HELLENIC REPUBLIC
UNIVERSITY OF IOANNINA
DEPARTMENT OF CHEMISTRY
SECTION OF INORGANIC AND ANALYTICAL CHEMISTRY

Physical Chemical Studies of Pigments of Archaeological Decorated Textiles and the Best Methods of Restoration and Conservation them

HANAA AHMED ABD El-HADY ELGAOUDY
Restorer at Egyptian Museum, Cairo, Egypt

PhD Thesis

Under Supervision
Prof Dr. Dimitra Kovala-Demertzi

IOANNINA 2013

Date of Application of Mrs. Hanaa Ahmed Abd El-Hady Elgaoudy: 2- 11- 2007.

Definition of Three Members of Supervision Committee from Γ.Σ.Ε.Σ.: 697 ^{A}/ 21-3 -008.

Three Members of Supervision Committee:

Supervisor:

Prof. Dimitra Kovala-Demertzi (Department of Inorganic and Analytical Chemistry – U.O. I

Members:

1- Prof. Mavroudis Demertzis (Department of Inorganic and Analytical Chemistry – U.O. I)

2-Assistant Prof. Varella Evangelia (Department of Organic Chemistry – A.U.Th)

Date of Define the Subject: 21- 3- 2008.

Subject: "Physical Chemical Studies of Pigments of Archaeological Decorated Textiles and the Best Methods of Restoration and Conservation them".

Definition of Seven Members Examination Committee from Γ.Σ.Ε.Σ.: 865^{A} /5 - 4 - 2013

1- Prof. Dimitra Kovala-Demertzi (supervisor)

2-Prof. Mavroudis Demertzis (member)

3-Assistant Prof. Varella Evangelia (member)

4-Assistant Prof. Nikolaos Kourkoumelis (Department of Medical physics, Ioannina University) (member)

5-Prof. Ioannis Plakatouras (Department of Chemistry, Ioannina University) (member)

6-Lecturer Dr. Emmanoul Manos (Department of Chemistry, Ioannina University) (member)

7- Assistant Prof. Konstantinos Ioannides (Department of Physics, Ioannina University) (member)

Approval of PH.D Dissertation with grade "Excellent" in 3 - 10 -2013.

President of Chemistry Department	**Secretary of Chemistry Department**
Prof. Tsikaris Vasileios	**Eleni Adamantiou**

ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ
ΣΧΟΛΗ ΘΕΤΙΚΩΝ ΕΠΙΣΤΗΜΩΝ
ΤΜΗΜΑ ΧΗΜΕΙΑΣ

Προς
το Τμήμα Χημείας
του Πανεπιστημίου Ιωαννίνων

Θέμα: << Απόφαση επταμελούς εξεταστικής επιτροπής ενώπιον της οποίας η **Hanaa Ahamed Abd El-Hady ElGaoudy** υποστήριξε τη διδακτορική της διατριβή>>

Σήμερα 03/10/13 και ώρα 12:00π.μ. έγινε δημόσια παρουσίαση της διδακτορικής διατριβής με θέμα: <<Physicalchemical studies of pigments of archaeological decorated textiles and the best methods of restoration and conservation them>>, από την υποψήφια διδάκτορα **Hanaa Ahamed Abd El-Hady ElGaoudy.** Η παρουσίαση έλαβε χώρα στην αίθουσα Φ2-145 του Τμήματος Χημείας , Πανεπιστημίου Ιωαννίνων , ενώπιον της κατά τον νόμο επταμελούς εξεταστικής επιτροπής.

Η **Hanna Ahmed Abd El-Hady Ahmed** ανέπτυξε επί μία ώρα τα κυριότερα αποτελέσματα της διατριβής της και στη συνέχεια απάντησε σε σειρά ερωτημάτων της εξεταστικής επιτροπής και του ακροατηρίου. Κατόπιν αποχώρησε η υποψήφια και το ακροατήριο και ακολούθησε σύσκεψη μεταξύ των μελών της εξεταστικής επιτροπής. Η επιτροπή έκρινε ότι η Διατριβή είναι πρωτότυπη και συμβάλλει στην πρόοδο της επιστήμης. Προχώρησε δε στην έγκριση αυτής με βαθμό <<Άριστα>> και αποφάσισε την απονομή του Τίτλου της Διδάκτορος στην **Hanaa Ahamed Abd El-Hady ElGaoudy** από το τμήμα Χημείας του Πανεπιστημίου Ιωαννίνων.

Τα μέλη της εξεταστικής επιτροπής

Δ. Κόβαλα-Δεμερτζή, Επιβλέπουσα Καθηγήτρια

Μ. Δεμερτζής, Μέλος της Τριμελούς Επιτροπής

Ε. Βαρέλα, Μέλος της Τριμελούς Επιτροπής, Επικ. Καθηγήτρια Τμήματος Χημείας Α.Π.Θ.

Ι. Πλακατούρας, Καθηγητής Τμήματος Χημείας Π.Ι.

Ν. Κουρκουμέλης, Επικ. Καθηγητής Τμήματος Ιατρικής Π.Ι.

Κ. Ιωαννίδης, Επικ. Καθηγητής Τμήματος Φυσικής Π.Ι.

Ε. Μάνος, Λέκτορας Τμήματος Χημείας Π.Ι.

HANAA AHMED A.H. ELGAOUDY

« Physical chemical studies of pigments of archaeological decorated textiles and the best methods of restoration and conservation them»

ISBN

I would like to dedicate this thesis

To

The spirit of my Father

My Greatest Mother

My Lovely Husband and sweet Kids

Dearest Brother and warmest Sisters

For their love, patience and support

Acknowledgements

I would like to take the opportunity to thank the people that have helped me during my postgraduate studies at the University of Ioannina. This Thesis would not have been possible without the help, guidance and supervision of my supervisor Professor Dimitra Kovala-Demertzi. I would like to thank her for her trust, her interest in the subject, for giving me the opportunity to work in her Lab, to develop this work and for her support and guidance during these years which made working in her lab a wonderful learning experience and easy. I will never forget. Also she has been a dedicated and gave me unlimited support, and she was a patient guide throughout this process.

Moreover, I am extremely thankful to Professor Mavroudis Demertzis and Professor Varella Evangelia for their interest and support in my work and for serving as members of the 3-member advisory committee. In particular, I am very much thankful to prof. Varella Evangelia for providing me with natural dyes for my research work; also she has helped and given me the opportunity to prepare the dyed samples in her Lab and for fruitful scientific discussions.

Throughout these years in Ioannina University, I should to thank and express my appreciation to all the people that I had met during my Ph.D. for their cooperation, pleasant company, conversations and help, also, for their attention and their valuable advices, My extended thanks to Prof. Nikos Kourkoumelis for his advices, scientific discussions, helping me in XRD analysis and for accepting to be one of the examination committee.

I must extend special thanks to Dr. Christina Papachristodoulou for her help in the (XRF) and XRD analysis.

I would like to thank the examination committee, Prof. Ioannis Plakatouras, Prof. Konstantinos Ioannides and Dr. Emmanoul Manos for their interest in the topic of the thesis and accepting to be the examination committee.

I would like to thank Anastasia Pournara for SEM images obtained on an electron microscope funded by the Network of Research Supporting Laboratories of the University of Ioannina. We also thank the Ring of Laboratory Units and Centers of the University of Ioannina for the FTIR, SEM, XRF and XRD measurements.

I am grateful to my colleagues, Malgorzata Staninska, Alexandra Primikiri and Stavroula Anastasopoulou for receiving me as a new graduate student in the Department. I have enjoyed a lot interacting with them and their companies.

It’s my immense pleasure to thank the Department of Chemistry, University of Ioannina where I have spent my four years for my doctoral studies.

I am grateful to the Greek State Scholarship Foundation (IKY) for a 4-years fellowship, for giving me the opportunity to complete my PhD study in Greece and financial support. Also, special thank to the staff in the section of foreigners for their help and the facilities they had offered.

Outside the realm of chemistry, I would like to acknowledge the support and encouragement of my father, mother, my brother and sisters, my uncles and all my relatives. I am truly fortunate to have their blessing and good wishes. Their support and encouragement are the strongest motivation for me to reach this accomplishment.

Especial thanks go to my dear husband, Tariq, for his continuous firm emotional supports and encouragement in all respects and my darling kids Al-Hasan and Kariema.

ELGaoudy Hanaa Ahmed
Ioannina, Greece, 2013

Table of Contents

Figures' index

Tables' index

ABSTRACT

Archaeologists in Egypt discovered ancient colored textiles in great quantities in comparison with the analogous uncolored ones. Furthermore, the latter are far more deteriorated. Most research investigations into archaeological linen have been concerned with manufacture, restoration, and conservation but little information is available about the properties of the fibers and particularly their chemical and physical properties after dyeing with natural dyes or painted with inorganic pigments. The main aim of this study is to evaluate the physicochemical properties of Egyptian linen textiles coloring with a variety of pigments and natural dyes used in ancient times after thermally aged to get linen samples which are similar as possible to the ancient linen textiles. The evaluations were based on Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-Ray Diffraction, Tensile strength and Elongation measurements. Results showed that beyond cosmetic reasons, colored textiles did indeed play a role as protecting agents affecting strength and reducing thermal deterioration. Specifically, in the molecular level, pigments and natural dyes under study seem to interact to cellulose and lignin compounds of the aged linen while in the macroscopic level tensile and elongation parameters are altered. Electron microscopy confirms that pigment particles are deposited on and between the fibers surfaces, while dye molecules are small enough to permeate the fibres with colour.

Moreover, this work is also focused on testing and analysis of some Archaeological samples from different places and periods of ancient Egypt to identify the pigments, dyes and binding media in order to understand the painting and dyeing techniques used in their decoration and to establish the degree of damage of the ancient fibres. Scientific analytical techniques have been employed for this purpose, such as FTIR, SEM, XRD and XRF. The results confirmed that all archaeological fibre textiles are made of linen and the blue dye of sample (N. R60-2) may be indigo, the dark red dye of sample (N. S-58) is cochineal dye and the black colour of sample (N. Z-57) is black charcoal. Scanning electron microscopy result shows that the fibres are severely damaged, consistent with loss of scale structure of linen fibre in according with XRD and FTIR results. XRD, XRF and FTIR results of ancient inorganic pigments confirmed that the red pigment is hematite, the yellow one is natrojarosite and the light green pigment is mixture of Egyptian blue, goethite and calcite.

The present work comprises of seven (7) chapters.

Chapter.1. Dealing with the theoretical background about the importance of archaeological textile materials and the linen fibers which were the most important fibers in ancient times, their chemical and physical properties. In addition the main deterioration factors of the cellulose fibers and methods of restoration and conservation of archaeological textiles.

Chapter.2. Dealing with distinguishing between Dyeing and Painting process, Natural dyes, their characterization, physical and chemical properties, the main classes of natural dyes according to their colours and also according to their methods of application.

Chapter.3. Dealing with the principal pigments which used in ancient times and their physical and chemical properties.

Chapter.4. Dealing with the experimental work, materials, preparation of tested dyed and painted samples. In this work we prepared some laboratory new painted and dyed linen samples. Accelerated thermal degradation at a constant temperature of 140°C in an electronic oven for 72 h was carried out to produce of an artificially aged model of linen fabrics similar as possible to the archaeological ones, taking into account that the thermal degradation increases with increasing temperature and the duration of ageing textiles. Furthermore, this chapter dealing with the scientific techniques used in the analysis of tested painted, dyed linen fibres and archaeological samples, such as Scanning Electron Microscopy (SEM) equipped with an EDS microanalysis detector, X-Ray Powder Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Tensile strength and elongation measurements and X-Ray Fluorescence (XRF).

Chapter.5-6. Dealing with the results and discussion of the previous scientific techniques which used in the analysis of experimental painted and dyed linen samples after thermal ageing (TA).

Chapter.7. Dealing with testing and analysis of some archaeological samples. In this part we studied five samples of archaeological textile fibers from different places and periods of ancient Egypt and also three inorganic pigments from tomb at al-Mina. The study focused on the identification of pigments, dyes, and binding media in order to understand the painting and dyeing techniques used in their decoration. The main aim in evaluating the historic textiles was to identify the fibers, to establish their degree of damage. The analytical techniques have been employed for this purpose, were Scanning Electron Microscopy

(SEM) equipped with an EDS microanalysis detector, X-Ray Powder Diffraction (XRD), X-Ray Fluorescence (XRF) and Fourier Transform Infrared Spectroscopy (FTIR). In addition the end of this part includes the discussion of the results.

ΠΕΡΙΛΗΨΗ

Οι αρχαιολόγοι στην Αίγυπτο έχουν ανακαλύψει αρχαία βαμμένα υφάσματα σε σημαντικές ποσότητες συγκριτικά με τα αντίστοιχα άβαφτα. Επί πλέον, τα τελευταία είναι πολύ πιο υποβαθμισμένα. Οι πιο πολλές ερευνητικές προσπάθειες σχετικά το αρχαιολογικό λινό έχουν ασχοληθεί με την παρασκευή, την αποθήκευση και την συντήρηση, αλλά λίγες πληροφορίες είναι διαθέσιμες σχετικά με τις ιδιότητες των ινών και ιδιαιτέρως τις χημικές και φυσικές τους ιδιότητες μετά το βάψιμο με φυσικές βαφές ή με ανόργανες χρωστικές ουσίες. Σκοπός της παρούσας μελέτης είναι να αξιολογήσει τις φυσικοχημικές ιδιότητες των Αιγυπτιακών λινών υφασμάτων, βαμμένων με ποικίλες ανόργανες χρωστικές ουσίες και φυσικές βαφές οι οποίες χρησιμοποιούνταν στην αρχαιότητα, μετά από θερμική γήρανση των λινών ώστε να είναι κατά το δυνατόν παρόμοια με τα αρχαία λινά υφάσματα. Οι αξιολογήσεις βασίζονται στο φασματοφωτόμετρο μετασχηματισμών Fourier (FTIR), στο ηλεκτρονικό μικροσκόπιο σάρωσης (SEM), στην περίθλαση ακτινών XRD και την αντοχή σε εφελκυσμό, και σε μετρήσεις επιμήκυνσης. Τα αποτελέσματα έδειξαν ότι εκτός από αισθητικούς λόγους, τα βαμμένα υφάσματα όντως διαδραμάτισαν ένα ρόλο ως παράγοντες προστασίας, επηρεάζοντας και περιορίζοντας την θερμική φθορά. Ειδικότερα, σε μοριακό επίπεδο, οι ανόργανες χρωστικές ουσίες και οι φυσικές βαφές φαίνεται να αλληλεπιδρούν με την κυτταρίνη και τη λιγνίνη των παλαιωμένων λινών, ενώ στο μικροσκοπικό επίπεδο οι εκτεινόμενες παράμετροι μεταβάλλονται. Το ηλεκτρονικό μικροσκόπιο επιβεβαιώνει πως τα σωματίδια της (ανόργανης) χρωστικής ουσίας είναι τοποθετημένα πάνω και ανάμεσα στις επιφάνειες των ινών, ενώ τα μόρια των (φυσικών) βαφών είναι αρκετά μικρά για να διαποτίσουν τις ίνες με χρώμα.

Επιπλέον, η εργασία αυτή επικεντρώθηκε σε δοκιμές και αναλύσεις μερικών αρχαιολογικών δειγμάτων από διαφορετικά μέρη και περιόδους της αρχαίας Αιγύπτου για να προσδιοριστούν οι χρωστικές, οι βαφές και τα διαβρωτικά μέσα, προκειμένου να κατανοηθούν η ζωγραφική και οι τεχνικές βαφής οι οποίες χρησιμοποιούνταν στην διακόσμηση τους και να καθοριστεί ο βαθμός ζημίας των αρχαίων ινών. Για το σκοπό αυτό έχουν χρησιμοποιηθεί οι επιστημονικές αναλυτικές τεχνικές όπως FTIR, ηλεκτρονικό μικροσκόπιο σάρωσης (SEM), περίθλαση ακτινών XRD και XRF. Τα αποτελέσματα επιβεβαίωσαν ότι όλα τα αρχαιολογικά υφάσματα είναι κατασκευασμένα από λινό, η μπλε βαφή του δείγματος (N. R60-2) μπορεί να είναι το λουλάκι, το σκούρο κόκκινο του δείγματος (N. S-58) είναι κοχενίλλη βαφή και το μαύρο χρώμα του δείγματος (N. Z-57)

είναι μαύρο κάρβουνο. Το αποτέλεσμα του ηλεκτρονικού μικροσκοπίου σάρωσης δείχνει πως οι ίνες είναι εντελώς κατεστραμμένες, σε συνδυασμό με την απώλεια της δομικής κλίμακας των ινών λινού σύμφωνα με τα αποτελέσματα XRD και FTIR. Τα αποτελέσματα XRD, XRF και FTIR των αρχαίων ανόργανων βαφών επιβεβαίωσαν ότι η κόκκινη βαφή είναι αιματίτης, η κίτρινη είναι “natrojarosite” και η φωτεινή πράσινη βαφή είναι μείγμα από αιγυπτιακό μπλε, γαιτίτη και ασβεστίτη.

Η παρούσα εργασία περιλαμβάνει επτά (7) κεφάλαια.

Κεφ.1. ασχολείται σε θεωρητικό υπόβαθρο με τη σημασία των αρχαιολογικών κλωστοϋφαντουργικών υλών και των ινών λινού που ήταν οι πιο σημαντικές κατά την αρχαιότητα, τις χημικές και φυσικές τους ιδιότητες. Επίσης με τους κύριους παράγοντες φθοράς των ινών κυτταρίνης και τις μεθόδους αποκατάστασης και συντήρησης των αρχαιολογικών υφασμάτων.

Κεφ.2. ασχολείται με την διάκριση μεταξύ των διαδικασιών βαφής και ζωγραφικής , τα φυσικά χρώματα, το χαρακτηρισμό τους, τις φυσικές και χημικές ιδιότητες, τις κύριες κατηγορίες των φυσικών βαφών ανάλογα με τα χρώματά τους, αλλά και σύμφωνα με τις μεθόδους εφαρμογής τους.

Κεφ.3. ασχολείται με τις κύριες χρωστικές ουσίες που χρησιμοποιούνταν κατά την αρχαιότητα, καθώς επίσης με τις φυσικές και χημικές τους ιδιότητες.

Κεφ.4. ασχολείται με την Πειραματική Διαδικασία, τα υλικά, την προετοιμασία των υπό εξέταση βαμμένων και ζωγραφισμένων δειγμάτων. Στην παρούσα εργασία ετοιμάσαμε στο εργαστήριο καινούρια ζωγραφισμένα και βαμμένα δείγματα λινού. Ταχεία θερμική αποικοδόμηση σε μία σταθερή θερμοκρασία 140 °C σε ηλεκτρονικό φούρνο για 72 ώρες, διεξήχθη για την παραγωγή τεχνητά παλαιωμένων λινών υφασμάτων, το δυνατόν παρόμοια με αυτές των αρχαιολογικών, λαμβάνοντας υπόψη ότι η θερμική αποικοδόμηση αυξάνεται με την αύξηση της θερμοκρασίας και τη διάρκεια της παλαίωσης των υφασμάτων. Επιπλέον, το κεφάλαιο αυτό ασχολείται με τις επιστημονικές τεχνικές που χρησιμοποιούνται στην ανάλυση των εξετασθέντων ζωγραφισμένων, βαμμένων ινών λινού και σε αρχαιολογικά δείγματα, όπως η ηλεκτρονική μικροσκοπία σάρωσης (SEM), εξοπλισμένο με έναν ανιχνευτή μικροανάλυσης EDS, περίθλαση ακτίνων X σε σκόνη (XRD), φασματοφωτόμετρο μετασχηματισμών Fourier (FTIR), αντοχή σε εφελκυσμό και φασματοσκοπία φθορισμού ακτίνων X (XRF).

Κεφ.5-6. ασχολούνται με τα αποτελέσματα και τη συζήτηση των προηγούμενων επιστημονικών τεχνικών που χρησιμοποιήθηκαν για την ανάλυση των εργαστηριακά ζωγραφισμένων και βαμμένων δειγμάτων λινού μετά την θερμική γήρανση.

Κεφ.7. ασχολείται με τον έλεγχο και την ανάλυση ορισμένων Αρχαιολογικών δειγμάτων. Σε αυτό το μέρος μελετήσαμε πέντε δείγματα αρχαιολογικών υφαντικών ινών από διαφορετικά μέρη και περιόδους της αρχαίας Αιγύπτου, αλλά και τρεις ανόργανες χρωστικές από τάφο στο al-Mina. Η μελέτη επικεντρώθηκε στον εντοπισμό των χρωστικών ουσιών, χρωμάτων, διαβρωτικών και δεσμευτικών μέσων, ώστε να γίνει κατανοητή ζωγραφική και οι τεχνικές βαφής που χρησιμοποιούνται στη διακόσμηση τους. Ο κύριος στόχος της αξιολόγησης των ιστορικών υφασμάτων ήταν να προσδιοριστούν οι ίνες και να διαπιστωθεί ο βαθμός της βλάβης. Οι επιστημονικές αναλυτικές τεχνικές που έχουν χρησιμοποιηθεί για το σκοπό αυτό είναι η ηλεκτρονική μικροσκοπία σάρωσης (SEM), εξοπλισμένο με έναν ανιχνευτή μικροανάλυσης EDS, περίθλαση ακτίνων X σε σκόνη (XRD), φασματοσκοπία φθορισμού ακτίνων X (XRF) και φασματοφωτόμετρο μετασχηματισμών Fourier (FTIR). Επιπλέον, στο τέλος αυτού του τμήματος γίνεται συζήτηση των αποτελεσμάτων.

CHAPTER 1

Linen Textiles

1.1. Introduction of the importance of textiles

The study of technology is an essential key to the understanding of people's culture. It is also an important aspect of craft manifestation. Textiles are an important source of reference for the cultural studies. During the Prehistoric and ancient periods, a large variety of indirect evidence is found in sculptures, paintings and literature to infer usage, trade etc. of textiles[1].

Textiles give us information about the technological skills of the people who made them, we can learn about a population from what they wore just as we learn from the tools and other gear they used on a regular basis[2,3].

Textiles often express who we are, our gender, age, family affiliation, social status, occupation, religion, and ethnicity. Knowledge of textile history is hence a key to our understanding of a multitude of human issues. After all, what separates us from other species is that we have and make ‘things’, and for the last 10.000 years textiles have been among our most indispensable things. In fact, textiles represent one of the earliest human craft technologies, certainly older than metallurgy, and they have been a fundamental part of subsistence, economy, and exchange. Textiles have an enormous potential in archaeological research, being able to tell about social, chronological, and cultural aspects of past societies, and at the same time giving us a unique opportunity to come very close to the prehistoric individual[4]**.**

Other studies have considered the relationship of spinning and weaving relevant with female’s ideology, because prominent female’s supernatural were often associated with textile[5]**.**

The archaeological textile studies are now recognized as a robust source of information for anthropological inquiry. Over the past two decades several important developments have taken place, enabling a more integrated approach to their study than in the past[6].

