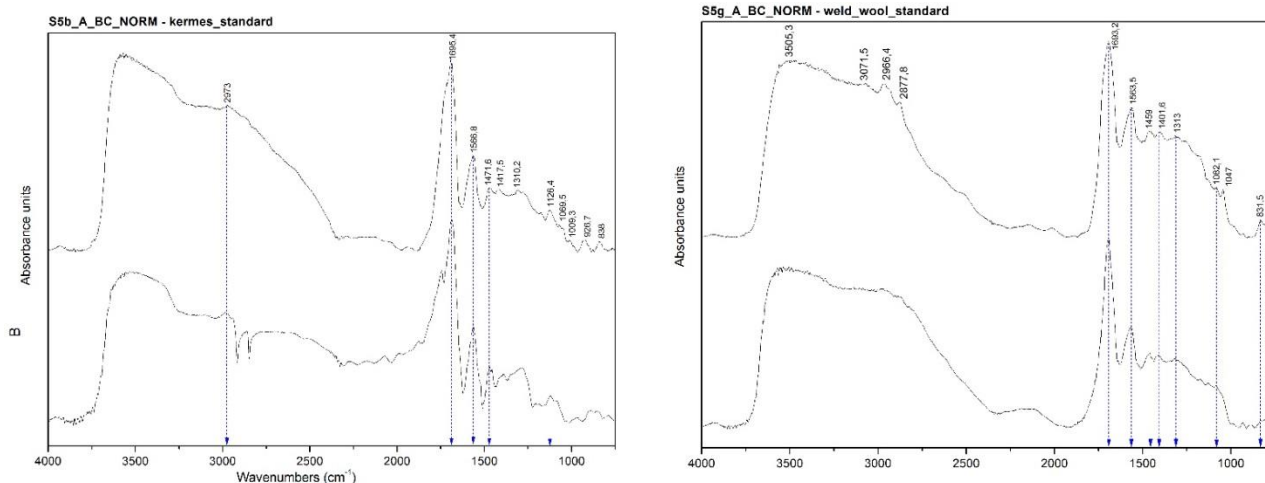


Figure 7. Left a) The characteristics of the wool fibre S1a can be observed (various scales on the surface) and b) The longitudinal form of the fibre S5a is presented as straight bundles with small lines parallel to the fibre axis, vertical bars in the X-form are also identified characterize the fibre as linen (Goodway, 1987).

Table 1. Final results from the Coptic textiles fibres.

Samples	Fibre (analytical technique)	Dye (analytical technique)	Colour
S1a	Wool (OM, SEM, FTIR)	Madder (FTIR)	Red
S1b	Wool (OM, SEM, FTIR, SERS)	-	-
S1c	Wool (OM, SEM, FTIR)	Indigo (RAMAN, SERS)	Violet
S1d	Wool (OM, SEM, FTIR)	-	-
S5a	Linen (OM, SEM, FTIR)	Undyed (OM, FTIR)	-
S5b	Wool (OM, SEM, FTIR, Raman, SERS)	Kermes (FTIR)	Red
S5c	Wool (OM, SEM, FTIR, Raman, SERS)	Undyed (OM, FTIR)	-
S6a	Wool (OM, SEM, FTIR)	Weld (FTIR)	
S6b	Blue fibre: wool (OM, SEM, FTIR)	Indigo (RAMAN, SERS)	
	Red fibre: wool (OM, SEM, FTIR)		
S7a	Wool (OM, SEM, FTIR)	Madder (FTIR)	
S7b	Blue fibre: wool (OM, SEM, FTIR)	Indigo (RAMAN, SERS)	
	Red fibre: wool (OM, SEM, FTIR)		
S10a	Wool (OM, SEM, FTIR)	Kermes (FTIR)	
S10b	Wool (OM, SEM, FTIR)	Indigo (RAMAN, SERS)	
S10c	Linen (OM, SEM, FTIR, Raman, SERS)	Undyed (OM, FTIR)	





**Figure 8.** a. The upper left  $\mu$ FTIR spectrum of sample S1a shows that the fiber has a protein origin and in particular is woollen (Odlyha *et al.*, 2007). In addition, madder was identified when the S1a spectrum is compared to a reference sample (lower spectrum) (Montazer and Paeninzadeh, 2004); b. The upper right Raman spectrum of sample S6b was optimized using the SERS technique and we were able to identify the indigo dye using a reference sample (lower spectrum in the same graph); c. On the lower left  $\mu$ FTIR spectrum of sample S5b kermes was identified when the S5b spectrum is compared to a reference sample (lower spectrum) (Lang *et al.*, 2002); d. On the lower right  $\mu$ FTIR spectrum of sample S5c weld was identified when the S5c spectrum is compared to a reference sample (lower spectrum) (Keyong Xu *et al.* 2009).

## 5. CONCLUSIONS

This study presents for the first time to the scientific community the so important collection of Coptic textiles of St. John monastery in Patmos providing valuable information regarding its state of preservation through the systematic documentation of the previous un-orthodox display methods. According to the detailed research, using various microscopic methods, we were able to identify and document previous alterations such as inappropriate adhesives, staples, unorthodox alterations etc., that will cause eventually further damage to the Coptic textiles. Therefore, it is of great importance that immediate action/treatment should be applied to remove the previous alterations. Furthermore, there is need for proper storage and display cases for these materials according to the current conservation and museological practices.

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Furthermore, detailed documentation of the deterioration agents and recording at a macro-scale was undertaken using high-resolution stereomicroscopic and microscopic (USB) methods providing information regarding the decoration, weaving patterns, condition (stains, tears) and past conservation treatments on the textiles which are all recorded.

Moreover, through the application of three different analytical techniques ( $\mu$ FTIR,  $\mu$ Raman and SARS) we were able to identify the dyes used on these textiles. In particular, we identified madder, indigo, granule (kermes) and weld which are common for this type of textiles. Finally, through the application of SARS technique we managed to avoid the fluorescence phenomenon and enhance the Raman spectra so as to make the particular peaks more visible and more identifiable.



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## APPENDIX

Accession number	Image	Description	Overall Dimensions	Fibres	Dyes
S.1		Basket surrounded by diamonds 5 <sup>th</sup> -6 <sup>th</sup> c. AD.	8.8 x 11.2 cm	Wool	Madder and indigo
S.5		Fragment of a textile representing a hunter over a red background. 5 <sup>th</sup> -6 <sup>th</sup> c. AD.	4.5 x 10.4 cm	Wool and linen	Kermes
S.6		Hunter. 5 <sup>th</sup> -6 <sup>th</sup> c. AD.	9.5 x 10.1 cm	Wool	Weld and indigo
S.7		Fragment of a tunic decorated with flower and human figures. 5 <sup>th</sup> -6 <sup>th</sup> c. AD.	31 x 14 cm	Wool	Madder and indigo
S.10		Fragment of a tunic. 5 <sup>th</sup> -6 <sup>th</sup> c. AD.	7.4 x 23.1 cm	Wool and linen	Kermes and indigo