1.2. Classification of Textile Fibers

Fibers used in textiles today can be divided into two major classes: natural and manufactured (man-made). Each of these main classes may be further subdivided into two general groups as shown in Figure 1.1.

The principal vegetable and animal fibers in use today are presented in Table 1.1.

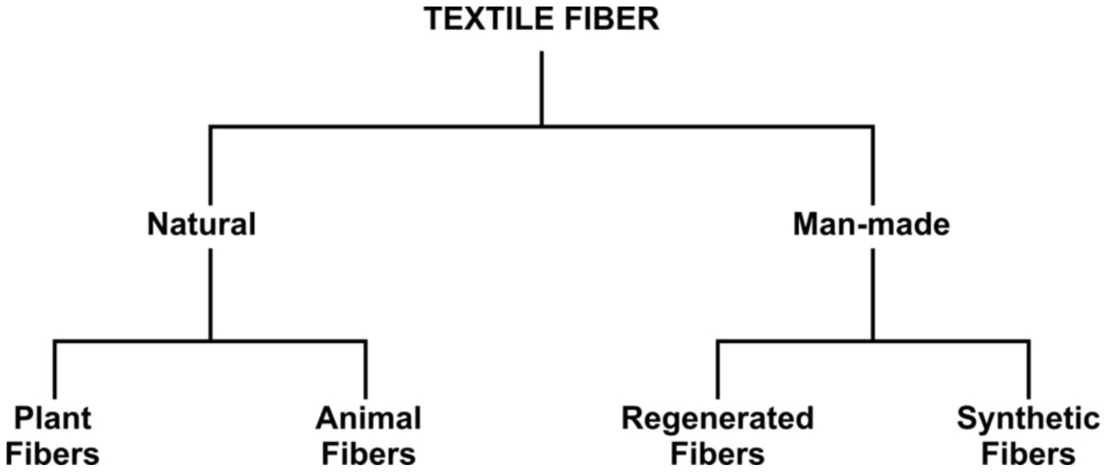


Fig.1.1. *Classification of Textile Fibers*

Table.1.1. *Natural textile fibres*

Vegetable (cellulose based)	Animal (protein based)
Cotton - *Gossypium*	Silk, cultivated - *Bombyx mori*
Flax - *Linum usitatissimum*	Silk, wild - *Tussah*
Ramie- *Boehmeria*	Wool - *Ovis aries*
Jute - *Corchorus*	Camel hair- *Camelidae*
Hemp - *Cannabis sativa*	Alpaca - *Auchenia paco*
Kapok - *Eriodendron anfractuosum*	Vicuna - *Auchenia vicuna*
	Llama - *Auchenia Llama*
	Guanaco - *Auchenia guanaco*
	Mohair - *Capra hircus angorensis*
	Cashmere - *Capra hircus laniger*
	Rabbit hair - *Lepus*

Table.1.2. *Principle manufactured (man-made) fibers*

Regenerated and cellulose derivative	Synthetic
Viscose rayon - regenerated cellulose	Nylon - polyamide
Cuprammonium rayon - regenerated cellulose	Polyester - polyethylene terephthalate
Cellulose acetate - cellulose ester	Acrylic - polyacylonitrile
Cellulose triacetate - cellulose ester	

From earliest times until the twentieth century, four fibers were in common use: Wool, silk, cotton and flax[7].

Seed fibres from cotton and stem fibres from flax were probably the first to be commonly woven into textiles. Linen (from flax) was the every-day fabric of ancient Egypt, and the plant was the first cultivated source of textile fibres in Europe. While cotton only became popular in Europe a few centuries ago, its history in Asia and the Central Americas dates back over 7.000 years. The spinning of animal fibres into threads and yarn seems to have developed relatively late on. In Mesopotamia, woven woolen cloth was being produced just 6.000 years ago, while the use of silk, in China, may only date from early in the 3rd millennium BC[4].

The word "textile" is derived from the Latin word, *texture,* means to weave. The term, however, is not confined to woven fabrics but includes many other forms of construction as shown in Figure 1.2[7].

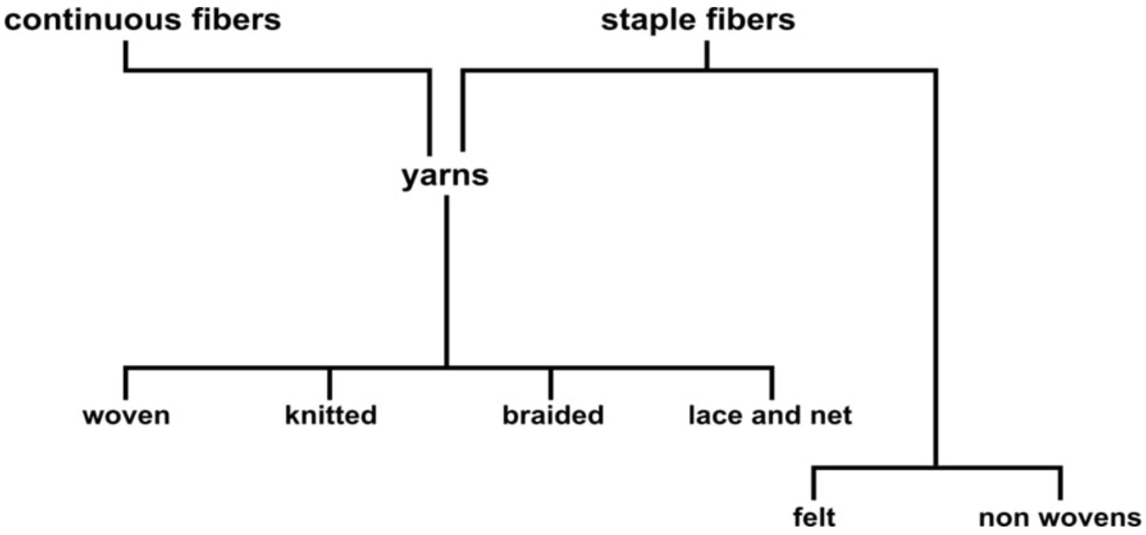


Fig.1.2. *Classification of textile materials*

1.3.Textile Technology

It is clear from textiles excavated from both tombs and settlement sites that, as early as the Predynastic period, the Egyptians were proficient spinners and weavers[8]. Information about the textile technology of Pharaonic Egypt derives both from the textiles themselves and from representation of the various stages of textile production, from the sowing of the flax-seed in the ground to the weaving material. Tomb-paintings and models are a particularly valuable source of information about the production of cloth, in particular spinning techniques and loom forms. The most important painting are in the Eleventh and Twelfth Dynasty tombs at Beni Hassan[9], the Eleventh Dynasty tomb of Dagi at Thebes[10], the twelfth- Dynasty tomb of Thuthotep at Deir El- Bersha , the Nineteenth-Dynasty tomb of Neferronpet at Thebes[11] and the Eighteenth-Dynasty tomb of Thutnefer at Thebes[12]. One of the most useful models of a spinning and weaving workshop is from the early Middle Kingdom tomb of Meketra at Cairo museum, Fig.1.3. Other models of this type are in the Metropolitan Museum, New-York.

In Ancient Egypt, textiles were used for many purposes, among them clothing, bags, sails, ropes, and nets. Ancient Egyptian textiles were primarily made of linen, which comes from the flax plant. Textiles were also made from palm fibers, grass, seeds, and much less frequently from sheep's wool and goat hair, where the fibers were spun on a spindle and then woven on a loom into the textile. In Pharaonic Egypt, textiles were usually created by women on looms in weaving workshops, which were usually housed in palaces and large estates.

Fig.1.3. *Models of a spinning and weaving workshop (Cairo museum, JE 46723)*

The majority of ancient Egyptian textiles are of linen which is made from the bast fibre, flax[13]. The Egyptians used linen from Pharaonic times onward. Linen was favored because it is strong and durable. The fibers are smooth and not easily abraded. Flax flourished in Egypt with the fertilizing annual floods of the Nile.

Fig.1.4. *Linen threads and tools which used in weaving textiles in ancient Egypt, case N. 7, second floor, Egyptian Museum.*

Linen could be woven in different levels of quality, from a very fine, sheer fabric, to a thick canvas-like fabric. Around 300 B.C., cotton was introduced from India, silk from China and sheep were imported. However, linen continued to be the most favored fabric because silk was very expensive. During Pharaonic times the Egyptians did not use wool because it was regarded to be ritually unclean. Linen garments were also cooler than wool garments, which was important in the hot climate of Egypt. However wool became common about the time of the ancient Greece and Roman conquest, around 30 B.C. The Romans liked wool and since Egypt was a major center of textile production for the Roman Empire, wool increased in use[14]. Wool has an advantage over linen in that it is easily dyed, while linen must first be soaked in an acidic mordant in order to take on a dye. Wool and linen were used both alone and in combination together in the same textile. Most commonly, weavers used linen as the background or main material, and wool as the material for the colorful narrow bands[15].

Textile manufacture was a major industry in Egypt, especially linen weaving. In the Ptolemaic and Roman periods (323 B.C) production was strictly controlled by the State, both for quality and the quantity produced[16].

Unfortunately, very little actual cloth has survived from Greek and Roman antiquity. Many textile tools, like looms "made of wood and thread" and spindles "made of wood" have also not survived. However, loom weights and spindle whorls are extremely common finds in ancient sites, so common in fact that until recently, archaeologists tended to give them little serious attention. Now, fortunately, cloth and textile artifacts are getting more serious attention from archaeologists[17].

In Ancient Greece, all thread and yarn would have been spun by hand using a distaff and spindle and all fabrics would have been manually woven on a warp-weighted vertical loom. Weaving was both a domestic and a commercial activity in Ancient Greece. The process of weaving fabric by Archaic and Classical Greek women and girls had a significant place in domestic life, in religious ritual, and in the literary mythology of the period. Homer describes Penelope, the devoted wife of Odysseus, busy at her loom day after day. The image that sparked the interest in this subject is a beautifully composed scene depicting women in various stages of working with wool, painted on a piece of terracotta pottery: a small Attic lekythos, or oil flask, dated from 550 to 530 B.C. The body of the vase illustrates five groups of women at various stages in the process of wool working[18], Fig.1.5. This lekythos seems to link weaving with marriage. Just above the loom on the shoulder of the vessel, there is a seated woman holding out her veil in a gesture associated with brides in Greek art.

Fig.1.5. *Lekythos or oil flask, 550 to 530 B.C.*

Later in the time of the Roman Empire, this changed and weaving became mainly the domain of male labor, although making clothes was still something women did[19].

Papyri recovered from the dry sands of Egypt provide considerable information on the production of textiles from the period of Greek rule, through the years of Roman control, down to the Byzantine era. However, the very nature of the papyrological documentation dictates that no complete and coherent picture of the industry at a given time ever obtains scattered in time and space, often fragmentary, seldom descriptive, generally concerned with economic transactions, fiscal matters, or topical Domestic issues, the papyri are imbued with the tantalizing quality of much of ancient daily life[20].

Textiles often present complex structures and represent the highest technological achievements of a culture, but due to their fragile and organic composition, they often do not survive, except in extra ordinary circumstances of extreme dryness, permafrost or anaerobic conditions[21].They are highly susceptible to damage from light, dirt, air-borne pollution, mould, insects and mechanical damage. They require carefully controlled, reliable temperature and humidity conditions[7].

1.4. Linen

1.4.1. Brief History

Linen is one of the earliest products known to civilization. It has been used for the production of fibers dating back several thousand years B.C. When man was in his earliest primitive state, living on the wide animals he hunted, the skins of those animals formed his only clothing. After a long period of history, man settled down, built himself permanent cities and cultivated the land. One of the products of the soil was flax, and out of the fiber from flax, linen was made. Linen is therefore the earliest known vegetable fabric to be woven and sometimes used as currency in ancient Egypt. Egyptian mummies were wrapped in linen because it was seen as a symbol of light and purity and as a display of wealth. Some of these fabrics, woven from hand spun yarns, were extremely fine and the fineness of the yarns in them cannot be produced even today on spinning machines, Fig.2.1.

Fig.2.1. *Piece of the fineness linen-Egyptian museum*

Flax, from which linen is made, is one of the oldest agricultural plants in the world. Over 5.000 years ago the Egyptians named it "woven moonlight", due to its very singular beauty.

When the tomb of the Pharaoh of the Exodus, Rameses ll, who died 1258 B.C., about 3.000 years ago, was discovered in 1881, the pure linen wrappings were in a state of perfect preservation. The mummy of “Kaboolie”, a daughter of a priest of Ammon, who died 2.500 years ago, is preserved in the library of Belfast, Ireland; the linen on this mummy is also in a state of perfection. Present research in Egypt has resulted in many wonderful discoveries and it is a matter of historical accuracy that when the tomb of Tutankhamon was opened, the linen curtains were found intact but all the other fabrics had crumbled to dust[22].

Fig.2.2. *Linen mummy shroud (with the mummy inside it), Egypt, about 1000 B.C. (Vatican Museum, Rome)*

There was a special type of cloth made for the gods and a type of linen to be worn by the priests or the kings in the "hall of the god". Two types of linen were specially made for royalty. The coffin texts specify five types of linen which were not used by the living. The other linens used for the dead only include the linen "rippling like water". Another type of linen occurs only in medical texts. There are many terms for strips or bandages of linen. Many types were used in mummification and each had its own name, most important in the ritual accompanying the preservation operations of dead body. Then there are the coloured stuffs. There was a "silver white" cloth, a green cloth and "lapis-lazuli" blue linen, the latter only in Greek times. Another blue cloth was made much earlier and dyed with a vegetable blue. In Greek times there was also yellow linen, and at least there were three red linens one of which was worn by priests[16].

Linen Derived from the stems of the flax plant, *Linum usitatissimum* is a member of the genus *Linum* in the family *Linaceae*[23].

The English word, linen is derived from the generic name, *linum*, and the term lint, from the old Scottish word, Lin[23].

Linen was a mainstay in textile media throughout Europe and the Mediterranean area from pre-history through modern times and flax was among the first plants cultivated by man, evidenced by ancient remains of spun and un-spun flax in Egypt, France, Turkey, Greece and Italy[24].

Flax is normally harvested at different times according to the use to which it is to be put. When the stems are green the fibers are soft enough for very fine thread, when they are yellow the fibers are stronger and suitable for good linen cloth, while when the flax is dead ripe the fibers are tough and can be made into ropes and mats. Ancient Egyptian linen varies considerably in texture, from the finest gauze to canvas-like coarseness and several different kinds of linen are distinguished in the lists of the Old Kingdom[25].

Fig.2.3. *Wall scene representing Sennedjem and his wife harvesting corn and flax in the fields of the afterlife, Deir el-Madinah, Luxor.*

Fig.2.4. *Harvest process of linen.*

The spinning and weaving of linen is depicted on wall paintings of ancient Egypt. As early as 3000 B.C., Mentioned several times in the Bible, it has been used as a cool, comfortable fiber in the Middle East for centuries as well[26].

Both Ancient Greeks and Romans imported their finest linen from Egypt where its wide cultivation attained great perfection and they greatly valued it as a commodity, but the cultivation of the plant was neglected by the Greeks, except for its seeds (linseed). The Greeks and particularly the Romans carried the weaving of woolen cloths to remarkably high standards[27].

Fig.2.5. *Child's mummy warping in linen textile, No.JE 28435, Greek-Roman period, Egyptian museum.*

1.4.2. Description of Flax fibers

Linen, or flax, is a bast (stem) fibre derived from certain varieties of *Linum usitatissimum*[28,29].

The flax plant is an annual and is grown both for its fiber and the seed. The flax flower is either blue or white**;** Fig.3.1.and a flax field in bloom is a very pretty sight**,** Fig.3.2.

Fig.3.1. *Flax flower*

Fig.3.2. *Flax field*

The quality of the finished linen product is often dependent upon growing conditions and harvesting techniques. Flax fibers vary in length from 2 to 36 inches and average 12-16 micrometers in diameter. There are two varieties: shorter fibers used for coarser fabrics and line fibers used for finer fabrics. Flax fibers can be identified by their typical "nodes"**,** Fig.3.3. which add to the flexibility and texture of the fabric. The cell walls of the flax fiber are thick and polygonal in cross-section. An immature flax fiber is clearly oval in cross-section, with a lumen much larger than in the mature fiber and with thinner cell walls[30], Fig. 3.4.

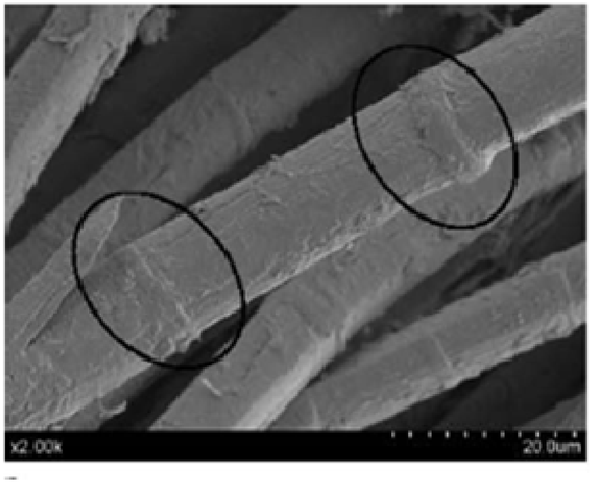


Fig.3.3. *SEM micrograph of the flax fibres showing the nodes*

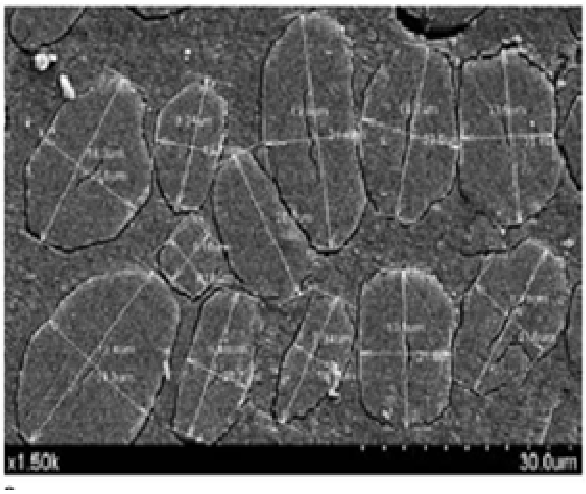


Fig.3.4. *Cross section showing bundles of Flax fibre cells with a lumen in the middle*

The fibers are cellular in nature being composed predominantly of cellulosic cell walls around a hollow lumen. In the case of flax fibers, bundles of these cells (ultimates) are cemented together by the lignaceous middle lamella[31,32].

1.4.3. Morphology of the Flax Plant

The morphology of the flax plant has been dealt with in a range of publications[33,34,35]. The stem is generally considered to be comprised of five layers: the epidermis, the cortex, the bast layer, the cambium layer and the interior woody tissue**,** Fig.3.5. each is described briefly below.

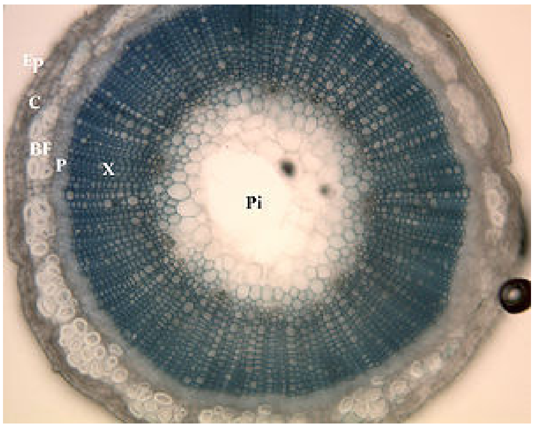


Fig.3.5. *Flax stem cross-section, showing locations of underlying tissues. Ep = epidermis; C = cortex; BF = bast fibers; P = phloem; X = xylem; Pi = pith.*

-The outer surface of the epidermis is covered with a thin layer of wax, which prevents excessive moisture evaporation and protects the plant. Bacteria enter the stem through this layer during retting[36].

-The next layer, the cortex, consists of circular cortical cells that are not lignified but contain pectin substances and coloring matter (eliminated ultimately by bleaching).

-In the third (bast) layer, fiber bundles run the full length of the stem and are found surrounded by parenchyma. A fiber bundle generally consists of between 10.0–40.0 ultimates or cells. Individual flax fibers that are 2.0–3.0 cm in length may range in diameter from 14.0– 30.0 micrometers, typically 14.0–17.0 micrometers[31, 34]. There may be between 15.0 and 40.0 bundles in the ring, depending upon the variety and agricultural variables. The ultimates are thicker near the plant root, thinner and longest near the apex of the stem. The primary walls of the cells (or ultimates) contain pectin substances with a trace of lignin, while the secondary wall contains mainly cellulose.

- The fourth layer, the cambium layer (phloem), consists of tender growth tissue, composed of thin-walled cells, that separates the fiber layer from the fifth layer.

-The latter consists of thick-walled cells first, then thin-walled cells, surrounding the pith cavity which is an air chamber extending through the length of the stalk.

The flax-fiber ultimates are thick-walled spindle-shaped cells with pointed ends and a small narrow lumen or canal inside the cell. The lumen is narrow but clearly defined and regular in width. It disappears towards the end of the fiber, which tapers to a point[37].

The ultimate fibers consist mainly of cellulose and are interconnected by middle lamellae which are considered to consist mainly of pectin, although some lamellae also contain lignin. Lignin is also to be found to a lesser extent in the flax ultimates, particularly in those from the lower portions of the stem[38].

The physical structure of flax-fiber ultimate is characterized by “displacements” or “breaks” in their surface layers. The presence of these transverse “dislocations” or “nodes”, often in the form of an “X”, is evident through microscopic examination. The walls of the flax ultimates have a spiral fibrillar structure, the external fibrillate running in a direction corresponding to an S-twist and this is the basis of the drying-twist test for the identification of flax[38].

Thus, if a wet flax fiber is held at one end and allowed to dry, the free end directed towards the observer, will be seen to move in a clockwise direction. This test may be applied to material at any stage of manufacture and is also successful on fibers that have been treated with caustic soda (mercerized)[31].

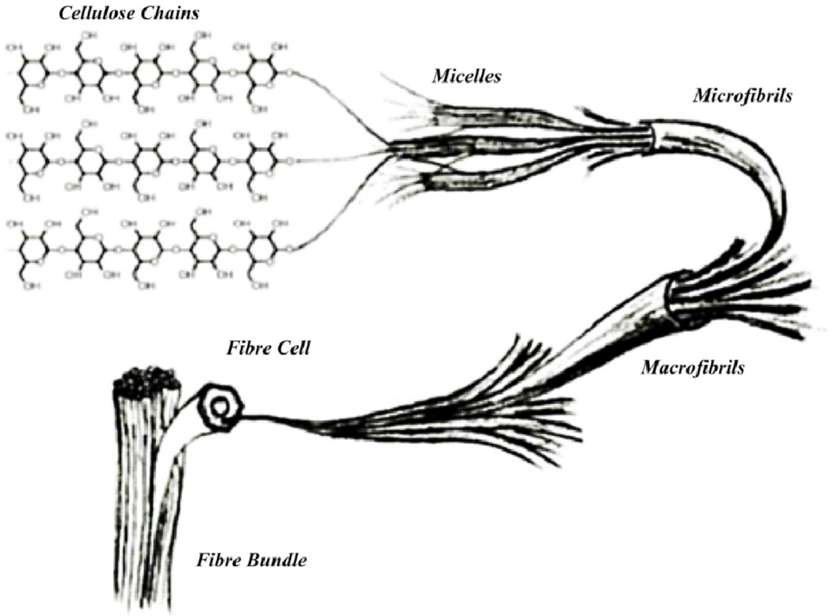


Fig.3.6. *Hierarchical microstructure of a linen fibre: from cellulose chains to the fibre*[39].

1.4.4. Extraction of linen fibers

Separating the linen fibers from the associated woody tissue was done since early antiquity by retting, a bacterial process that softens and decomposes woody tissue and separates the linen fiber bundles into single strands.

Two slightly different retting processes seem to have been practiced: land (or dew) retting and water retting. In land retting, soil fungi soften and degrade the woody tissue that holds the linen fibers together; in water retting the woody tissue is degraded by bacteria. After retting for a more or less extended period of time, lasting for several days (water retting is much faster than land retting) the woody tissue is broken down and softened by the activity of the microorganisms. The partly decayed stems are then beaten and shaken (the operation is known as scutching) to remove the decayed woody tissue. The detached linen fibers are heckled (to separate long and short fibers) and are finally dried. The length of linen fibers is variable and may have reached in antiquity lengths of up to 30.0 cm [24].

1.4.5. Physical properties of Linen

Linen has a number of properties that makes it useful for various industrial applications, use in home furnishings and apparels. Some of them are:

Strength: Linen is a durable and strong fabric, one of the few that is stronger wet than dry fiber; it is two-three times as strong as cotton. It is second in strength to silk.

Elasticity (elongation): Elasticity is the extent to which a fiber can be elongated or stretched and then returned to its normal condition and size. Linen is the least elastic natural fabric. Because linen fibers have a very low elasticity, the fabric will eventually break if it is folded and ironed at the same place repeatedly.

Resilience: Resilience refers to the extent to which a fabric can be deformed by crushing or compressing it, and finally returning it to its original condition. Linen is quite stiff and wrinkles easily.

Absorbency: Absorbency refers to the extent to which moisture can penetrate into a fiber. The fiber absorbs moisture and dries more quickly. It can gain up to 20% moisture without feeling damp. When freed from impurities, linen is highly absorbent and will quickly remove perspiration from the skin. It is excellent for manufacturing towels and handkerchiefs[23, 40].

Although linen fibers have higher crystallinity, their relatively higher moisture regain is due to the presence of non-cellulosic substances, especially hemicellulose and pectin which are hydrophilic[41].

Heat Conductivity: Heat conductivity refers to the extent to which heat can be conveyed through a fiber. It is most suitable for use in summer, as the fiber allows the heat to escape. Linen is less likely to cling to the skin; when it billows away, it tends to dry out and become cool so that the skin is being continually touched by a cool surface.

Luster: Linen fabrics have a high natural luster and their natural color ranges between shades of ivory, tan or grey. Although not good for the fabric, pure white linen is created by heavy bleaching.

1.4.6. Chemical properties of Linen

The cell walls of flax, Fig.3.7., as with all plant fibers, are largely composed of polysaccharides, principally cellulose (62.1%), along with hemicelluloses (16.7%) and pectin (1.8%) and a smaller proportion of lignin (2.0%), proteins, pigments, waxes and minerals [35, 36]

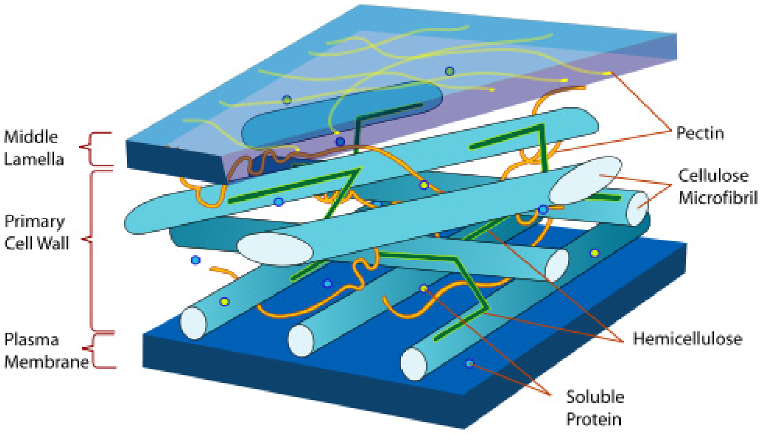


Fig.3.7. *Plant cell wall diagram showed location and arrangement of cellulose microfibrils in the plant cell wall*[42]**.**

Cellulose the main component in linen fibers is a natural, linear polymer: a polysaccharide built of up to several thousand β- D-glucose units, Fig.3.8. D-glucose $(C_6H_{12}O_6)_n$ is a saccharide containing five hydroxyl functional groups and an aldehyde group [43]**.**

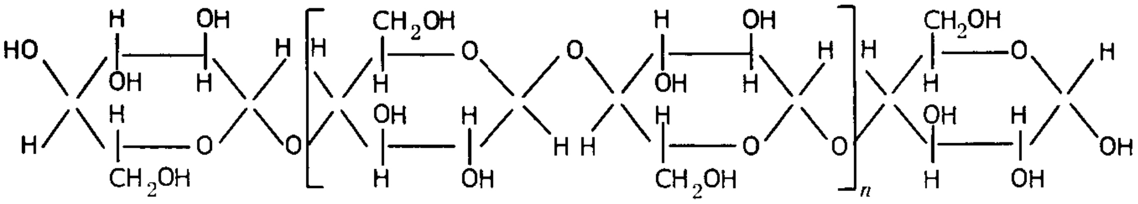


Fig.3.8. *Four of as many as 1500 glucose units that may make up a cellulose polymer. Because of the length of its molecules, cellulose makes excellent natural fibers as, for example, those of cotton and linen.*

In the polysaccharide cellulose, the glycosidic hydroxyl group on carbon-1 of one unit undergoes a condensation reaction with the hydroxyl group on carbon-4 of another unit, and forms (1-4) glycosidic ether bonds[43].

The molecules of cellulose are long, straight and unbranched polymers[24]. Due to the fact that the cellulose polymers are of organic origin, the main constituent atoms are carbon and hydrogen. The chemical bonds between the atoms are typically covalent bonds. The cohesion of the fibre materials is provided not only by the covalent bonds between their constituent atoms but also by intra-and intermolecular secondary (physical) bonds such as hydrogen secondary bonds. These bonds can be formed between suitable atoms or groups of atoms of the same chain (intramolecular secondary bonds) or between different chains (intermolecular secondary bonds). Secondary bonds, as well as some special non-covalent bonds, stabilize the secondary structure of one polymer chain, and the connections between two or more polymer chain which is called the tertiary structure of the polymer[43].

The large number of hydroxyl groups allows for hydrogen bonding, both inter-and intermolecular, Fig.3.9. This means that the linear chains align themselves side by side to form microfibrils with high tensile strength which in turn align themselves more or less along the axis of fibers. This strength is important in cell walls[43].

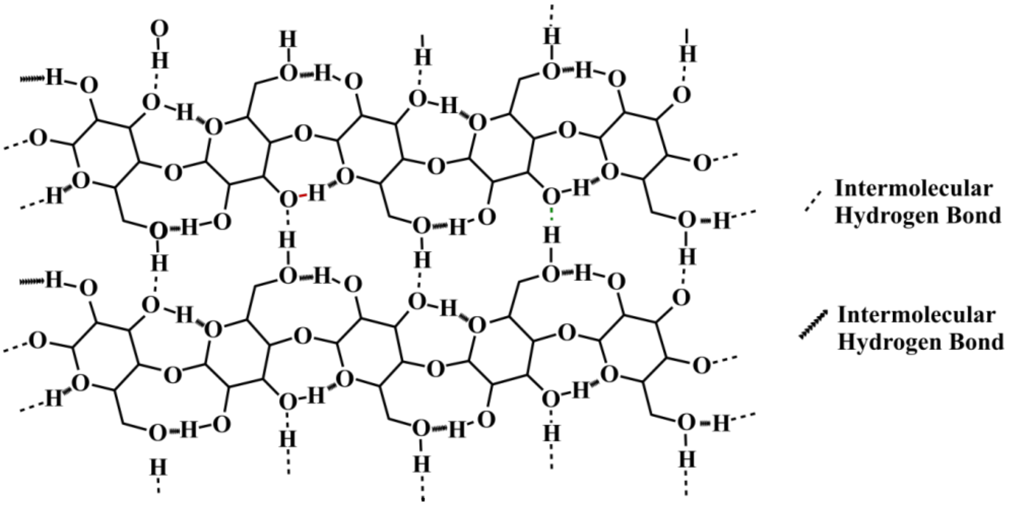


Fig.3.9. *Hydrogen bonding between cellulose chains*[39]

Cellulose exhibit both crystalline (well-ordered) and amorphous (non-ordered) regions. The structure of cellulose is often described by reference to the theory of “fringed micelles”: the long line cellulose chains pass through micelles (crystalline fractions) which continue into the fringes (amorphous regions). The stiffness of the polymer is due to the crystalline fractions while the flexibility of the cellulose is providing by the amorphous regions where segments are able to move. The crystalline/amorphous ratio of cellulose varies with different cellulosic fibres[43]. Cellulose of linen fibres is much more crystalline, (degree of crystallinity, typically about 70%) resulting of the high arrangement of the molecules which results from hydrogen bonding involving the hydroxyl groups. This intermolecular association leads to a high crystallinity which is sufficiently ordered for cellulose to give an X-ray diffraction pattern which results in the suitability of cellulose as a structural material in plants and also lends it a high degree of chemical resistivity[44]. This high crystallinity requires a temperature of 320°C and pressure of 25 MPa to become amorphous in water[45].

Accordance with the literature, it has been established that no degradation takes place until 200°C. Above this temperature thermal stability gradually decreases and the cellulose decomposition occurs. Generally, at temperatures less than 100°C the water loss in all the samples takes place[46].

Typically, for undegraded linen cellulose, the degree of polymerization (DP, the number of glucose units that make up one polymer molecule) is of the order of 10.000-20.000 cellobiose units (cellobiose is the identical repeating unit of cellulose [39,47]

In general, the DP of cellulose varies depending on its source. The mechanical properties of cellulose “based fibre”, such as tensile strength are very dependent on its DP. Its chemical properties depend on the glycosidic ether bonds between its units[47].

Effect of chemicals: Linen is resistant to dilute acids, but it is damaged by diluted hot and cold concentrated acid. Linen has a good resistance to alkaline solutions, so that the quality of its properties doesn’t less by laundered repetition. Also, the organic solvents which used in dry cleaning relatively affected on linen fabrics[48].

Also perspiration and bleaching can damage linen. Linen is relatively easy to take care of since it resists dirt and stains, has no lint or pilling tendencies and can be dry cleaned, machine washed or steamed. Linen should not be dried too much by tumble drying; it is much easier to iron when damp. Today linen is usually an expensive textile, and is produced in relatively small quantities. It has a long “staple” (individual fiber length) relative to cotton and other Natural fiber[32]. Linen is a difficult fiber to dye because the cellular structure is permeated by a kind of natural wax which prevents chemicals and dyes from crossing the cell structures[25], therefore so many of the surviving ancient textiles were undyed, Although the Egyptians are known for their love of color and for paintings on the walls and floors of the houses, temples and tombs[14].

1.5. Deterioration factors of cellulose fibres

1.5.1. Effect of moisture

When cellulosic materials are in contact with water vapor or liquid water, water molecules penetrate the capillaries and pore (by means of capillary forces) and diffuse into the amorphous regions. Water disrupts the interchain bonds because the hydrogen bonding is of low density in the amorphous parts in comparison with the crystalline regions. Water molecules form new hydrogen secondary bonds with the hydroxyl groups of cellulose chains. Cellulose may contain different quantities of water depending on its condition and environment. Cellulose can bond water in three different ways:

a- Structural water refers to a one-molecule layer of water, present in the amorphous region, structural water is already present in the fiber during fibre formation, and can only be evaporated from the cellulose at a temperature well above 100ºC.

b- Bound water refers to the moisture absorbed by cellulose and includes structural water. Bound water is considered as condensed liquid water, whether it originates from atmospheric humidity or is taken from liquid water. Bound water may fill whole capillaries, causing considerable swelling. Part of the bound water can be evaporated by air drying; all bound water can be dried out by heat and/or by keeping the material in an environment with a relative humidity below 30% for a long time. If this happens, the material is said to be desiccated.

c- Excess water refers to liquid water that has penetrated the material and bonded loosely to cellulose. This causes the most swelling. Excess water can be eliminated by pressure or centrifugation.

Cellulose exhibits hysteresis on absorption and desorption of water, in a similar way to other organic materials. Bound water in the cellulose polymer acts as a “plasticizer”, (Materials consisting of small molecules which fill the free volume of the polymer prevent the chains in the amorphous regions from fitting close together). As long as cellulose-based materials contain the equilibrium moisture content in an environment of 45-65% relative humidity, they remain soft and flexible, due to the presence of considerable amount of plasticizer in their amorphous regions. On desiccation (resulting from high temperatures or a relative humidity below 30%) most of the bound water evaporates, and the cellulose may dehydrate, resulting in an inflexible, often powdering material.

Steam can dissolve harmful soils in the textiles and it can result in the bleeding of dyes, the corrosion of metals and the swelling of binding media. Too much water in the cellulose causes swelling. The swollen material is more accessible to chemical and biological agents, thus the deterioration of cellulose is accelerated in damp and wet conditions. The swelling of cellulose on wetting is accompanied by shrinkage on drying. If drying of wet cellulosic fibres is carried out too rapidly or too high a temperature, the shrinkage can cause considerable changes in the dimensions and flexible properties of the fibres.

Shrinkage is due to the formation of many new hydrogen secondary bonds between neighbouring cellulose chains on drying. During dehydration strong intercellulose hydrogen bonds bring the molecules tightly together, eliminating moisture and causing extreme shrinkage and making it almost impossible to rehydrate. Thus, the proportion of amorphous/crystalline regions changes to a higher crystalline percentage. This explains the limited flexibility of dehydrated cellulose in comparison with the original flexibility of the fibres.

1.5.2. Effect of ultraviolet radiation and light

Pure native (untreated) cellulose absorbs ultraviolet radiation strongly below 200 nm, slightly between 200 and 300 nm and very weakly up to 400 nm. The fact that cellulose absorbs mainly in the far ultraviolet region can be explained by the strong chemical bonds throughout its polymer. The aldehyde groups at the chain ends are responsible for absorbance close to the visible region.

After absorbing electromagnetic radiation, free radical photochemical reactions start in the cellulose. These reactions are greatly accelerated in the presence of moisture and catalysts. Well-known catalysts of photo-oxidation are compounds of heavy and transition metals, such as iron, copper, manganese, cobalt, lead and tin. Such impurities, often originating from the textile objects themselves (e.g. iron stains, dye mordants, certain pigments and the corrosion products of metal decorations) enhance the speed of photodeterioration.

The most common photochemical damage is done to cellulose by photo-oxidation, this process can occur simultaneously by two main routes:

a- Oxidation of the hydroxyl side groups, which results in changes to colour, polarity, solubility and in the absorption- desorption properties of the cellulose to water.
b- Rupture of the glycosidic ether bonds between the units of the cellulose, causing a decrease in DP, thereby changing its mechanical properties, solubility and other properties.

The photo-oxidation of cellulose is a heterogeneous reaction, which may be limited initially to the amorphous regions spreading slowly to the well-ordered crystalline regions. The reaction rate depends on many factors, including the condition of the cellulose, the wavelength and the intensity of the radiation, the amount of available oxygen, the temperature, and the moisture content of the material and the presence of catalysts. The product of the oxidation is called “oxicellulose”. Oxicellulose containing a considerable number of carbonyl groups can be recognized by its yellow, yellowish brown or brown colour.

1.5.3. Effect of heat

Cellulose may become desiccated as a result of heat treatments. If sufficient activation energy is present, a condensation reaction may occur between two hydroxyl groups of two cellulose chains to form cross-links. The more cross-links formed between cellulose chains, the stiffer the textile becomes. The fibres will also lose some of their original ability to bond water.

Free radical thermal oxidation reactions occur in similar way to photo-oxidation, they cause thermal oxidation of the hydroxyl side groups and chain scission of the cellulose polymer. Both cross-linking and chain scission result in a rigid, fragile, yellow/brown material with weakened mechanical strength.

Treatments at high temperatures may cause rupture of certain bonds of cellulose, this rupture results in the elimination of small deterioration products, including carbon monoxide, carbon dioxide, water and glucose derivatives.

Cellulose is particularly heat-sensitive after irradiation by electromagnetic radiation, because of the presence of activated chemical bonds, as well as peroxides and hydroperoxides (the primary products of photo-oxidation).

Thermal deterioration, like photo-oxidation, is accelerated in the presence of moisture and catalysts.

1.5.4. Effect of acidic solutions

Cellulose is particularly sensitive to acids. Dilute solutions of acids penetrate the amorphous regions firs and carry out acid hydrolysis of the accessible cellulose polymer.

The acid hydrolysis may remain limited to the amorphous regions or it may extend to the well-organized crystalline regions, depending on the type and concentration of the acid, the temperature, the duration of the hydrolysis and other factors, including the condition of the cellulose.

The rate of the acid hydrolysis is also controlled through the sequence of three discrete stages: an initial rapid stage in which a limited number of glycosidic bonds are rapidly broken, a second stage where the hydrolysis of the glycosidic ether bonds available in the amorphous regions of the cell wall leads to a rapid fall in DP of the cellulose until nearly all glycosidic bonds in the amorphous regions of the cell wall have undergone acid hydrolysis, and a third stage where hydrolysis takes place very slowly by attacking the glycosidic ether bonds on the margins of crystalline micelles. As these micelles are accessed through oxidation reactions and swelling or other physical processes, their hydrolysis becomes more possible. The product of acid hydrolysis is called “hydrocellulose”, which is a rigid, brittle and mechanically weak material which may turn to powder.

1.5.5. Effect of alkaline solutions

Native cellulose resists alkaline treatments. For example, the process of making cotton crepe using an 18-20% solution of the strong base sodium hydroxide changes the crystal structure of cellulose but does not cause significant changes in the colour or mechanical properties of the fibre. Alkaline attack the glycosidic ether bonds between two anhydroglucose units of cellulose but unlike acid hydrolysis, alkaline degradation is not random. The attack by the alkaline is limited to the last unit of the chain because the reaction is controlled by the hidden aldehyde group. Extreme swelling of cellulose may occur in strong alkaline solution (10-22% potassium hydroxide). Under this extreme condition, cellulose may swell enormously but will not dissolve. On drying, this cellulose adopts different crystalline state called cellulose II[39,42].

1.5.6. Biological deterioration

Textiles are in most cases subject to rapid decomposition and are rare finds in an archaeological context[49]. Fungi, bacteria and other micro-organisms decompose the cellulose of the fibers by means of their enzymes. The degrading processes involve rupture of the glycosidic ether bonds of the polymer. The aim of the living organism is to break down cellulose into small products (possibly to glucoses) which are suitable nutrients. The collective name for enzymes which decompose cellulose to cellobiose or glucose is cellulase. The most common chemical reaction accelerated greatly in the presence of a particular enzyme (hydrolysis) in humid condition. The enzymatic hydrolysis of cellulose is often accompanied by oxidation, because several bacteria and micro-organisms produce hydrogen peroxide during the decomposing process. The acidic products of metabolism excreted by certain micro-organisms can cause acid hydrolysis of cellulose[42].

1.6. Scientific methods of restoration and conservation of Archaeological textiles

1.6.1. Introduction

Conservation is an interdisciplinary field that needs to take into account such disciplines as the humanities, the arts, the sciences and technology and crafts. Although the actual conservation intervention is or should be carried out by trained conservators, the degree of that intervention cannot be decided by the conservator alone. The reason for this is that conservation is not merely a technical operation on a cultural object. Rather, it is a cultural operation carried out by technical means.

Thus, when a conservation intervention is being planned on an object, it is important that as much information as possible about that object be available to the conservator. For example, this includes the anamnesis of the object, i.e., its history, starting with provenance, its historical context, including the available technology and materials available at the time the particular object was created, its subsequent use and the conditions under which it was kept there. It is clear, therefore, that the contribution of historians and art historian is critical for conservation. Furthermore, the study of the object, its constituent materials and any deterioration process that may be affecting it, requires the contribution of the sciences to effectively identify any changes and decay it may have suffered. Based upon the scientific information acquired, an appropriate conservation method can then be devised[39].

1.6.2. Preliminary examination

Any conservation intervention needs to follow a logical procedure. This starts with the visual assessment and the compilation of all the relevant historical data available, including its recent history and information on any previous conservation intervention. Then a diagnosis as to the state of conservation of the object is required. Is the object sound? Does it suffer from any deterioration? If so, what are the causes? These questions, as well as the identification of the constituent materials require the support from various analytical techniques. The results from these analyses serve various purposes. In the first place, they have to correlate with the historic information available. Second, is the object in question in a sound condition or does it show some deterioration? If so, is that deterioration active or is it the remnant of a previous decay process that has now ceased? These are fundamental questions that need to be addressed so as to determine if a conservation treatment is required or not and should a treatment be necessary, the most appropriate method and material need to be determined. Finally, and as a result of this preliminary examination and study, a condition report needs to be prepared including any recommendation regarding subsequent treatments or the conditions under which the object should be stored or displayed[39].

1.6.3. Cleaning process

Cleaning operations are the most important processes used in the treatment and maintenance of the ancient textiles which often have dust and stains and foreign materials both from factors of deterioration or the environment which the object was extracted from it[50]. Due to the physical nature of textiles, such as its ability to bind with the dirt which settles in the holes located between the fibers, as well as inter-plainer spacing between the threads, which eventually leading to the accumulation of dust and dirt on the surface of the textile[51].

The amounts of material that adhere to the surface of the textile depend on physical properties of fibers such as fibers diameter, the degree of harshness or smoothness, and duration of exposure to air pollutions[52]. The process of cleaning ancient textiles of the dirt is necessary for several reasons:

1- The tiny particles of dust adsorbed the moisture and acid gases from the atmosphere. This is leading to concentration of acidic solutions between and around the fiber, which speeds up the chemical reaction rates.

2- Dirt distorts and blurs the appearance of textile features.

3- Dirt reduces the flexibility of the textile and lead to brittle and fracture.

4-Dirt encourages the growth of insects and micro-organisms which causing textile damaging.

Therefore, it is necessary to clean textiles, whether it is displayed or stored or will be addressed in treatment and maintenance[53].

Cleaning archaeological, degraded linen is the most difficult problems faced by the restorer, due to the fact that linen fibers are rigid in nature, and get hard after ageing, which lead to brittle and decreasing the strength. The cracks found on the linen fibers increase the strength of link dirt and stains with weak fiber making it difficult to remove[54].

The most important methods used in the process of cleaning archaeological linen textiles are:

1.6.3.1. Mechanical cleaning

Mechanical cleaning means surface cleaning of textiles, is the removal of loose dirt outstanding on the textile surface. This dirt is often dust and sand as well as the remnants of insect waste. The process of mechanical cleaning aiming to prepare the textiles for displaying if their condition permit, or prepared them for other clean-up operations if the mechanical cleaning does not achieve the purpose[55]. The main methods used to clean ancient textiles mechanically are:

1.6.3.1.A. Cleaning using soft brushes

A very soft brush is used to remove outstanding dust and dirt of the textiles surface. The cleaning must be done in part -part of the piece, so as to collect dirt, which is sucked by using a vacuum cleaner. Taking into account not forming a dust cloud, to not return and settle again on the surface of the textiles. Preferably a brush with long white hair and it has to be changed when it's color changes[56].

1.6.3.1.B. Cleaning using a vacuum cleaner

In this way a piece of the textile is placed between two layers of nylon mesh with large openings in order to protect and prevent tearing textiles, at the same time allow the absorption of dust and dirt[57]. A vacuum suction must be used with controlled low absorption strength, and a vacuum hose nozzle should not be adjacent to the surface of the textiles directly, but must be used for a suitable distance. As well as the Micro-Vacuum Suction Tweezers-unit can be used to clean dust and dirt outstanding archeological textile surface, taking into account wearing gloves and masks protection during the cleaning process[58].

1.6.3.2. Chemical cleaning

In most cases mechanical cleaning process is not enough to remove dirt and stains of the surface of ancient linen textiles. In this case, resort to the process of chemical cleaning. The main methods of chemical cleaning which suitable with the state of archaeological, brittle linen textiles are:

1.6.3.2.A. Dry Cleaning

Dry cleaning is known as the French cleaning, because it is first known in France. Dry cleaning means a process to remove stains and dirt from the surface of textiles with organic solvents[59].The main advantages of dry cleaning, it does not cause wetting of the fibers, does not lead to a change in its original form and does not affect the dyes which are affected by water solutions, in addition, organic solvents have a great affect to remove stains, especially of fatty acids. In spite of all advantages of the process of dry cleaning, but it have many flaws, the most important are: the organic solvents are expensive, their severe toxicity, and most organic solvents are flammable which displays the effects of textile as well as restorers to the dangers of fire[60].

The most important organic solvents used in cleaning ancient textiles are: Ethyl alcohol (C_2H_5OH), Benzene (C_6H_6), Carbon tetrachloride (CCL_4), Mineral turpentine oil, di, tri, tetra ethylene chloride (C_2Cl_4 - C_2HCl_3 -- C_2 H_2Cl_2) and Trifluor trichloroethane (Cl_2FC-$CClF_2$) which known commercially as Volclene Arklone. It has excellent properties in the melting of dirt fatty acids, it is one of the most reliable modern solvents and it does not cause the removal of dyes comparing with other solvents[57].

The effective of dry cleaning, is dependent on the effectiveness of detergents, which depends on several factors, including mechanical movement, temperature degree, the duration of immersion, and drying and the degree of dirt. In the case of archaeological textiles that have cuts and tears, it is necessary to be put between two layers of nylon mesh in order to maintain the tearing parts during cleaning process[53].

1.6.3.2.B. Wet cleaning

The wet cleaning using water as a basic solvent, it is one of the most common methods used in the cleaning of archaeological textiles. However, some researchers in the past believed that the aqueous solutions reduces the strength of the fibers and increase their weakness, but in the same time they stress that the alternative systems using methyl alcohol (IMS), and other safe organic solvents given the less degree of cleaning, also until recently remained strongly believes that the addition of glycerine to the aqueous solutions used in cleaning linen fibers increases the strength and durability of fibers. However, (Cook, et al, 1996) demonstrated in a recent study that glycerine does not give any significant improvement in the durability and strength of fiber, but it may increase the effectiveness of washing to clean and remove certain types of stains[55].

In a recent study carried out on a variety of archaeological weak textile samples, it clears that the linen and cotton fabrics, is one of the most vulnerable types of archaeological textiles suitable for wet cleaning with water solutions. As the study pointed out that the mechanical properties of flax and cotton were not affected despite the use of tap water in the processes of cleaning and rinsing. The scientific results have confirmed that the wet cleaning of weak linen textiles using water increases the durability and strength of linen fiber, because the water would bring coherence between the hydrogen bonds[61].

The water used in the cleaning of ancient textiles must be, distillery, preferably ethyl alcohol + distilled water at 1: 1 in cleaning ancient painted linen textiles with pigments, as the water increases strength and durability of fiber and helps to remove dirt and dust and Ethyl alcohol, helps to not delay the drying period, In addition, it sterilizes the textiles from the effect of remnant of fungi[56].

In the case of painted textiles, preferably the process of cleaning by using suction table, which has the ability to control widespread of the solutions, and prevent them to access to the pigments which used in coloring textiles. At the same time allow using aqueous solutions without causing any damage of archaeological textile piece[57].

1.6.3.2.C. Cleaning by enzymes

For 25 years, enzymes have been used in conservation. Their characteristics and applications have been discussed in numerous articles and books, and they have been shown to be a valuable tool for conservators. The information found in the literature, however, can be fragmentary, perplexing or downright contradictory, because conservators generally use enzymes as a “last resort”.

Enzymes which digest starch and protein have become widely accepted as some of the most useful reagents available to conservators. Similarly, for the removal of adhesives from textiles and other absorptive papers, application of enzymes can be a method that is at once the most efficacious and the least disruptive to the textiles fibres. Extremely thick accretions which would require inadvisably long or repeated bathing times in traditional washing solutions are also more efficiently removed by enzymes, because they catalyze a degradation reaction of the components of paste and glue. Enzyme preparations can be dissolved in water and applied locally or in overall treatments. Enzymes have been used in cellulosic poultices and in mixtures of water and organic solvents, although it should be noted that the later procedure may not be advisable. A rinse step is an essential part of an enzyme treatment and adjustments of temperature and PH can increase an enzyme's efficiency[62].

1.6.3.3. Laser cleaning

Laser-based techniques are widely used in the conservation of cultural heritage objects as advanced cleaning tools. Laser cleaning is an established method for the restoration of metal artifacts and for the selective removal of black crusts, or other surface deposits, from stone, marble sculptures, or architectural surfaces. Laser cleaning is controllable with a high precision, reducing the risks of damaging the bulk material below. Recent advances in laser cleaning methodologies exploiting dual wavelength schemes and the use of ultra short pulsed. Lasers are making this method a reliable alternative to traditional cleaning procedures. This is mainly based on the possibility of micrometric control of the amount of material removed and the possibility of implementing online diagnosis of the cleaning process.

Laser cleaning of architectural surfaces and sculptures is a well developed procedure, while laser cleaning of photosensitive organic materials is still a subject of investigation in various laboratories. Successful implementation of laser based techniques in the field of cultural heritage relies on understanding the interaction between laser light and the materials which constitute the object or artwork. Organic substrates are encountered in art and historical objects such as paintings, ancient parchments, paper documents and textiles. Laser cleaning of fibrous substrates such as parchment, documents and textiles involves the selective removal of surface deposits via essentially a thermal evaporation process[63].

1.6.4. Humidification process

It is necessary to try to flat wrinkles and bends existing in linen textiles so as not to cause further break down and fracture of the fibers and to facilitate the process of displaying or storing the object. The process of flatting must be done after the lifting of the textiles humidity, especially in the case of its much dryness. If these process was did without raising the moisture content, it will lead to the rupture of the fibers and may lead to damaging completely.

The process of Humidification of archaeological textile piece is carry out by placing it on a stretched tightly nylon network and then placed inside the humidification Chamber. The nylon network allows the passage of moisture, so that the whole textile is prone to wet steam[56].

Thus, the moisture content of flax fiber is increased and the fiber become more flexible so we can flat the wrinkles easily, without causing any damage to the fibers. Loads of glass or lead are placed to fix the fibers in their proper situation, as well as the fringes are organized individually in the right places, taking into account that the flatting process must be done slowly and very carefully[62].

After the end of humidification and flatting process, the face of the textile piece is covered by a nylon network and takes it out of the humidification chamber, and placed it inside the laboratory, so the linen fibers can restore the balance with the surrounding atmosphere.

It is necessary to note that the humidification process is carried out when the simply mechanical cleaning of the archaeological piece is enough and there is no need for a wet cleaning process, followed by a process of consolidating and displaying or storing the archaeological textile piece[58].

1.6.5. Drying process

After the completion of wet cleaning, we must not let archaeological textile wet long time after washing but should be dried immediately and must be dried at room temperature, as the moderate drying helps to remove only excess water. Permanently must be excluded the use of thermal iron because the damage caused by it is irreversible. However, in some cases resort to some other aid to speed up the drying process, using dried air or infrared lamps or by using the heat surfaces with controlled temperature, we resort to such methods in the cold country or in the case of thick textiles, such as carpet which may remain for several days without fully drought, which prone the textile piece of biological attack. It must be emphasized to use only safe methods to accelerate the process of drying so as not to subject the object to deterioration[57].

There are several methods used in drying ancient textile, the method of drying depend on the case of textile piece, such as drying by air, heat and by solvent. The later method is used for drying fragile pieces that do not bear the sudden drying, in this method the object is soaked in a bath of ethyl alcohol and water by 1:1 and in the bath of pure ethyl alcohol. Followed by immersion in xylene and then drying. But the defects of this method, it can lead to melt some of the natural oils found in the fibers which leads to deteriorate fibers[51].

1.6.6. Consolidating the colors which used in the decoration of the archaeological textiles

After completion of the mechanical cleaning process, before starting the other steps of treatment, consolidate the colors used in decoration should be done, in order to fix it and to not affected by other stages of treatment "if needed". The process of consolidating are done by using an appropriate material such as Baraloid B72 2% dissolved in xylene, Plexisol and Beva.

Baraloid B72 2% has good properties after ageing; it has a little gloss, stable flexible, and therefore has been used successfully in the consolidating of Ancient Egyptian colors. The slow evaporation of xylene help colors to absorb Baraloid completely. The process of consolidating should be done by using high quality soft brushes, and should be done on the front and back of colored decorations. Also start from mid-colored part, to the farthest (from the middle to the outside) so as to prevent the spread of consolidate solution outside the border of colors and then let the color to dry completely before starting the other phases of treatment[57].

1.6.7. Consolidation and fixation of ancient textiles on a new holder

The process of consolidating the linen textiles are one of the most important archaeological phases of treatment and maintenance, because most of these textiles are fragile and friable in the form of parts and need to be consolidated. Therefore, the consolidating of these textiles is one of the following basic cleaning and drying steps[60]. Taking into account when choosing the method of consolidation to be easy to apply, fit the case of the object to be treated, and be easy to use inside the museum or the lab without needing to have great potential and costs[64]. The most important methods used to consolidate the general archaeological textiles are (1) Consolidating by needle, (2) Consolidating by fixing on a new holder. (3) Consolidating by solvents.

The different way of consolidating depends on the type of textile and its damage conditions, as well as depends on the conditions of the textile after that if it will be displayed or stored[42].

1.6.7. A. Consolidation by needle

This method is safer and more used to consolidate the archaeological textile, where as it is a reversible. If the sewing done without care and precaution and by untrained hands , it will lead to damage of textile, as in the case of using thick yarn and many stitches or pulling the threads much more than necessary, thus resulting in a ruptures of archaeological textiles. Therefore, sewing must be done using fine needles and fine stitches which are not be seen to the audience, and must not pull strings too much. To complete the restoration and consolidation successful must be based on the experienced, aware of major types of needles, threads and types of backgrounds fibers which will be used for this purpose, methods of processing and dyeing. Ancient textiles which containing many cuts and tears can consolidate them by the needle methods. In this case sewing is not done on the textile piece directly, but through a network of thin Nylon bobbin placing on the top of the textile[57].

1.6.7. B. Consolidating by adhesives

This method of consolidation is the best way that suits the state of most of archaeological linen textiles. The main advantages of this method are: carried out in a single step in a very short time, does not cause any staining or damage of archaeological textile, save the effort and the expensive labors, consolidation is done without use of water, The decorations of archaeological textile are shown clearly through the cloth holder which does not hide what is beneath and preserving the fabric and proves its case over time[65]. Some of the best resins used for consolidation are Mowilith DMC2, Beva 371. Paraloid F10, Lascaux 360 HV and 498 HV[66].

The methods of consolidation by adhesive on a new holder are being applied in two steps: 1- Preparation of the new holder. There are two methods for the preparation of a new holder which used as background. The first one is carried out by making adhesive layer on the warp and weft threads without clogging pores and spaces between the threads. The second is carried out by making the non-thick layer of adhesive on the holder.

2- Fixing the archaeological textile piece on the new cloth holder which previously prepared with the adhesive. There are four main methods used to fix the archaeological textile piece on the new holder. (1) By heating, (2) humidity, (3) activate the adhesive using poultice of its dissolvent (water or organic solvent)[67]. The later method takes about 10 minutes to complete the paste operation, which is done by permeating the solvent vapor through the holes in the Core -Tex to the new cloth holder which contains the adhesive. Thereby acting steam to activate the adhesive, a paste operation of the new holder with the archaeological textile piece is done without any penetration of the adhesive within the fibers. The pressure from the weight of the glass board helps to complete the paste operation well[66]. (4) By solutions of adhesives. The purpose of this method is to bind a single broken fiber from each other and to return the physical forces to the fibers or textiles by solutions of adhesives. This method is applied by using soaking or spraying with guns or by using a brush. In this case, the adhesive must be dissolved in an appropriate concentration of a suitable solvent to be able to penetrate enough into the fibers. Taking into account, when applying the method of consolidation by spray the strength of exit solution must be controlled to not weaken and deteriorate the fabric[41]. In This method of consolidation the selection of resin type depends on the fabric. There is no doubt that the silk textile needs resins which are different from the linen fabrics. As well as the main objective of consolidation plays a major role in choosing the type of the used resin and the methods of consolidation.

The most conservators prefer the method of consolidation by spraying, as they see it is giving an opportunity to build the polymer within the fiber of the textiles. Whether the consolidation is applied by soaking or spraying, should be extremely cautious in the application. It must not be implemented only after extensive study, as the used resins will penetrate into the fiber and cannot be removed completely. So it should use only those materials that have been proven successful in tests[66].

1.6.8. Displaying

The methods of displaying and storing archaeological flat textiles are Different than these used with the ancient three-dimensional textiles, such as tunics and dresses[57]. The most appropriate methods to display the archaeological flat textiles are:

1.6.8.A. Displaying under glass

This method is safe, easy and convenient to display the archaeological flat textiles, because it does not require several operations and archaeological textile be displayed readily without damage[51].

1.6.8.B. Displaying using a Nylon Net

This method is used for displaying flat, weak and fragile textiles. In this method the piece of fabric is placed between two layers of nylon network[57].

1.6.8.C. Displaying on a wooden frame

This is the easiest methods used in displaying the archaeological textiles. It is preferred in the case of controlling indoor air conditions of temperature, humidity and free from dust and pollutants. This method helps to ventilate the textile continuously which reduces the infection of textile with micro-organisms. On the other hand this method is not preferred in open places where there are Dust and dirt, which can be deposited within and between the woven fibers, which leads to damage and erosion of textile[57].

1.6.8.D. Displaying by Hanging with Velcro

This method is used with archaeological flat textiles which are light weight and in Good state. It is done by using the two faces Velcro tape, one of them is smooth and the other is rough which contains the adhesive[68].

1.6.9. Storing archaeological, flat textiles

There should be no difference between the quality of the displaying and of storage; both of them are useful for the archaeological textile piece. generally, the ideal storage areas must be on a high degree of cleanliness, temperature and humidity must be in the best grades between 16- 20°C of the temperature and about 50 - 55% relative humidity, the processes of conservation must be done continuously to ensure the safety of stored objects, the preservation of monuments within the stores must be organized and visible, because the effects of accumulation monuments lead to exposure them to further damage as the difficulty of access, and the impossibility of handling when need them. Avoid using plastic folders to store fabric, as the atmosphere inside the bags over time rise a temperature and humidity degrees, causing the growth of fungi. Preferably using a paper sheets treated with Fungicide within the content of textiles and cover the surface of archaeological textile with dark, neutral pH cloth or paper to prevent the effect of light and protect the surface of the accumulation of dust. Avoid using any wood in the storage of textiles especially cotton and linen, because wood contains acids, resulting in damaging the fibers. Storing the similar monuments together, because in the case of storing different materials together it could lead to damage one of them, such as storing of oak which gives the fumes of acetic acid next to fabric, this is lead to change the color and weaknesses of textiles. Scientific documentation of all stored archaeological artifact must be done to find and study them easily[67].

1.6.9.A. Flat Storage

Generally, this method is safe and easy to store flat textiles. A small flat textile pieces are placed on the shelves and drawers horizontally. There are different types of these cabinets and drawers, some of them are made of solid wood and others are made of special types of plastic. There are also some boxes and drawers are made of non-rust metal (stainless steel). Prefer to use stainless steel cabinets than wood cabinets .The drawers must be easy slide, shallow and the textile must be placed unfolded within drawers or on shelves[69].

1.6.9.B. Storing flat textile by folding

This method is the best method to store large textiles and mummy's wrappings. It allows storing a large amount of textiles in the very narrow space. In this method a circular cylinder or rod form is used to wrap the textile around it[76].

1.6.9.C. Storing flat textile by hanging

This method is used to store textiles which could not be wrap on a cylinders because they have folds or decoration or in the case of large size textiles which cannot be stored flat or on the shelves. Take into account when applying this method the textile piece would be hung on the warp yarn which is more strength and resistant, because the real weight of the fabric will be carried on these threads, otherwise the fibers will be damage over time[70].

1.7. References

---

[1] M.J. Herskovits, "Man and His works, the Science of Cultural Anthropology", 3rd ed., New York 402-420 (1952).

[2] J. Kathryn, "Scraps of Prehistoric Fabric Provide A View of Ancient Life" Ohio State University, London, 9-13(2005).

[3] C.M. Baldia, K.A. Jakes, "Photographic Methods to Detect Colorants in Archaeological Textiles," J. Archaeological Science 34: 519-525 (2007).

[4] E.A. Strand, K.M. Frei, M. Gleba, U. Mannering, M.L. Nosch, I. Skals, "Old Textiles New Possibilities", European J. Archaeology, 13:149, 150-173 (2010).

[5] S.D. McCafferty and G.G. Mccafferty, " Spinning and Weaving Tools from Santa Isabel, Nicaragua, Ancient Mesoamerica", J. Cambridge University Press, U.S.A. 19(1), 143–156 (2008).

[6] R. Good, "Archaeological Textiles: A Review of Current Research", Annual Review of Anthropology 30: 209-226 (2001).

[7] A. Anthony, W. Smith, "An Introduction to Textile Materials: Their Structure, Properties and Deterioration", Journal of the Society of Archivists 20(1), 25-39 (1999).

[8] G. Caton-Thompson, E.W. Gardner, "The Desert Fayum", 4th ed., London: Royal Anthropological Institute of Great Britain and Ireland, London 154-160 (1934).

[9] P.E. Newberry, "El Bersheh I, Beni Hassan I". EEF, G. Willoughby Fraser, London, (Vol: 2,3: part 1,2), 28-30 (1893).

[10] N.G. Davies,"Five Theban Toms," London: EES, 14: 55-70 (1913) .

[11] N.G. Davies, "Seven Private Tombs at Kurnah," New York: MMA, 8: 403-456 (1948).

[12] N.G. Davies, "Two Ramesside Tombs at Thebes," New York: MMA, 1: 621-633 (1927).

[13] P.T. Nicholson, I. Shaw, "Ancient Egyptian Materials and Technology," 1th ed., Cambridge University Press, 268-298 (2000).

[14] J. Dunn, "Ancient Coptic Christian Fabrics," J. American University in Cairo Press, 2: 187-207 (2002).

[15] R.J. Forbes, "Studies in Ancient Technology," Leiden, E.J. Brill, Netherlands 6: 27 -38 (1964).

[16] G.E. Bowen, "Texts and Textiles: A Study of the Textile Industry at Ancient Kellis", J. Anthropologica. 24: 18-28 (2001).

[17] C. A. Hop, G. Bowen, "Text & Textile: An Introduction to Wool-Working for Readers of Greek and Latin Supplementary", BACE, Oxford, 1-8 (1943).

[18] G.S. Beadle, "A Picture of Women Weaving in the History Art and Literature of Ancient Greece," The Costume Institute, J. The Metropolitan Museum of Art, New York 14: 166 (2007).

[19] S. Scaevola, M. Harlow, "Clothing in ancient Greece and Rome," Magazine History Today 52(1)12-18 (2008).

[20] R. Choeon, A. Kirstein, S. Layton, "Weavings from Roman, Byzantine and Islamic Egypt," The Board of Trustees University of Illinois, 51: 36-40 (1999).

---

[21] C. Biera, M.M. Dusenbury, “Textiles”, Magazine of The Oxford Asian Textile Group, 42: 213-217 (2009).

[22] H.L Sine-Gunnsdottir, J.M. James, “A Short History of Linen,” Janis M. James, 1-11 (2007).

[23] Z. Goffer, “Archaeological Chemistry”, 2nd ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 353-360 (2007).

[24] T.H.L. Ivegard Sask, “The Problem of Fixing Dye In Linen”, London, Thames and Hudson LTD.75-92 (1978).

[25] A. Lucas, “Ancient Egyptian Materials and Industries”, 4th ed., Edward Arnold & Co. London, 140-149 (1962).

[26] N. Evbryk, “How Products are Made”, Oxford University Press, 4: 214-224 (1996).

[27] E.J. Charles-Singer, A.R. Holmyard-Hall and T.I. Williams, “A history of Technology,” Oxford, Clarendon press, 2: 252-57 (1957).

[28] D.M. Catling, J.E. Grayson “Identification of Vegetable Fibres,” London: Archetype LTD. new ed., 125-130 (1998).

[29] J.A. Marshall, “The Identification of Flax, Hemp, Jute and Ramie in Textile Artifacts”. MSc. dissertation, University of Alberta, Dep. of Culture, 36-50 (1992).

[30] I.T. Hamilton, “Linen Textiles”, ISRN Biotechnology, 15(2) 30–34 (1986).

[31] S.K. David, M.T. Pailthorpe, “Classification of Textiles Fibres: Production, Structure, and Properties, In: Robertson J and Grieve M,” Forensic Examination of Fibers” New York, London, 132-155 (1999).

[32] J.W.S. Hearle, R.H. Peters, “Fibre Structure,” Textile Institute, Butterworths, London 35: 524-562 (1963).

[33] S.K. Batra, “Fibre Chemistry” in Handbook of Fibre Science and Technology, M. Lewin & E.M. Pearce, Marcel Dekker Inc., New York and Basel 6: 727-807 (1995).

[34] J. Cook, “Handbook of Textile Fibres: Natural Fibres”, 5th ed., Merrow Publishing Co. Ltd., Shildon, Co. Durham, UK. 79–117 (1984).

[35] H.R. Mauersberger, “Matthews Textile Fibres,” 6th ed., John Wiley & Sons Inc, New York, 283-299(1954).

[36] A. Dujardin, “Retting of Flax”, 2th ed., Flax Development Committee, Belfast 5: 281 (1948).

[37] M.A. Hann, “Innovation in Linen Manufacture,” Taylor & Francis Group 3: 24-30(2005).

[38] F. Sadov, M. Korchagin, A. Matetsky, “Chemical Technology of Fibrous Materials,” revised edition, MIR Publications, Moscow, USSR, 512-520 (1978).

[39] M. Eric, M. Jones, “Conservation Science, Heritage Materials”, The Royal society of Chemistry, Cambridge, UK. 43-55 (2006).

[40] E.J.W. Barber, “Prehistoric Textiles,” 4th ed., Princeton University Press, U.S.A, 374-385 (1992).

[41] N. Reddy, Y. Yang, “Properties and Potential Applications of Natural Cellulose Fibers from Cornhusks,” journal of The Royal Society of Chemistry (7)190-195 (2005).

[42] S. Pérez, W. Mackie, “Structure and Morphology of Cellulose,” in "Polysaccharides: Structural Diversity and Functional Versatility", Dimitriu Eds., Marcel Dekker, 641-68 (2001).

[43] S.J. Maills, W. Raymond, “The Organic Chemistry of Museum Object,” 1th ed., Butterworth- Heinemann, London 69-80 (1994).

---

[44] M. Lewin, E.M. Pearce, “Handbook of Fiber Chemistry”, 2nd ed., New York, Marcel Dekker Inc. 436-453 (1998).

[45] S. Deguchi, K. Tsujii, K. Horikoshi, C. Commun, “Cooking Cellulose in Hot And Compressed Water”, Chemical Communications, Cambridge, England 31: 3293–95 (2006).

[46] E. Princi, S. Vicini, E. Marsano, V. Trefiletti, “Influence of the Artificial Weathering on Thermal Stability of Paper-Based Materials,” Thermochimica Acta. 468: 27–34 (2008).

[47] K. Dieter, B. Heublein, H. Peter Fink, A. Bohn, “Cellulose: Fascinating Biopolymer and Sustainable Raw Material,” J. Polymer Science, 44: 3358-98 (2005).

[48] A. Naik, “Characterization of Natural Fibers: Experimental Method”, Euro Mediterranean Post- Graduate Advanced School, Italy 122-136 (2001).

[49] U. Mannering, G.R. Possnert, J. Heinemeier, M. Gleba, “Dating Danish Textiles and Skins from Bog Finds by Means of 14C AMS,” J. Archaeological Science 37: 261–268 (2010).

[50] M. Flury- Lemberg, “Textile Conservation and Research,” 2nd ed., The J. Paul Getty Trust, USA, 5-24 (1989)

[51] J. Smith, “Cleaning,” In Textile Conservation: Advances in Practice, 1th ed., Crafts Council Conservation Science Teaching Series, London, 342-360 (1983).

[52] H. Judith , H. De-Graff, “ Cleaning Ancient Textile”, In Conservation And Restoration of Textile , C.I.S.S.T, Lombardy Section, Milan , Italy, 612-620 (1980).

[53] K. Finch, G. Putnman, “The Care and Preservation of Textiles,” B.T. Batsford LTd, London, 213-228 (1985).

[54] W.D. Cook, L. Hillyer, “The Cleaning of Degraded Linen,” The Conservator London 20:1, 13-16 (1996).

[55] P. Singer, A. Wylie, “ The Conservation of A fourth Century Ad painted Egyptian Shroud,” In Conservator., London 19: 58-64 (1995).

[56] Sh. Landi, “The Textile Conservators Manual,” 2nd ed., Butter Worths, London 263-282 (1998).

[57] H. Morgan, P. Cruick Shank, “The Conservation of the Shroud of Resti an 18th Dynasty, Linen Book of the Dead”, Conservation in Ancient Egyptian Collections, London 23: 17-23 (1998).

[58] H.J. Plenderleith, A.E.A. Werner, “The Conservation of Antiquities and Works of Art,” 2nd ed., London, 189-164 (1971).

[59] E.R. Beecher; “The Conservation of Textile,” Cultural Property ICROM, UNESCO 14: 256-280 (1979).

[60] H. De-Graaf; “Some Recent Development In Cleaning Ancient Textile” In Conservation And Restoration of Textile , C.I.S.S.T, Lombardy Section, Milan , Italy 711-723, (1980).

[61] Y. Shashoua, “Investigation Into The Effects Of Cleaning Old, Dyed, Naturally Soiled Textiles By Aqueous Immersion, In: Preprints Of The 11th Triennial Meeting Of The ICOM COMMITTE For Conservation, Edinburgh 315-319 (1996).

[62] A. Harby, “Development of Biotechnological Process for Restoration of Historical Textiles,” PHD Thesis, (NTUA), School of chemical engineering 32-38 (2009).

[63] N. Carmona, M. Oujja, H. Roemich, M. Castillejo, “Laser Cleaning of 19th Century Congo Rattan Mats”, J. Applied Surface Science 257(23) 9935-9940 (2011).

---

[64] J.E. Leene, “Restoration and Preservation of Ancient Textiles, and Natural Science”, Recent Advances In Conservation”, IIC, Rome Conference, 132-190 (1963).

[65] M.A. Keyserlingk, “The Use of Adhesives In Textile Conservation”, In: ICOM Preprints, 9th Triennial Meeting, Dresden 35(9) 307-312 (1990).

[66] C.V. Horie, “Materials for Conservation – Organic Consolidates Adhesives and Coating,” 2nd ed.,Velson Horie, Elsevier LTD, 105-121(2010).

[67] M. Takami, “The Conservation of A Korean Painted Silk Banner, C: 1800: Paint Analysis and Support Via Solvent Reactivated Acrylic Adhesive”, 13th Triennial meeting of the ICOM Committee for Conservation, 747-754(2002).

[68] K.N. Smith, “Systems for Storage and Display Textiles”, In A practical Guide to the Conservation and Care Of Collections, Western Australian Museum 116-125 (1998).

[69] E.V. Johnson, “Museum Collections Storage”, UNESCO, United Nation 34-40 (1979).

[70] M. Cathy, “A Method of Mounting and Storing An Archeological Textile,” ICCROM Publication, London, 75-82(1990).

CHAPTER 2

Natural Dyes

2.1. Distinguishing between Dyed and Painted Fabrics

Two main methods for coloring textile materials are recognized in ancient times, dyeing and painting. By dyeing yarns fabrics are colored throughout to the same color, whereas by painting the textile material is given a colored design or pattern by using a mixture of a pigment and a binding medium and may be applied directly to the textiles or onto a painting ground[1].

In the process of dyeing, each fiber should be left with the dye uniformly distributed throughout its substance, rather than largely confined to its outer surface[2].

The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber[3]**.** It will also usually exhibit some substantively for the material being dyed and be absorbed from the aqueous solution. All dyestuffs are organic compounds, on the other hand pigments are generally inorganic compounds composed of particles that are insoluble in the application medium. They have no substantively for the material. Since the particles are too large to penetrate into the substrate, they are usually present on the substrate surface. The pigment is therefore easily removed unless fixed with an adhesive "binding media"[4,5].

Colour on textiles can be achieved by the use of organic or inorganic colorants, be pigment or dye, each requiring significantly different application techniques due to their physical properties, but also leaving specific chemical signatures behind. Pigments are large in molecular size and coat fibre surfaces while dye molecules are small enough to permeate the fibres with colour. Mineral pigments may be somewhat limited in range of composition while organic colorants may be more difficult to identify, not only because a single plant or animal source may yield multiple colour constituents, but also because these constituents decompose into many different components. Furthermore, a single colour constituent might be obtained from several different sources. Often colorants are combined and additional dyeing aids such as mordants, chelating agents, or pH-altering agents are added to aid in binding dye to the fibres[6].

2.2. Natural dyes

Dyes are organic coloured compounds which can bond to natural and synthetic fibers and make them colored[7].

Natural dyes, dyestuff and dyeing are as old as textiles themselves. Man has always been interested in colours, the art of dyeing has a long past and many of the dyes go back into prehistory[8].

Archaeologists have found a number of ancient pieces of dyed fabric and other evidence for ancient textile dyeing. Sheep's wool that was dyed red with madder and blue with indigo was found at Kahun, an Egyptian town for pyramid workers, dating to 1890 B.C. Egyptian tomb paintings at Beni Hasan also show nomadic people wearing multi-colored garments and shoes, and a model dating to 2000 B.C from the tomb of Meketra at Thebes shows a weaving workshop where cloth was dyed.

Fig.4.1. *Wall scene probably showing work in a dye shop, New Kingdom, Turin museum*

Ancient people may have gotten the idea to dye fabrics when they noticed stains on their clothing after eating or working with different plants, berries, and mollusks. They began to use these plants and animals to dye fabrics[9].

Ancient Egyptians and Ancient Indians were among the first people to perfect the dyeing process by recognizing which plants were most useful and what methods of dyeing produced the best results. The oldest known dyed fabric dates as far back as 6000 B.C. Several thousand years later more evidence appears of Ancient Egyptians that using plants to create natural dyes for their clothing. They are well known for creating several different red dyes and for inventing the process of mordanting[10,11].

Surviving textiles suggest that dyeing techniques were introduced into Egypt from Western Asia from the New kingdom onwards[1].

From Roman times the art of dyeing was well established in Egypt. Coptic textiles illustrate well the range of dyes being used in the late Roman, early Byzantine and early Islamic periods[12].

In the history of Greece[13], B. Curtius expresses his opinion that the art of dyeing fine woolen goods was brought to Greece from Phoenicia with the cult of Aphrodite. This assumption, which makes Phoenicia the original home of purple-dyeing, can only hold good for articles distinguished by artistic perfection, as the art of dyeing plain textiles with natural dyes had long been known to Greece. On more than one occasion Homer mentions dyed textiles in a manner which leaves no room for doubt[13]. Two Greek papyri, dating from about the third or fourth century A.D., which were found in Egypt, probably at Thebes, describe the process of dyeing and the natural of the colors used at that period[14].

Natural dyes have been widely used in textile and decorative products because of their beauties and effects on human beings since the ancient times[15]. A good quality dye was considered to be as valuable as precious metals like silver and gold[16].

Because of the wide range of colors possible with natural dyes, medieval and cultural dye recipes were carefully protected and rarely recorded so that dyers could maintain a competitive advantage over their competition. Unfortunately, when dyers switched to synthetic dyes, their knowledge of the traditional craft of natural dyes died with them[17].

2.2.1. Characterization of natural dyes

A dye can be defined as a highly coloured substance used to impart colour to an infinite variety of materials like textiles, paper, wood, varnishes, leather, ink, fur, foodstuff, cosmetics, medicine, toothpaste, etc. As far as the chemistry of dyes is concerned, a dye molecule has two principal chemical groups, viz. Chromophores and Auxochromes groups[8,18].

Chromophores groups are the special groups or structures causing colour in organic materials. They are usually an aromatic ring, is associated with the colouring property. It has unsaturated bonds such as $–C=C$, $=C=O$, $–C=S$, $=C–NH$, $–CH=N–$, $–N=N–$ and $–N=O$, whose number decides the intensity of the colour.

Auxochromic groups are functional groups which modify the light absorbance of the organic compound. Auxochromes shift the absorption of the compound to longer wavelengths of light and carry out a bathochromic effect, a hypsochromic effect is the name given to the reverse shift. The addition of amino, hydroxyl, carboxyl, alkyl groups and halogens to the chromophoric system of a molecule shift the colour from yellow to red, and from red to green, and are therefore bathochromic groups, an amide group causes a hypsochromic effect. The real colour of an organic molecule is determined by its chromophoric and auxochromic groups. Coloured organic compounds without sufficient polar auxochromic groups in their chemical structure (e.g. indigo) are non-water-soluble materials and cannot bond strongly to fibres. Dyestuffs are held in place mainly by secondary bonds (in certain cases salt linkages) between the polar groups of the substrate and the auxochromic groups of the dyestuff (e.g. direct or acid dyes). The presence of polar auxochromic groups makes a dyestuff water-soluble and suitable for fast dyeing[7].

2.2.2. Advantages and limitations of natural dyes

Natural dyes are less toxic, less polluting, less health hazardous, non-carcinogenic and non-poisonous. Added to this, they are harmonizing colours, gentle, soft and subtle, and create a restful effect. Above all, they are environment friendly and can be recycled after use.

Although natural dyes have several advantages, there are some limitations as well. Tedious extraction of coloring component from the raw material, low colour value and longer time make the cost of dyeing with natural dyes considerably higher than with synthetic dyes. Some of the natural dyes are fugitive and need a mordant for enhancement of their fastness properties. Some of the metallic mordents are hazardous. Also there are problems like difficulty in the collection of plants, lack of standardization, lack of availability of precise technical knowledge of extracting and dyeing technique and species availability. Tyrian purple is obtained from the rare Mediterranean mollusk *Murex brandavis*. In order to obtain 14.0 g of the dye about 1.200 mollusks are needed[8].

2.2.3. The main sources of natural dyes in the different period of ancient times

A wide variety of plant and animal sources are known as potential sources for the production of textile dyes[19.]

2.2.3.1. Vegetable or plant dyes

Vegetables dyes can be found in almost any plant. The dyes were extracted from the roots, trunk bark, and branches of trees, the stems, leaves, flowers, and fruits of plants. Historically, the most important were madder, woad, indigo, safflower, turmeric, saffron and henna. All the dyes obtained from natural sources are rather impure[3].

2.2.3.2. Animal dyes

One of the earliest and most important of the animal dyes came from several species of snails found along the shores of the Mediterranean. Animal dyes were extracted from the bodies of insects and mollusks, and the eggs of insects, as Kermes, Cochineal and Tyrian purple[20,21]

2.3. Classification of natural dyes

Dyestuffs can be classified according to their origin, "natural or synthetic", to their method of application, "mordant, direct, vat dyes", or according to the chemical class their chromophores belong to. They can also be classified on the basis of their color.

Classifying them accordingly to the application method gives information on the technologies and procedures adopted in the production of dyed textiles. Classifying dyes on the basis of the chemical class their chromophores belong to is useful for the analyst in order to choose the right sample extraction procedure to recover the chromophores from historical samples and to develop the right identification procedure[22].

2.4. The main classes of natural dyes according to their colours

2.4.1. Blue Dyes

The most common sources of the blue color of Egyptian textiles are indigofera species, such as indigo and the *Istis* species, such as woad. It is clear from New Kingdom finds, especially those from the tomb of Tutankhamon and the roughly contemporary workmen's village at Amarna that both dark and light blue yarns were available[1].

2.4.1.A. Indigo

History

The name indigo comes from the Roman term indicum, which means a product of India. This is somewhat of a misnomer since the plant is grown in many areas of the world, including Asia, Java, Japan, and Central America. Another ancient term for the dye is nil from which the Arabic term for blue, al-nil, is derived. The English word aniline comes from the same source.

Fig.5.1. *Indigofera plant*

The color indigo, often associated with political power or religious ritual, has held a significant place in many world civilizations such as Mesopotamia, Egypt, Greece, Rome, Mesoamerica, Iran, and Africa for thousands of years. The dye is first mentioned in a written source for Western Europe in the histories of Herodotus (writing around 450 B.C.), who described its use in the Mediterranean area. In the excavation of Thebes an indigo garment dating from 2500 B.C. was found, for example “furthermore”, the Hindu god Krishna is most often depicted in blue, human sacrifices were often painted blue in ancient Mayan culture, and the Virgin Mary is regularly imagined draped in blue clothes in Christian art.

The Romans used indigo as a pigment for painting and for medicinal and cosmetic purposes. It was a luxury item imported to the Mediterranean from India by Arab merchants[22].

The blue compound indigo is one of the oldest dyes known to humans. There is written evidence of use of indigo dating back 4.600 years[23]. The ancient Egyptian imported indigo from India and over a hundred years ago Thomson and Hera path identified it on ancient Egyptian fabrics, though unfortunately the date of the material is not stated[14].

Also indigo was a tattooing agent in Britain when Roman colonization occurred. For centuries indigo has been used to dye the uniforms of British and American sailors. The selection of blue apparently dates back to King George II and a meeting of British naval officers in 1745. The officers were directed to appear before the Admiralty, each wearing their favorite uniform. According to one story (described by William F. Leggett in Ancient and Medieval Dyes, 1944) an enterprising captain chose the blue colors used in the riding habit of the Duchess of Bedford, a favorite of the King, and who just happened to be the wife of the first Lord of the Admiralty[24].

A variety of plants have provided indigo throughout history, but most natural indigo is obtained from those in the genus *Indigofera*, fig.5.1., which are native to the tropics. In temperate climates indigo can also be obtained from woad (*Isatis tinctoria*). The plants of the genus *Indigofera* produce a much stronger dye that those of the *Isatis* (woad) family; however, dyer’s woad is much more easily cultivated and therefore more widely used than *Indigofera*, which needs a tropical climate[25].

Although the dye in both types of plants is the same, namely indigo, in the *Indigofera* plants the dye is about 30.0 times more concentrated than in woad plants[3].

Indigo blue has been traditionally extracted from the leaves and to some extent from the midribs of the plant. After the leaves and midribs have been collected, they are soaked in water, the mixture of water and plant tissue is then pounded into a paste that is left to ferment for a few days. Following the fermentation process, the liquor is filtered out of the solid residue and exposed to air; oxygen in the air oxidizes the dye, which precipitates out of solution as a powdery dark blue solid that is then separated by filtration from the liquid and finally dried.

Scientific Classification[26].

INDIGOFERA	
Kingdom	*Plantae*
Division	*Magnoliophyta*
Class	*Magnoliopsida*
Order	*Fabales*
Family	*Fabaceae*
Subfamily	*Faboideae*
Tribe	*Indigofereae*
Genus	*Indigofera*

Properties

Indigo ($C_{16}H_{10}N_2O_2$)[27], is an aromatic compound, Fig .5.2.,[28] derived from the precursor indole and along with the betalains. Indigo is one of the few notable nitrogen, containing pigments of plants[29].

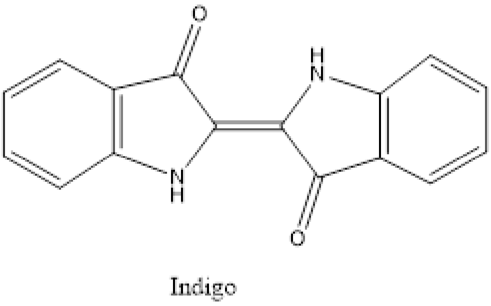


Fig.5.2. *Chemical structure of indigo dye*

The dye is composed of a mixture of two different organic substances: Indigo blue "indigotin" the major component, and small amounts of indigo red, chemically known as indirubin. Trace amounts of indirubin are probably present in all samples of the natural blue dye. Some indigo plant varieties, such as some from Java, are particularly rich in indirubin, containing as much as 6% indigo red[3].

The indigo possesses a number of properties which have not been incorporated in any other single dyestuff. These properties include its attractive shade, the ability to build up heavy navy shade, the dipping, the ability to dye cotton from a cold dye bath and good general fastness properties. The outstanding characteristic that makes indigo so special is its property of maintaining its tone after repeated severe washings and exposure to light .Although indigo dyed fabric can lose its depth of color, the tone is still pleasing. The fashion world calls it “that been-in-the-sun looks”[30].

Indigo was classified as vat dyes because they cannot be used for dyeing without prior chemical modification to make it soluble. Thus, during the dyeing process indigo is first chemically reduced (with an alkaline solution made from wood ash, plant ash, lime, or stale urine) to its colorless intermediate, *leuko indigo*, which is soluble in water. Yarn and/or textiles dipped in the colorless solution absorb the reduced leuko indigo, which, when exposed to air, is oxidized and yields the characteristic indigo blue color[11,31] that was not soluble in water, so it would not wash out of the fabric[9]**.** Most blues used in ancient Egypt would have been produced in this manner[1].

Indigo is odorless and non toxic, It is one of fastest dyes against photo oxidative fading, due to its high stability. Knowledge of the use of indigo as a dye is widespread in all cultures around the world, in the form of lumps; it was ground and applied with a binding medium. In some cases, it was adsorbed onto white chalk-containing clay: the most famous example of this practice is Blue Maya[22].

2.4.1.B. Woad

Dyer's wood (or glastum) is the common name of the flowering plant *Isatis tinctoria* in the family *Brassicaceae*.

History

The first archaeological finds of woad seeds date to the Neolithic and have been found in the French cave of l'Audoste, Bouches du Rhone (France). In the Iron Age settlement of the Heuneburg, Germany, impressions of the seeds have been found on pottery. The

Hallstatt burials of Hochdorf and Hohmichele contained textiles dyed with woad. It was used to dye the robes of the high priests of Jerusalem in Biblical times[20].

Woad was certainly cultivated in the Fayum province of Egypt in early Christian times, that is from the first to the fourth century A.D., and probably earlier and therefore, what has been assumed to have been Indian indigo on ancient Egyptian fabrics may have been woad, more particularly since Indian indigo, although known to the Romans of Plinys time was only used as a pigment for painting and not as a dye. Vitruvius (first century B.C.) mentions the scarcity of indigo and the use of woad as a substitute in painting. Pfister examined a large number of dyed woven woolen fabrics chiefly from Arsione Upper Egypt, ranging in date from the third century A.D. to the seventh on which he identified the blue color as woad[14]. Woad is a fascinating and tantalizing dye to use. It grows in southern Europe, in the temperate zone. In some parts of the world it is classed as a noxious weed. Woad was grown in the British Isles in Hampshire, the Midlands and Yorkshire and Ireland. In the eighteenth century Somerset and East Anglia became the main areas for woad cultivation. In Europe Woad is extensively used in place of Oriental Indigo, mostly in the textiles. In painting and illuminations it was often employed as surrogate of Azurite and Lapis lazuli. It originates from the fresh leaves of *Isatis tinctoria L*. and derives its hue from the Indigotin molecule[32]. Woad/indigo lakes are largely used in Russian icon painting and miniature, pure or combined with orpiment, verdigris, or verdigris and saffron to yield green[33].

Scientific Classification[34]

WOAD	
Kingdom	*Plantae*
(unranked)	*Angiosperms*
(unranked)	*Eudicots*
(unranked)	*Rosids*
Order	*Brassicales*
Family	*Brassicaceae*
Genus	*Isatis*
Species	*I. tinctoria*
Binomial name	*Isatis tinctoria*

Properties

Fig.5.3. Wood plant

Woad does not produce as much indigotin as indigo, though the chemical composition is the same. The woad plant is a biennial. Its leaves are pale green, growing on an erect stem which can reach over 1 m in height; there is a mass of yellow flowers, Fig.5.3. which turn to purple seed pods. A blue dye can be made from the green leaves of woad[31].

The dyeing powder is extracted from the leaves after a long and complicated treatment. The leaves are harvested at maturity from the basal rosette and are subsequently smashed or ground in mills in order to extract the pulp. The crushed leaves are sprinkled with water and the first fermentation takes place.

After this, they are rolled into small balls which can be stored and transported in this form. The desiccated balls of woad are thereafter ground with a quern or crushed with a mallet, then dampened with water and a second fermentation takes place. When dried, this paste called “a granat” represents the concentrated dyeing stuff, or pastel, which is ready for use[35].

The result was a dark clay substance which as the dye. It was used as the basis for many “sad colors” as the dark blue could be reduced to different shades and used as a fixer of other colors[36].

Recently, scientists have discovered woad might be used to prevent cancer, having more than 20.0 times the amount of glucobrassicin contained in broccoli. Young leaves when damaged can produce more glucobrassicin, up to 65.0 times as much[37,38].

2.4.2. Red Dyes

Quite a variety of red dyes of both vegetable and animal origin were used in antiquity, although only a few of them ever attained practical importance. Among these were madder of vegetable origin, probably the most widely used and in its heyday also the most important red dyes and kermes and cochineal, both derived from the bodies of insects[39,40].

2.4.2.1. Red vegetable Dyes

2.4.2.1.A. Madder

History

A bright red dye comes from a plant of the same name also known as "dyer's root"[20]. Historically, Madder (*Rubia tinctorum L.*) is one of the oldest and most used dyes in red lakes from antiquity to the nineteenth century, with ample geographical distribution, spanning Eastern and Western cultures[32].

It is also the most important red dye structures obtained from plants are based on the anthraquinone and naphthaquinone[41], Fig.6.1, 6.2.

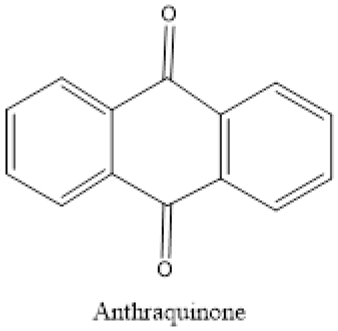


Fig.6.1. *Chemical structure of Anthraquinone*

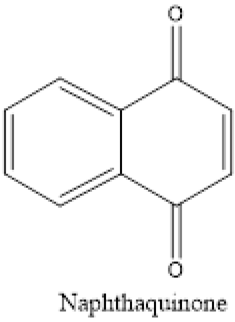


Fig.6.2. *Chemical structure of Naphthaquinone*

The dyes were obtained from the roots of different 35.0 species of the Rubiacea family including madder (*Rubia tinctorum L.*), Fig.6.3. This order found naturally in Palestine and Egypt, abundant in Asia and Europe, and extensively cultivated in the ancient world, was widely used for production of the dye since remote antiquity. The use of madder for dyeing seems to have originated in the Middle East: it was identified in many textiles found in Egyptian tombs and in woolen fabrics from the Judean Desert in Palestine[42,43].

Fig.6.3. *Madder plant*

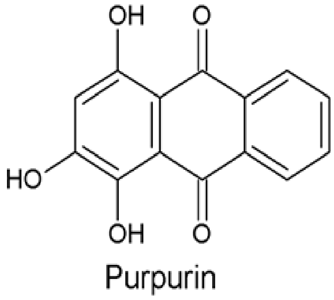
Ancient Egyptian mummies have been found wrapped in cloth dyed from the madder plant. Chemical test of red fabrics found in the tomb of King Tutankhamon in Egypt show the presence of alizarin[11,44]. It was also used by the ancient Persians, Greeks, and Romans. In the first dye trade document written in Greek, there is a record of trade in this root between India and Asia Minor. After the collapse of the Roman Empire in the fourth century A.D. and for almost eight centuries we know little of madder being grown in Europe[31]. Madder from other varieties of *Rubiacea* plants were used by the Incas in ancient Peru[42,43].

Scientific classification[45]

MADDER	
Kingdom	*Plantae*
(unranked)	*Angiosperms*
(unranked)	*Eudicots*
(unranked)	*Asterids*
Order	*Gentianales*
Family	*Rubiaceae*
Subfamily	*Rubioideae*
Tribe	*Rubieae*
Genus	*Rubia*

Properties

The chemical investigation of madder dates back to 1826. The identification of alizarin ($C_{14}H_8O_4$) an organic compound as the main chromophore of the dye extracted from *Rubia tinctorum*[9], and purpurin ($C_{14}H_8O_5$), Fig.6.4, 6.5[28], also an organic compound that resembles alizarin as the main one in the roots of *Rubiaceae* plants from South America[46].



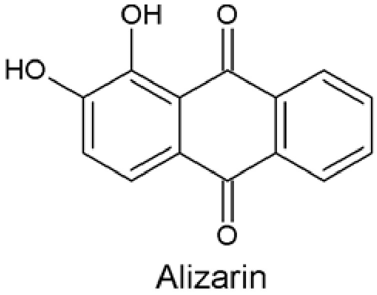


Fig. 6.4. *Chemical structure of purpurin* ***Fig. 6.5.*** *Chemical structure of Alizarin*

Madder, also known as Turkey red, is a scarlet dye extracted from perennial herbaceous plants of the order *Rubiacea*, of which there are about 35.0 species[39, 40]. The plant is varying in height from 1.0 to 3.0 meters[31]. The dye is concentrated mostly in the roots of the plants, older roots being richer in the dye than young ones. After removal from the soil the roots are washed with water, dried, and chopped. The dye is extracted from the plant tissue with hot water, in which it is soluble, but precipitates as a powder when the solution cools down. The powder is then separated from the liquor and finally dried.

Dyeing with madder yielded brilliant and permanent red, when the dye was used in conjunction with different mordant, however, it provided a variety of hues. Madder was also used for the preparation of red lakes, as for example, that applied to colored Greek terracotta statuettes[39,47] for many generations and up to the present time madder has also enjoyed popularity in the Middle East for its medicinal properties[48].

2.4.2.1.B. Henna

History

Henna is another ancient red dye of vegetable origin, which was not widely used for dyeing textiles but mainly for staining human hair, skin (mostly the hands), and nails. Henna is derived from the small shrub *Lawsonia inermis* and from other species of *Lawsonia* plants that are native to the Middle East, northern Africa, Persia (Iran), and India[49]. Henna has been used for body art and hair dye since the Bronze Age, henna has had a recent renaissance in body art due to improvements in cultivation, processing, and the Diasporas of people from traditional henna using regions[50].

An orange-red color on mummy wrappings of 21th Dynasty date, P.fister found to be due to henna, probably mixed with red color obtained from the flowers of Carthamus tinctorus[14].

Henna was used as a hair dye in Indian court records around 400 CE [50] and also some brides use henna to stain a beautifully intricate design on their hands. The Berbers of North Africa believe henna represents blood and fire, and that it links humankind to nature. Henna is used in Berber marriage ceremonies because it is thought that it has special seductive powers and that it symbolizes youth. Henna dye is used to stain leather and horses' hooves and manes[51].

In Rome during the Roman Empire, and in Spain during Convivienca**,** It was listed in the medical texts of the Ebers Papyrus (The Ebers Papyrus was written around 1550 B.C. in Thebes, Egypt) and by Ibn Qayyim al-Jawziyya (14th CCE (Syria and Egypt) as a medicinal herb[52,53]. In Morocco, wool is dyed and ornamented with henna, as are drumheads and other leather goods[51]**.**

Scientific Classification[54]

.

HENNA	
Kingdom	*Plantae*
Division	*Magnoliophyta*
Class	*Magnoliopsida*
Order	*Myrtales*
Family	*Lythraceae*
Genus	*Lawsonia*
Species	*L.inermis*
Binomial name	*Lawsonia inermis*

Properties

The dye is derived from the leaves of the plant *Lawsonia inermis*, Fig.7.1. To extract the dye, Lawsonia roots are soaked in water and ground into a paste, which is soluble in water and henna is, therefore, obtained as a powder, after filtering the solution and evaporating to dryness.

Fig.7.1. *One year old henna plant*

Since ancient times textile dyeing is commonly addressing wool or silk, and consists in boiling the powdered dry leaves even without mordant, except for the inherent tannins, in a slightly acidic water bath. Depending on tannin concentration, tints are reported to range from reddish brown to orange yellowish[55].

Henna yields bright orange hues when applied directly to fibers or textiles, but yellow or brown when applied in conjunction with different mordant[49], and also mixed with indigo or other plant material to obtain a greater color range[56].

The coloring matter in henna is the organic compound Lawsone ($C_{10}H_6O_3$) (2-hydroxy-1,4-naphthaquinone), Fig.7.2. a potential redox mediator in biochemical fuel cells. Its derivatives were already clinically proved to treat successfully cerebral toxoplasmosis in childhood and adult HIV infections and were tested as efficient inhibitors of the respiration of tumor cells[57].

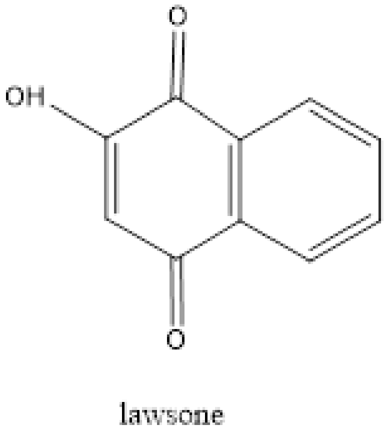


Fig7.2. *Chemical structure of Lawsone*

Other chemicals active in henna include the naphthaquinone juglone (also found in walnuts) several flavonoids and tannins. The leaves and young twigs are pulverized into a fine powder, sometimes with various other plant additives. This is then made into a paste with hot water and then spread or painted into designs on the area of skin to be dyed, usually be left overnight. The action of the active components when mixed with hot water and applied to hair seals the oils and tightens the hair cuticle giving a rich, healthy shine.

Medically henna has been used internally and externally for the treatment of jaundice, leprosy, smallpox and the fruit is thought to have properties that regulate menstruation. Henna extracts show antibacterial, antifungal, and ultraviolet light screening activity. The flowers possess a pleasant aroma and crude perfumes are produced in some major growing areas by preparing a suspension of comminuted flowers in vegetable oil[58,59].

2.4.2.2. Red insect dyes

The red dyes of scale insect origin are of great importance in the history of early textiles and lake pigments. They have received a good deal of attention in the last few years from the point of view of their specific insect origins (rather confused in the past) and their identification on textiles, for this can be valuable evidence for disputed questions of age and place of origin. The most important insect dyes are: kermes, Cochineal, and Lac[60,61].

2.4.2.2.A. Kermes

History

Kermes is a scarlet dye, it is probably the earliest one on which there are records. Derived from the insect *Kermococcus vermilia Planchon* (formerly known as *Coccus ilicis*), which lives on oak trees of the species *Quercus cocciferaea*. The insects are round, smaller than a pea**,** Fig.8.1. It is widely distributed in Armenia, the Middle East, northern Africa, and Spain. Kermes seems to have been the most important red dye known to the ancient Babylonians and was also used by the Egyptians, Greeks, Hebrews, and Phoenicians[62,63].

Fig.8.1. *Kermococcus vermilia Planchon insect*

Moses mentioned its use in Egypt, and other writers referred to it as captured booty in 1400 B.C. Kermes was the main insect red dye in Europe and in Asia, and when the shellfish purple dyeing declined it took its place in the garments worn by high clergymen. It was widely replaced by carminic acid, the major constituent of all cochineals, but the various species have characteristic fingerprints of anthraquinone, minor components (including the laccaic acids) which allow them to be distinguished in historical samples[48].

In ancient times, these insects were thought to be of a vegetable nature, and were used in medicine[14].

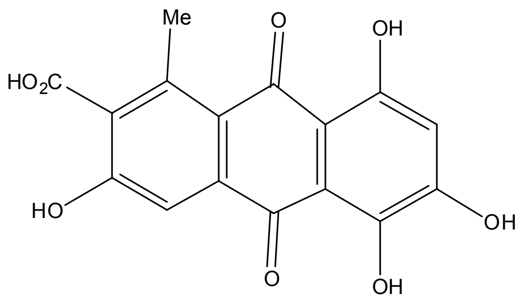
Scientific Classification[64]

KERMOCOCCUS VERMILIA INSECT	
Kingdom	*Animalia*
Phylum	*Arthropoda*
Class	*Insecta*
Order	*Hemiptera*
Family	*Kermesidae*
Genus	*Kermes*
Species	*K.vermilio*
Binomial name	*Kermes vermilio*

Properties

Kermes varied in color from bluish-red to brilliant scarlet depending on the mordant use[36]. To prepare the dye, the female insects are collected prior to hatching eggs and killed either by exposure to the vapors of vinegar or by immersion in a solution of vinegar in water. Crushing the bodies of the dead insects and then adding to them a vinegar–water solution results in the dissolution of the dye; when the water evaporates, kermes precipitates as a powdery residue[62,63].

The coloring matter in kermes is the organic compound kermesic acid (<70%) ($C_{16}H_{10}O_8$)[28,41] Fig.8.2.



Kermesic acid

Fig.8.2. *Chemical structure of kermesic acid*

The use of kermes was not restricted to the dyers alone, for in ancient times the extract was also used as a medicament. It was applied as astringent to wounds and as a cure for congestion of the eyes. The famous Arab doctor Abu ben-Masouiach, praised kermes as a medicine to stimulate the heart, and it was used in Europe until the 18th century as a cardiac drug. F. Silvestri, the great Italian entomologist, confirms that the most prescribed medicine during the 8th and 9th centuries was "Alkermes" (extract of kermes) and he commented that the colour and the aroma of the "liqueur" must have contributed to its effectiveness[65].

2.4.2.2.B. Cochineal

History

Fig.9.1. *Coccus cacti, insects*

Cochineal derived from the bodies of insects, was known for many centuries to the pre-Columbian inhabitants of the Americas. Its native habitat seems to have been Mexico, although there is evidence that it was also used for dyeing in Peru during the Inca period[66]. Cochineal was apparently unknown outside the American continent until the beginning of the sixteenth century, when following the Spanish conquest of Mexico, it was brought to Europe. It has been suggested, however, that a red dye similar to cochineal may have been derived from a variety of insects native to the Ararat valley in Turkey[60].

In ancient Mexico cochineal was extracted from the dried bodies of *Coccus cacti*, insects Fig. 9.1. which live on the cactus plant *Nopalea cochenillifera*.

Cochineal dye was used by the Aztec and Maya peoples of Central and North America and was first imported to Europe in the 1530s from Spanish conquests in America. Carmine was used as a dye and a lake pigment in ancient Egypt, Greece and near East and is one of the oldest organic pigments; Recipes for artist's use of carmine appear in many early painting and alchemical handbooks throughout the Middle Ages[67].

Scientific Classification[68]

COCCUS CACTI INSECTS	
Kingdom	*Animalia*
Phylum	*Arthropoda*
Class	*Insecta*
Order	*Hemiptera*
Family	*Dactylopiidae*
Genus	*Dactylopius*
Species	*D. coccus*
Binomial name	*Dactylopius coccus*

Properties

To obtain the dye, the insects were first collected, when the females were fully developed and just before the egg lying began, when they are about 90.0 -110.0 days old, the insects had to be harvested. This is the stage when their red dye content is highest. The collected insects are then killed, either by immersion in hot water followed by drying, or dried directly by exposure to the sun[65].

The dye which is soluble was then extracted from the dead insects by immersing them in water. After filtering out the exhausted solids from the solution, the water was evaporated and the dye was obtained as a red powder.

The little cochineal bug will give the most color when ground into a fine powder. Obtainable colors are dark burgundy to bright red to soft lilac and pink[30]. It took about 70,000 dried insects to make one pound of dye[24].

The coloring matter in cochineal is the organic compound carminic acid [$C_{22}H_{20}O_{13}$][41,63] Fig. 9.2.

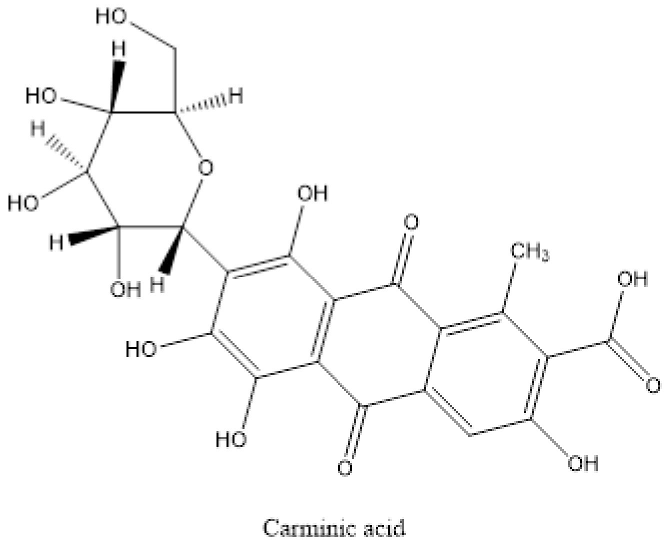


Fig.9.2. *Chemical structure of carminic acid*

Carminic acid (CA) is one of the best natural dyes from the technological point of view because it is fully soluble in water, stable against oxidation, light and high temperatures. It is highly appreciated by its good tinctorial qualities, and the colour hues can vary from red to yellow according to the pH value of the medium. It is extensively used in food, cosmetic and pharmaceutical industries, as well as in dyed handmade textile products. As an internationally allowed food colorant, CA is used in many products such as jams, ice cream, dairy products, canned food, meat products and beverages[69,70].

Carmine is one of the very few pigments considered safe enough for use in the cosmetics industry for hair and skin-care products, lipsticks, face powders, rouges, and blushes industry, these products the cochineal serves no directly useful purpose. Its use is to make the products more attractive and therefore to sell better, this it does very effectively[71,72]. A bright red dye and the stain carmine used in microbiology are often made from the carmine extract too[73].

2.4.2.2.C. Lac dye

History

Lac was a product not only of India but also of china and most other south-east Asian countries, and it was used in Middle Eastern countries from early times. It was well known in Egypt in early Arab times and it has been found in Persian and Egyptian carpets of the fifteenth and sixteenth centuries. It seems to have been extensively used in European dyeing practice only in the late eighteenth century, though cited in commercial documents from the fifteenth. It was later, like the other old world insect dyes largely displaced by cochineal[41].

Scientific Classification[74]

KERRIA LACCA INSECT	
Kingdom	*Animalia*
Phylum	*Arthropoda*
Class	*Insecta*
Order	*Hemiptera*
Suborder	*Sternorrhyncha*
Superfamily	*Coccoidea*
Family	*Kerriidea*
Genus	*Kerria*
Species	*K. lacca*
Binomial name	*Kerria lacca*

Properties

Fig.10.1. Kerria lacca insect

Lac is derived from lac resin, the hardened secretion of the lac insect, the only known resin of animal origin. The lac insect, *Kerria lacca*, Fig.10.1, formerly known as *Laccifer lacca*, is a natural parasite of a variety of trees in large areas of southern Asia. Three different products are derived from lac resin: lac dye, lac wax, and shellac.

To obtain the lac resin, twigs encrusted with the secretion of the insects are cut down from the trees, and then the incrustation is separated from the twigs, washed with water and filtered. The wax and shellac which are insoluble in water, remain as a solid residue of the filtration, while the soluble red dye (lac) is obtained as a powder when the water from the filtered solution is evaporated.

The coloring matter in lac dye is an organic compound known as laccaic acid[3, 41] Fig.10.2

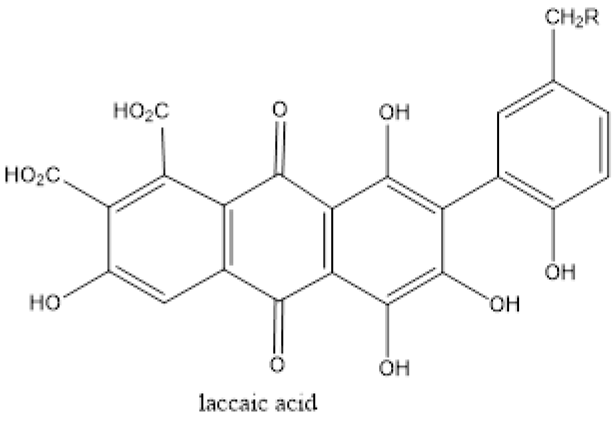


Fig.10.2. *Chemical structure of laccaic acid*

Lac is a natural polymer with atoxigenic, renewable and naturally degradable characteristics. Nowadays, more and more attentions are paid to environment protection and resource conservation. Also it is used in medicine as hepatoprotective and antiobesity drug[75].

2.4.2.2.D. Purple Dyes

History

Two dyes were extensively used in antiquity for dyeing purple: Archil and Tyrian purple. Archil, also known as argol or lichen purple, is derived, as its name suggests, from a variety of lichens. The best-known variety, *Lecanora tartara*, grows on rocks in many Mediterranean islands. The preparation of the dye entails a rather involved sequence of operations beginning with maceration of the lichens, followed by oxidation of the macerated product and then fermentation of the oxidized solution, during which a powdery residue is formed. The residue is archil which is finally dried. Tyrian purple also known as royal purple and purple of the ancients, was undoubtedly one of the most renowned and highly valued ancient dyes which had a high standing as a symbol of wealth and distinction. Cloth dyed with Tyrian purple was very costly and it seems that only royalty and priests could afford it[76,77]. During the early Roman Empire period, only kings and priests could wear purple dyed fabrics[48].

The production of Tyrian purple flourished, as the name suggests, in the ancient town of Tyre in southern Lebanon, on the shore of the eastern Mediterranean Sea. Quite accurate information about the importance of purple in the ancient world has long been available, but only during the twentieth century did its composition, the way it was produced and its true appearance become known in 331 B.C. Alexander finds 190.0 years old purple robes when he conquers Susa, the Persian capital. They were in the royal treasury and said to be worth $6 million (equivalent) which makes it priceless. During the 2nd and 3rd Century A.D. Roman graves found with madder and indigo dyed textiles, replacing the old Imperial Purple (purpura) which was too expensive for the average people. Because of that, a 3rd Century papyrus found in a grave contains the oldest dye recipe known for imitation purple called Stockholm Papyrus. It is a Greek work. In 273 A.D. Emperor Aurelius refused to let his wife buy a purpura-dyed silk garment. It cost its weight in gold. Late 4th Century Emperor Theodosium of Byzantium issued a decree forbidding the use of certain shades of purple except by the Imperial family on pain of death. During 400 A.D. *Murex "the* mollusk from which purple comes" becoming scarce due to huge demand and over harvesting for Romans. One pound of cloth dyed with Murex worth $20,000 in terms of our money today[77]. Because of the heavy demand for purple and its high price, many substitutes designed to either dilute the dye or imitate its color were used in the ancient world. Thus mixtures of indigo and other dyes that yield shades of purple were often used as substitutes. At the time of the decline of the Roman Empire the manufacture and use of Tyrian purple seems to have subsided being gradually replaced by dyes easier to produce, such as archil, kermes, and madder. It has been suggested that a purple dye similar in composition to Tyrian purple was produced in the South American continent from the mollusk *Purpura patula*[78,79,80].

Properties

Tyrian purple, also known as royal purple, shellfish purple, imperial purple or purple of the ancients, is an organic dye that has been used since antiquity and has an important historical value. It can be obtained from various species of mollusks, such as *Murex brandaris.M,* Fig.11.1, *trunculus, Purpura haemastoma and P. lapillus*; the dye is not present in the live mollusk, as it is generated by enzymatic hydrolysis of precursors found in the animal's hypobranchial glands, followed by photochemical conversion to the purple pigment[81].

Fig.11.1, *Murex brandaris,M mollusks*

The dye is one of the components of a colorless secretion, when the secretion is exposed to oxygen in the air and to solar radiation it acquires color, turning first yellow then green and finally purple[82].

Only very small amount of Tyrian purple, often less than 1.0 mg can be extracted from each mollusk, making this dye rare and costly. The main chromophore of Tyrian purple is organic compound 6,6'-dibromoindigotin ($C_{16}H_8Br_2N_2O_2$)[41] Fig.11.2.

but the different types of mollusks provide dyes of varying composition whose components can also include 6-monobromoindigotin and indigotin, some isatins as well as smaller amounts of indirubins[81,83].

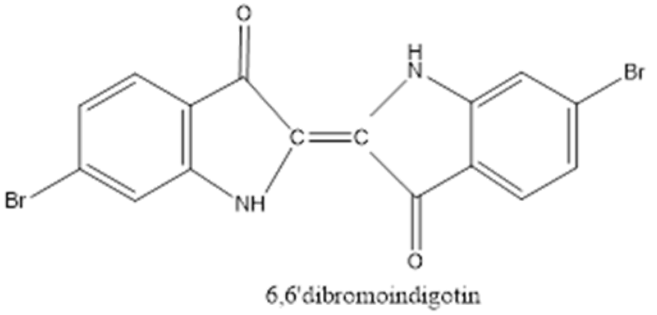


Fig.11.2. *Chemical structure of 6, 6'-dibromoindigotin*

The dyestuff was used in ancient times for both textile dyeing and pigment preparation.

Purple-dyed fabrics actually had a reddish shade tending toward violet[79]. Pharmacological inhibitors of GSK-3 which extract from Tyrian purple are being developed as potential drugs against diabetes, neurodegenerative diseases, cancer, inflammation, and infectious diseases[84].

2.4.3. Yellow Dyes

The natural yellow dyes are mostly flavonoids compounds, which are widely distributed in the vegetable world[41]. The basic skeleton of the flavonoid group of dyes is flavonol[7] Fig.12.1.

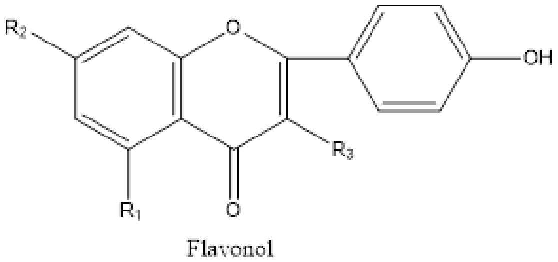


Fig.12.1. *Chemical structure of flavonol*

A number of yellow dyes were known in antiquity; weld and saffron seem to have been the most widely used, but barberry root, turmeric, Persian berries and safflower have also been identified in ancient fibers.

2.4.3.A. Saffron

The word saffron originated from the 12th-century old French term saffron, which derives from the Latin word *safranum*. *Safranum* is also related to the Italian zafferano and Spanish azafrán[85]. Safranum comes from the Arabic word aṣfar (أصْفَر), which means "yellow" via the Persian paronymous zaafarān (زَعْفَرَان) [86,87].

History

Saffron a rare and costly dye in antiquity as well as in modern times has been valued not only for dyeing textiles but also as a coloring and a fragrance in food[3].

The history of saffron in human cultivation and use reaches back more than 3.500 years and spans many cultures, continents and civilizations. Saffron is native to Southwest Asia, but was first cultivated in Greece[88].

Saffron has a long history of use as a direct dye. Evidence of its use dates back to Egyptian times, it was very popular in Persia in Classical times. It was later replaced by cheaper dyes, like weld, with better fastness properties[48]. Saffron played a significant role in the Greco-Roman classical period (8th century B.C. to the 3rd century A.D). However, the first known image of saffron in Greek culture is much older and stems from the Bronze Age. A saffron harvest is shown in the Knossos palace frescoes of Minoan Crete[89], which depict the flowers being picked by young girls and monkeys. The ancient Greeks and Romans also prized saffron for its use as a perfume and deodorizer. They scattered it about public spaces such as royal halls, courts and amphitheatres. When Emperor Nero entered Rome they spread saffron along the streets and wealthy Romans made daily use of saffron baths. In late Ptolemaic Egypt, Cleopatra used a quarter-cup of saffron in her warm baths because of its coloring and cosmetic properties. She also used it before encounters with men, believing that saffron would give lovemaking more pleasure. Egyptian healers used saffron as a treatment for all varieties of gastrointestinal ailments[90].

Scientific Classification[91]

SAFFRON	
Kingdom	*Plantae*
Order	*Asparagales*
Family	*Iridaceae*
Subfamily	*Crocoideae*
Genus	*Crocus*
Species	*C. sativus*
Binomial name	*Crocus sativus*

Properties:

Saffron is obtained from the stigmas of the flowers of *Crocus sativus L.* It is considered to be the most expensive world's spice. The flower of Crocus sativa is a light purple Fig.12.2 but it is the thread-like reddish colored stigma of the flower that is valued both as a spice and as a natural colorant. Saffron is hand harvested in the autumn and the stigma is laboriously separated to yield the reddish colored spice. It takes in excess of 70,000 flowers to yield just one pound (0.45 kilo) of saffron spice.

Fig.12.2. *Flower of Crocus sativa*

The odor of saffron is sometimes described as like the “sea” air. The natural color is a powerful yellow in applications such as for saffron rice[92].

The coloring matter in saffron is the organic compound crocin ($C_{20}H_{24}O_4$-glycoside) Fig.12.3 and crocetin[41,93] Fig.12.4.

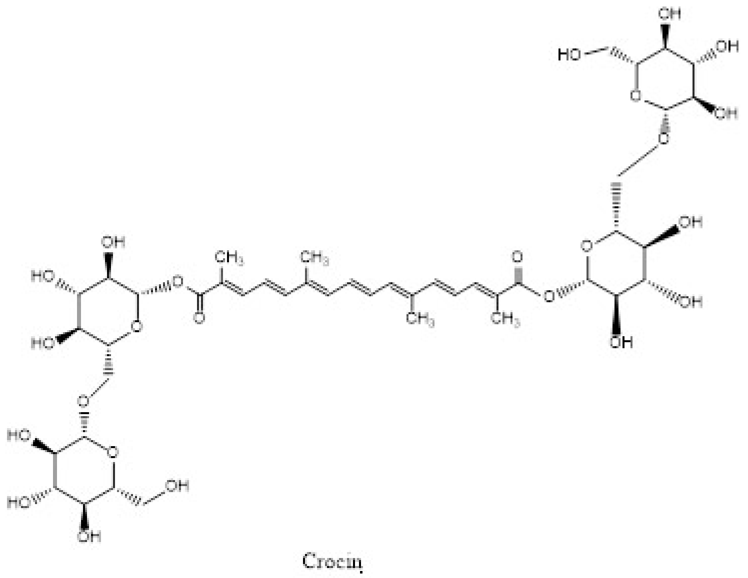


Fig.12.3. *Chemical structure of crocin*

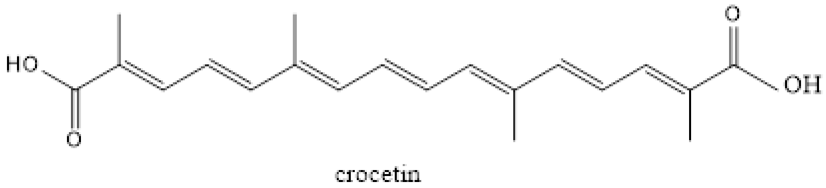


Fig.12.4. *Chemical structure of crocetin*

There are no references in the literature to the use of other parts of the plant, like leaves or petals, although the toxic effect of the bulb on animals has been described[94]. Because of its rarity and high cost, saffron was and still often replaced or adulterated with the more common safflower and/or turmeric[3,48].

Saffron is characterized by a bitter taste and an iodoform, or hay-like fragrance; these are caused by the chemicals picrocrocin Fig.12.5 and safranal. It also contains a carotenoid dye, crocin, which gives food a rich golden-yellow hue[86].

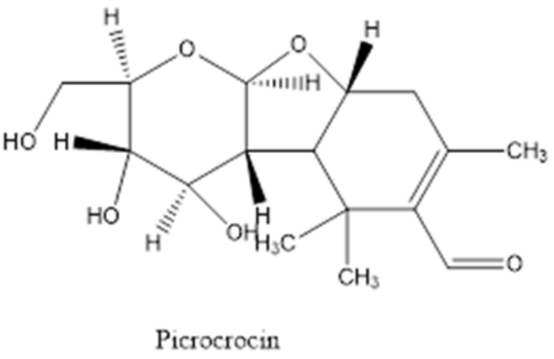


Fig.12.5. Chemical structure of picrocrocin

In addition, saffron contains proteins, sugars, carotenes-vitamins, flavonoids, amino acids, mineral matter, gums and other chemical compounds. These traits make saffron a much-sought ingredient in many foods worldwide[95]. Saffron also has medicinal applications. In general, the medicinal use of saffron has decreased in recent decades and its uses have been reduced to that of a dye and spice. According to some authors it is only used for its coloring properties. Independent of its use as a dye and scent, saffron is also of interest because of its vitamin content with a content of about 1.00 pg riboflavin; it constitutes a good source of this vitamin. There are many studies on saffron toxicity. Its innocuousness has been demonstrated by dixfSrent tests. The classic one reports a complete lack of toxic effects[24,94]. Advanced pharmacological studies have verified its anti tumor affects, free radical scavenging properties and hypolipaemic effects. It is useful in neurodegenerative disorders accompanying memory impairment[95].

2.4.3.B. Safflower

History

Safflower is one of humanity's oldest crops. Chemical analysis of ancient Egyptian textiles dated to the Twelfth dynasty identified dyes made from safflower and garlands made from safflowers were found in the tomb of the pharaoh Tutankhamon, also safflower seeds were placed in his tomb for him to use in the afterlife[10,11]. Many years ago Thomson suggested that the yellow dye of the ancient Egyptians was derived from the safflower, but he was unable to prove this, though it has since been established definitely by Hubner who identified it on fabrics of twelfth dynasty date. Hubner found also that another and slightly different shade of yellow of the same date was iron buff[14]. John Chadwick reports that the Greek name for safflower occurs many times in Linear B tablets, distinguished into two kinds: a white safflower which is measured and red which is weighed. The explanation is that there are two parts of the plant which can be used; the pale seeds and the red florets. Safflower was also known as carthamine in the 19th century. It is a minor crop today, with about 600,000 tons being produced commercially in more than sixty countries worldwide. India, United States and Mexico are the leading producers with Ethiopia, Kazakhstan, China, Argentina and Australia accounting for most of the remainder. Safflower has been cultivated since antiquity in Egypt and South East Asia and later in Europe. It is still cultivated but for the oil rich seeds rather than as a source of dye[48].

Scientific Classification[91]

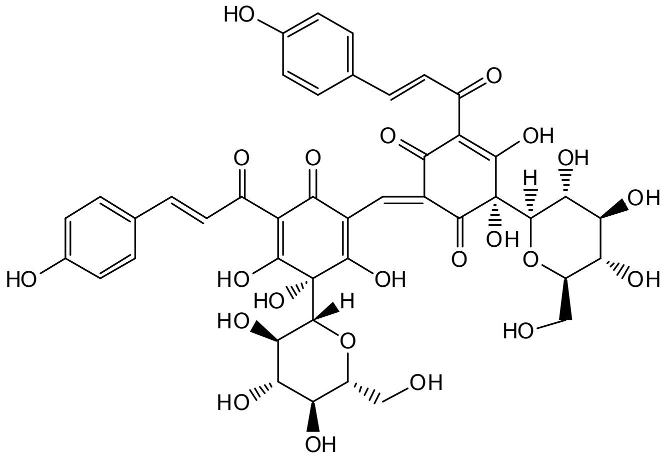
SAFFLOWER	
Kingdom	*Plantae*
(unranked)	*Angiosperms*
(unranked)	*Asterids*
Order	*Asterales*
Family	*Asteraceae*
Tribe	*Cynareae*
Genus	*Carthamus*
Species	*C. tinctorius*
Binomial name	*Carthamus tinctorius*

Properties

Safflower plant, Fig.13.1 is an annual plant, it grows to 1.0 m in height. It consists of a water soluble yellow and a water insoluble red component. This dye is found in the floret heads which are about 2.5 cm. The floret are carefully picked by hand, thoroughly dried in the sun or first washed to remove the fugitive yellow dye, thus leaving the insoluble red dye[31].

Fig.13.1. *Safflower plant*

The florets contain two different types of organic coloring matter: a red chromophore carthamin ($C_{43}H_{42}O_{22}$) Fig.13.2. has been used frequently for dyeing purposes; because of the beautiful pink shades it produces as a direct dye on silk.



Carthamin

Fig.13.2. Chemical structure of Carthamin

Carthamin was first isolated by Perkin and Kametaka in 1910[48], and a few yellow ones (safflower yellow A, safflower yellow B, and precarthamin) rarely used as dyeing materials with a mordant. These chromophores are very sensitive to sunlight, pH, and oxygen. Carthamin is hydrolyzed to carthamidin at low pH and bleaches when exposed to light[96,22].

2.4.3.C. Turmeric

History

Turmeric or curcuma, also known as Indian saffron, is obtained from the ground roots of *Curcuma domestica Valet*, or *Curcuma longa L.*) a plant growing abundantly in the East Indies and China. It was used as a direct dye on cotton, wool or silk, mainly in combination with other dyes[48].

The history of turmeric dates back to the pre-historic era and duly recognized in Ayurveda for their medicinal properties like antiseptic qualities for cuts, burns and bruises. The brides in India are also smeared with turmeric before their marriage to impart glow to their skin and make it impeccable. Turmeric became known as Indian Saffron, since it is widely used as an alternative to far more expensive saffron spice[97].

Scientific Classification[91]

TURMERIC	
Kingdom	*Plantae*
Order	*Zingiberales*
Family	*Zingiberaceae*
Genus	*Curcuma*
Species	*C. longa*
Binomial name	*Curcuma longa.*

Properties

Turmeric *(Curcuma longa*) is *a rhizomatous herbaceous perennial* plant Fig.14.1 which is native to Tropical South Asia. It needs temperatures between 20°C and 30°C, and a considerable amount of annual rainfall to thrive. Plants are gathered annually for their rhizomes and re-seeded from some of those rhizomes in the following season[98].

Fig.14.1. *Turmeric (Curcuma longa) plant.*

Its rhizomes are boiled for several hours and then dried in hot ovens, after which they are ground into a deep orange-yellow powder commonly used as a spice in curries and other South Asian and Middle Eastern cuisine for dyeing and to impart color to Mustard condiments. Its active ingredient is curcumin and it has an earthy, bitter, peppery flavor and a mustardy smell[99].

The coloring matter in turmeric is the organic compound curcumin ($C_{21}H_{20}O_6$)[28,48] . Fig. 14.2.

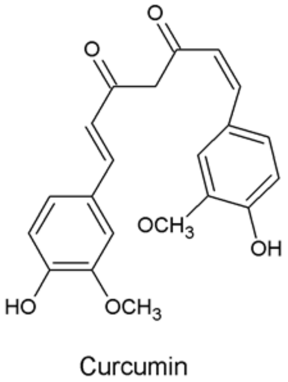


Fig.14.2. Chemical structure of curcumin

Curcumin is not very lightfast. Cotton, wool and silk may be dyed with curcuma without prior mordanting. Turmeric is thought to have many medicinal properties and many in India use it as a readily available antiseptic for cuts, burns and bruises. It is also used as an antibacterial agent. Safety evaluation studies indicate that turmeric is well tolerated at a very high dose without any toxic effects. Thus, both turmeric and curcumin have the potential for the development of modern medicine for the treatment of various diseases[100].

Turmeric is one such perennial herb. Its rhizomes and oils have great importance. It is extensively used as spice in domestic cooking. In combination with other natural dyes, it is also used as a coloring agent for textiles, pharmaceuticals, confectionary and cosmetics. In Indian system of medicine, turmeric rhizomes are used in stomachache, as a blood purifier, carminative, appetizer and tonic. Turmeric is also used in drugs against cancer, dermatitis and high cholesterol level. The essential oil extracted from turmeric also possesses anti-inflammatory, antifungal, antihepatotoxic and antiarthritic activities. It is also well known for its anti-carcinogenic, anti-microbial, anti-parasitic, anti-mutagenic, anti-inceptive and anti-cancer properties as well as for the formation of sunscreen[101].

2.4.3.D. Weld

History

Fig.15.1. Weld plant

Weld extracted from *Reseda lutea L.* is one of the oldest natural dyestuffs known in Europe and it has been used since the beginning of the Christian era to dye textiles and later on as an organic pigment in medieval manuscripts as well as in easel paintings[102]. During several Neolithic excavations a yellow dye was found, it was created from the seeds of *Reseda lutea*, more commonly known as the weld plant[11,26]. Fig.15.1. Weld plant also known as "dyers rocket" because of the speed and height that it grows to. It was originally from the Middle East, North Africa, and the Mediterranean area, but has subsequently spread throughout Europe and also was used in early Anatolian carpets alike. In the former case it was always the main yellow dye though after the discovery of America it was partially replaced by fustic[103].

The Romans dyed the robes of the Vestal Virgins and wedding clothing with this magic herb. It was a favored dye in Persia in the Dark Ages and widely use in Europe as a dye in the middle Ages. Weld is a more concentrated yellow dye than most dye flowers but was superseded by tropical dye plants after the European invasion of the New World[104].

Scientific Classification[91]

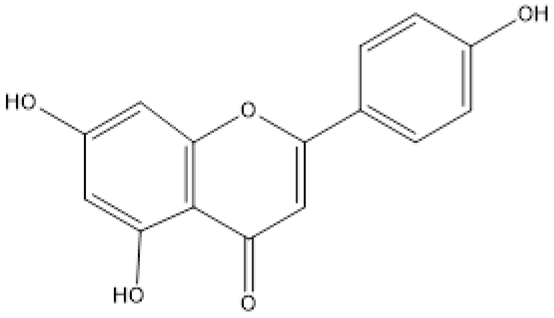
WELD	
Kingdom	*Plantae*
(unranked)	*Angiosperms*
(unranked)	*Rosids*
Order	*Brassicales*
Family	*Resedaceae*
Genus	*Reseda*
Species	*R. lutea*
Binomial name	*Reseda lutea*

Properties

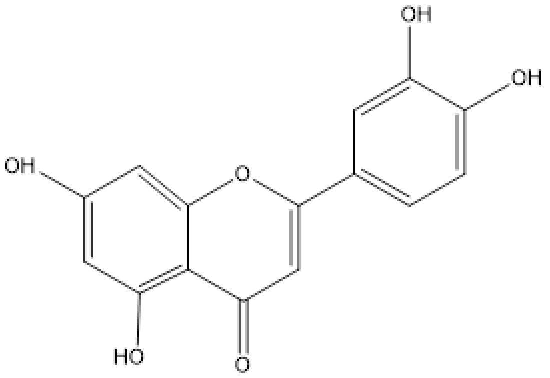
Weld is a weedy plant that was used in the past as a source for a brilliant yellow dye. It was harvested by cutting and binding the flowering stalks together after the flowers were nearly finished blooming. Apparently, most of the dye is contained in the seeds. The dye is distributed throughout the entire plant, although it is concentrated in the upper branches and seeds. To extract it, the leaves and stems of dried plants are washed with boiling water, in which the dye is soluble. After the solution cools, the dye precipitates as a yellow powder**.**

Dyeing with weld yields the purest and fastest shades of yellow used in conjunction with different mordants, however, it provides a variety of hues[3]. It gives a bright yellow with alum and tartar as mordant. With chrome it yields an old gold shade, with tin it produces more orange colored yellows, with copper and iron olive shades[48]. Weld was also frequently used with woad or indigo to give fast green dyes and mostly used to colour silk and wool[32].

Weld dyeing properties depend on the two main organic components luteolin (Lu) ($C_{15}H_{10}O_6$) and apigenin ($C_{15}H_{10}O_5$) (Ap) hydroxyflavonoids, Fig.15.2, 15.3 that are generally present in a ratio of about 9: 1.



Apigenin



luteolin

Fig.15.2, 15.3. *Chemical structure of luteolin and Apigenin*

In the last few decades, a growing interest on flavonoids has been demonstrated because of a large spectrum of biological and pharmaceutical properties such as their well-known antioxidant activity. Interestingly, in very recent applications, these natural dyes have been used as an alternative to synthetic photo-sensitizers in dye-sensitized solar cells. Despite the large number of experimental studies on the antioxidant properties of apigenin and luteolin, only a recent paper by Favaro et al., has reported an exhaustive spectrophotometric and fluorometric study of the two main components of the yellow color extracted from weld[104]

2.4.3.E. Fustic

History

Fig.16.1. *Chlorophora tinctorial tree*

Old fustic is the golden yellow wood of a large tree called Chlorophora tinctorial Fig.16.1 which grows wild in the West Indies and tropical America. It was first brought to Europe by the Spaniards at the beginning of the sixteenth century. Fustic is sold in the form of wooden chips. Old fustic and young fustic there may be confusion over these names. Young fustic *(rhus corinus or Venice sumach*) is growing in Italy and the south of France. The root and stem are used for dyeing a golden yellow to orange on wool mordanted with tin and the color is fugitive.

Old fustic is available ground or as wood chips and also as an extract[31].

Scientific Classification[91]

FUSTIC	
Kingdom	*Plantae*
(unranked)	*Angiosperms*
(unranked)	*Rosids*
Order	*Rosales*
Family	*Moraceae*
Tribe	*Moreae*
Genus	*Maclura*
Species	*M.tinctoria*

Properties

Morin is the main component of old fustic[41] Fig.16.2. Morin is an important bioactive compound by interacting with nucleic acids, enzymes and protein[105].

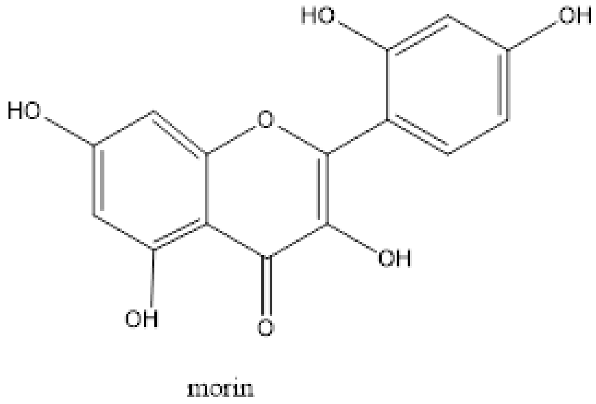


Fig.16.2. *Chemical structure of morin*

It is a flavone that exhibits antiproliferative, antitumor, and anti-inflammatory effects[106]. It yields a range of colors from strong dark yellows to an attractive peach color on silk, cotton and wool and it has good light-fastness[31].

2.4.3.F. Barberry root

History

Fig.17.1. *Berberis vulgaris*

Barberry root is a yellow–red dye that has been used since prehistoric times. The history of *berberis vulgaris* might be as old as barbarians but it is rather a sophisticated plant and is serving human in one way or the other. The Italians call the barberry Holy Thorn, because it is thought to have formed part of the Crown of Thorns[107]. *Berberis vulgaris,* Fig.17.1 is a deciduous shrub growing up to 4 m high. The leaves are small oval with a serrated margin; they are borne in clusters of 2-5 together, subtended by a three-branched spine 3-8 mm long. The flowers are yellow, the fruit is an oblong red berry, ripening in late summer or autumn and they are edible but very sour and rich in Vitamin C.

The dye is extracted with hot water from the stems, bark, and roots of *Berberis vulgaris*, a bush that grows indigenously in Europe as well as in North America.

Scientific Classification[91]

BARBERRY ROOT	
Kingdom	*Plantae*
Division	*Magnoliophyta*
Class	*Magnoliopsida*
Order	*Ranunculales*
Family	*Berberidaceae*
Genus	*Berberis*
Species	*B. vulgaris*
Binomial name	*Berberis vulgaris*

Properties

The coloring matter in the dye is the organic compound berberine ($C_{20}H_{19}O_5N$)[28] Fig.17.2.

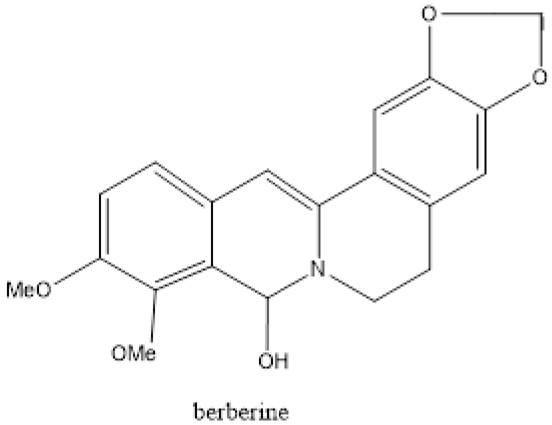


Fig.17.2. *Chemical structure of berberine*

Silk and wool can be dyed directly with barberry root, yielding a yellow color, however, for dyeing cotton, a mordant is required to attach the dye to the substrate fibers[3].

Barberries have long been used as an herbal remedy for the treatment of a variety of complaints. The main chemical constituent berberine possesses a wide range of biochemical and pharmacological activities, such as anti-diarrheal, anti-arrhythmic anti-inflammatory, fever reducing and analgesic (pain-reducing) effects[92].

2.4.4. Green Dyes

In addition to dyeing blues and reds, the ancient Egyptians also carried out a process called double dyeing (two layers dyeing or topping) where by the fibres, threads or cloth were first dyed one colour and then dyed again with a different dyestuff in order to obtain another colour[1].

It seems that no green dyes were known in the ancient world. Most ancient green colored textiles appear to have been obtained using mixtures of dyes having complementary colors, such as yellow and blue. Examination of green textiles from Egypt, for example, revealed that the color was obtained by mixing indigo blue with a yellow dye[108].

2.5.The main classes of dyes according to method of application

2.5.1. Direct dyes

Also known as substantive dyes are applied directly to the fiber in the aqueous solution in contact with the material[4].

Direct dyes bond to fibers with secondary bonds. They are usually large, linear, flat, water-soluble molecules. Direct dyes diffuse into the fibers from hot water solutions. The flat shape of this class of dye facilitates effective diffusion and gives them an affinity for cellulose fibers. Direct dyes are particularly suitable for dyeing cellulose fibers but rare for silk or wool, because the many polar hydroxyl side groups of the cellulose form hydrogen secondary bonds with the polar auxochromic groups of the dyestuff, while the non-polar parts of the planar molecule are kept in place by *van der Waals* forces[7].

Direct dyes usually are less wash and light-fast than vat or mordant dyes. Examples of direct dyes include madder (*Rubia tinctorum L.*), turmeric (*Curcuma longa*) and saffron (*Crocus sativus*)[48].

2.5.2. Vat dyes

Vat dyes are non-water-soluble dyes without sufficient auxochromic groups in the molecule[7]. Vat dyes derived their name from the container in which they were developed. A vat dye is also a substantive dye because it too requires no prepping of the fibers to be dyed. They were among some of the earliest dyes to be applied to fibers[3].

Vat dyes are water-insoluble but under alkaline reduction conditions, they can be converted into a water-soluble form is known as its “leuco” form. The leuco form of the dye diffuses into the fiber and when exposed to air it oxidized back to the original non-water-soluble dyes and these pigment aggregates are trapped in the fiber [48].

Indigo and woad are the most important examples of vat dyes in ancient times, urine provide the alkali and fruits provided the reducing agent. In industrial times sodium hydroxide (NaOH) and sodium dithionite ($Na_2S_2O_4$) have been used for the alkaline reduction. Changing in the chromophoric structure of indigo caused by the reduction reaction results in *leuco*-indigo, which is yellow. The yellow *leuco*-indigo penetrates the fibres and oxidizes back to blue indigo on exposure to air. Due to the absence of auxochromic groups, vat dyes bond to fibres mainly by *van der Waals* forces and some dipole bonds. Their good wash fastness is due to their limited water-solubility. They have poor wear resistance, as is well known from the ease with which the colour can be rubbed from the surface of indigo-dyed denim jeans. Some kinds of ancient purple, such as that from the mollusk *Phyllonotus trunculus*, were also applied as vat dyes[7].

2.5.3. Mordant dyes

Mordant dyes (the vast majority of natural dyes) require the treatment of the textile fibers with a solution of mordant (generally a metal salt). The auxochromic groups of several dyes are enable the formation of complex compounds with certain metal ions. They are called mono- di- and polyfunctional mordant dyes, depending on the number of auxochromic groups suitable for forming complexes with metal ions. The yarn or fabric can be impregnated with the aqueous solution of a metal salt, known as the mordant[7].

The mordant (whose name is derived from the French verb mordre meaning ‘to bite’) are substances mostly mineral salts or metal oxides, which form chemical bridges between dyes and dyed fibers[3]. This allows the cloth or yarn to accept the pigments from natural dyestuffs and encourages them to hold these pigments so they can accept color and remain fast[109].

When the pre-mordanted fabric was soaked in a hot bath of a suitable natural dye, the dye penetrated into the fibres and reacted with the metal ions present. This reaction formed the strong bonds between the dye and fibre by the metal ion, and also form a large complex molecule which result in decreased the water solubility of the dye so the colour was less likely to bleed out on washing[3,4,48]. The presence of certain functional groups in suitable position in the dye molecule causes its coordination to the metal ion. Generally, two hydroxyl groups or a hydroxyl group with a carbonyl, nitrous or azo group in adjacent position are responsible for coordination[110].

The mordanting treatment processes invented by Ancient Egyptians[26]. The exact period when Egyptians started to use mordants is open to doubt because the contaminants occurring naturally in the Egyptian sand can make it difficult to detect such substances[1].

Nevertheless, it is likely that the Egyptians used alum, which is a naturally occurring salt[1,14]. The large amount of aluminum and calcium in the colored linens from Tutankhamon’s tomb that have been analyzed suggest the use of aluminum and calcium salts as mordants[111].

In Roman times the ability to obtain multicolored effects by the use of different mordants was well established[14].

The type of mordant applied will determine the final colour of the dyed fabric[19]. The different mordants produce a wide range of hues from a single dyestuff of a remarkable resistance to wet treatments, but the shades lack brilliancy[116]. This explain how a dyeing workshop in the middle ages using no more than 10.0-12.0 natural dyes could produce a wide range of colours[7]. Madder *(Rubia tinctorum L.)* for example, dyes brick–red on aluminum, violet on iron and pink on a tin mordant. The colour is not only affected by pre-mordanting the textile fibre, mordanting after dyeing is also done and can result in a change of colour[112].

The light fastness is influenced by internal factors: the chemical and the physical state of dye, the dye concentration, the nature of the fibers, the mordant type. The light fastness of a dyed fiber usually increases with increasing dye concentration, the main cause being an increase in average size of the submicroscopic particles which the dye forms in the fiber. A Light fastness of dyes textiles is related to the chemical structure and physical characteristics of the fiber itself. Padfield and Landi stated that indigo is much more light resistant on wool than on cotton. The fastness of a mordant dye depends on the mordant and mordanting method, because different metal dye complexes are formed, which may differ in their stability to light and also because the metal may have a positive or negative catalytic effect on the photochemical degradation of the dye. Cox-Crews, in a study on 18.0 yellow natural dyes, concluded that the mordant is more important than the dye itself in determining the light fastness of colored textiles. Use of tin and alum mordant results in significantly more fading than when chrome, iron or copper ones are used. External factors such as the source and the intensity of illumination, the temperature and the humidity, the atmospheric pollution can affect the reaction as well[113].

The most common mordants are:

- Alum: (Aluminum Potassium Sulfate $AlK(SO_4)_2.12H_2O$).

This is the most widely used mordant. Be careful not to use too much with wool, otherwise you will get a sticky feeling that doesn't come out.

- Copper: (Copper Sulfate $CuSO_4$)

This mordant is used to bring out the greens in dyes. It will also darken the dye colors, similar to using tin, but is less harsh.

- Chrome: (Potassium Dichromate $K_2Cr_2O_7$)

Chrome brightens dye colors and is more commonly used with wool and mohair than with any other fiber.

- Iron: (Ferrous Sulfate FeO_4S)

Dulls and darkens dye colors. Using too much will make the fiber brittle

- **Tin:** (Stannous Chloride $SnCl_2. 2H_2O$).

Tin will give extra bright colors to reds, oranges and yellows on protein fibers. Using too much will make wool and silk brittle. To avoid this you can add a pinch of tin at the end of the dyeing time with fiber that was premordanted with alum. Tin is not commonly used with cellulose fibres[77,117].

The mordants may be applied to the substrate before dyeing (pre-mordanting) during dyeing (simultaneous mordanting) or after dyeing (post-mordanting). Premordants, as the mordant applied before the dyes are known, seem to have been the most commonly used in antiquity. Many dyers prefer to mordant a large quantity of textiles at a time, other dyers mordant only what they plan to dye or mordant while dyeing. Post-mordanting is used to shift hue and is usually used to achieve a color not possible with any other combination of dye or mordant[17]. Some mordants not only are instrumental in attaching the dye to the fibers but also alter the shade and even the hue of some dyes, a single dye often provides a range of hues when used with different mordants. The color or hue of textiles dyed with madder, weld and logwood for example, are determined by the chemical nature of the mordant used[3].

2.5.4. Acid (anionic) dyes

This class of dye has a strong affinity for the protonated amine groups of protein fibres. The name originates from the dyeing process, in which acids (usually acetic acid, occasionally sulphuric acid) are added to the dyebath. This is required to protonate the amino groups of polyamide fibres and the proteins of silk or wool fibres. The acid dye ionizes to a negatively charged anion in water, which can bond to the positively-charged protonated amino groups of protein fibres by salt linkages. In addition to the salt linkages, hydrogen, dipole and van der Waal bonds are also formed between the dye and the fibre polymer.

Most modern acid dyes are applied in the form of their sodium salt, which can be easily ionized. The majority of natural plant and insect dyes can be applied as acid (anionic) dyes.

2.5.5. Basic (cationic) dyes

Basic dyes ionize in water to cations, and show great affinity to the ionized carboxyl groups of protein fibres. Neutral or slightly alkaline conditions promote the ionization of the carboxyl end and side groups of proteins into negatively charged groups. This can be achieved at a pH above the isoelectric region of the protein fibres of silk or wool. A buffer of acetic acid and sodium acetate is added to the dyebath to provide a slightly alkaline pH.

Many modern basic dyes become positive ions after the ionization of the halogen ion attached to their positively charged protonated amino groups.

In the dyeing process, salt linkages are formed between the negatively charged carboxyl residue and the positively charged ion of the dye.

The only natural dye that belongs to this dye class is berberine. Cellulose fibres can be dyed with basic dyes after having been impregnated with tannins (Gallic and ellagic acid), which provide the ionizable carboxyl groups in the material.

2.5.6. Oxidation dyes

Oxidation dyes are colourless compounds or compounds with a pale colour, they form coloured dyestuffs during the dyeing process of the fibre, the most important group of synthetic amines in the presence of oxidizing agents and catalysts. One of the best known oxidation dyes is Aniline black.

The ancient purple of the mollusk was applied as an oxidation dye. It has been found that a blue intermediate product developed from precursors present in the juice by enzymatic oxidative and photochemical reactions, dyed wool from an acid dyebath, it then oxidized to the reddish-purple colour typical of dibromindigotin.

2.5.7. Reactive dyes

The very high wash fastness of reactive dyes is due to the covalent bond formed between the dye and the fibre during dyeing. The chromophoric part can be an azo compound or an anthraquinone; it can also be a premordanted or a phthalocyanine compound. The bridge couples the chromophoric part and the reactive group. The reactive group can undergo a substitution or addition reaction with suitable functional groups of the fibre. Reactive dyes containing unsaturated reactive groups are used to facilitate the addition reaction. Dyeing with reactive dyes is carried out in three main steps:

1- Diffusion of the dye onto the fibre in the presence of salt.

2- Reaction by the addition of an alkali, e.g. sodium carbonate.

3- Washing off the hydrolysed but not reacted dye.

2.5.8. Disperse dyes

Disperse dyes were developed for acetate fibres. They are small, non-water-soluble or slightly water-soluble coloured compounds. The finely ground dye can be used from its dispersion, and is usually effective with synthetic fibres, which can resist the high temperature required by the dyeing process. There is a wide range of disperse dyes; those with azo chromophoric structures are well known[7].

2.6. The process of dyeing

Dyeing can be carried out at any of the following stages in the textile manufacturing stage:

1- The fibers can be dyed before they are spun. Fiber dyeing provides a deep penetration of the dye into the fiber, giving even color and excellent color-fastness.

2- The yarn can be dyed after spinning but before the product is woven or otherwise fabricated. This is called package dyeing.

3- Before the fabric is finished, it can be dyed in lengths (piece dyeing).This process allows manufacturers the opportunity to produce fabrics in their natural colors, and then dye them to order.

In cross-dyeing, fabrics of two or more fibers can be dyed so that each fiber accepts a different dyestuff and becomes a different color, through the use of appropriate dyestuffs for each fiber. The ancient literature is “with rather few exceptions” tacit about dyeing and dyers[114]. It is essential for the correct identification of the fiber or other fabric to be made before dyeing commences[115].

Fig.18.1. *Dyed linen tunic of Tutankhamon, No. JE 62625, Egyptian museum, New kingdom.*

Fig.18.2. *Piece of dyed Linen textiles, JE 59117- SR 4 / 2133, Egyptian museum, Greco-Roman periods, Saqqara.*

Fig.18.3. *Fragment of undyed and polychrome linen cloth with inscriptions, New kingdom, 18th dynasty, reign of Thutmose IV, Egyptian museum, Cairo, JE 46527.*

Fig.18.4. *Child's tunic, dyed linen, 6th-7th centuries, No.1522-1899, Coptic museum, Egypt.*

Fig.18.5. *Shirt, polychrome wool and undyed linen, tapestry woven, TM 169, Coptic museum.*

Fig.18.6. *Tunic, dyed wool and undyed linen, Byzantine period, 4th century A.D. JE 65775, Egyptian museum, Cairo.*

2.9. References

---

[1] P.T. Nicholson, I. Shaw, “Ancient Egyptian Materials and Technology”, 1th ed., Cambridge University Press, 104-119 (2000).

[2] A.W. Smith, “An Introduction to Textile Materials: Their Structure, Properties and Deterioration”, Journal of the Society of Archivists 20(1) 25-39(1999).

[3] Z. Goffer, “Archaeological Chemistry”, 2nd ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 365-378 (2007).

[4] A.D. Broadbent, “Basic Principles of Textile Coloration”, 1th ed., Society of Dyers and Colorists, 210-234 (2001).

[5] X. Zhang, R. Laursen, “Application of LC–MS to the Analysis of Dyes in Objects of Historical Interest,” International Journal of Mass Spectrometry 284: 108–114 (2009).

[6] C.M. Baldia, K.A. Jakes, “Photographic Methods to Detect Colorants in Archaeological Textiles,” J. Archaeological Science 34: 519-525 (2007).

[7] A. Timar-Balazy, D. Eastop, “Chemical Principles of Textile Conservation”, 1th ed., Butterworth-Heinemann, London, 67-97 (1998).

[8] R. Siva, “Status of Natural Dyes and Dye-Yielding Plants in India”, Review Articles, Vellore Institute of Technology, India, Current Science 92(7) 916-924 (2007).

[9] L. Fruen, “Ancient Dyes” in The Real World of Chemistry,” 6th, Hunt Publishing (5)7872-9677 (2002).

[10] H. Abrams, “Colors: The Story of Dyes and Pigments,” 1th ed., New York: Harry N. Abrams, 13-35 (2000).

[11] C. Sandall, “Abrief Englightenment on Natural Dyes”, Technology and Science, Archetype, 213-221 (2007).

[12] J. Wouters, “Dye Analysis in a Broad Perspective: a Study of 3rd to 10th Century Coptic Textiles from Belgian Private Collections”, in: Dyes in History and Archaeology 13: 38-45(1994).

[13] G.A. Faber, “Dyeing and Tanning in Classical Antiquity,” Ciba Review, Basle 4 (1938).

[14] A. Lucas, “Ancient Egyptian Materials and Industries “, 4th ed., Edward Arnold & Co., London, 150-259 (1962).

[15] A. kbari, “Natural Dyes”, 2nd ed., Technology and Science, Archetype Publications 312-323 (2007).

[16] K.M. Frei , I.V. Berghe, R. Frei, U. Mannering, H. Lyngstrøm, “Removal of Natural Organic Dyes From Wool Implications For Ancient Textile Provenance Studies”, J. Archaeological Science 37: 2136-2145 (2010).

[17] S. Kadolph, “Natural Dyes: A Traditional Craft Experiencing New Attention”, International Journal for Professional Educators 75(1) 14-17 (2008).

[18] K.V. Krishnamurthy, “Methods in Cell Wall Cytochemistry”, 6th ed., CRC Press, Boca Raton, 413-430 (1999).

[19] V. Berghe , M. Gleba , U. Mannering, “Towards the Identification Of Dyestuffs In Early Iron Age Scandinavian Peat Bog Textiles,” J. Archaeological Science 36 :1910-1921(2009).

---

[20] J. Poulin, “Natural Dyes”, J. Canadian Association for Conservation 32: 48-56 (2007).

[21] D. Corinne, “The Story of Dyes and Dyeing,” J. Chem. Ed., 26: 583-87 (1949).

[22] I. Degano, E. Ribechini, F. Modugno, and M.P. Colombini,” Analytical Methods for the Characterization of Organic Dyes in Artworks and in Historical Textiles,” Applied Spectroscopy Reviews, 44: 363-410, (2010).

[23] W.D. Cooke, A. Brennan,“The Spinning of Fine Royal or Byssos Linen”. Archaeological Textiles Newsletter, 28: 2390-97 (1990).

[24] H. Gram, “Natural Dyes”, J. American Botanical Council (32)30, 1513-1523 (1994).

[25] G. Smith, Beer, “A History of Suds and Civilization from Mesopotamia to Microbreweries,”1th ed., Avon, New York, 230-238 (1995).

[26] R. Kamal, M. Mangla, “Cancer Chemopreventive Activity of Rotenoids from Derris Trifoliate”, Journal of biosciences 18: 93-101(1993).

[27] J.H. Robin Clark,” Pigment Identification by Spectroscopic Means: An Arts/Science Interface”, Académie des sciences / Éditions scientifiques et médicales Elsevier SAS. 5 : 7-20 (2002).

[28] Z.C. Koren, “Dyes in History and Archaeology”, Textile Research Associates York, 13: 27-30 (1994).

[29] K.M. Davies, “Plant Pigments and Their Manipulation”, Blackwell Publishing Ltd.14: 1460-1494 (2004).

[30] H. Wickens, “Natural Dyes for Spinners and Weavers”, BT Batsford Limited, London. 5: 92-96 (1993).

[31] C. Robin, “Links to Naturally Dyed Textile Sources. Natural Dyes International, 28: 342-350 (2007).

[32] S. Acquaviva, E. D’Anna, M.L. De Giorgi, A. Della Patria & P. Baraldi, “Physical and Chemical Investigations on Natural Dyes,” Applied Physics A, 100: 823–828 (2010).

[33] E. Kampasakali, V. Evangelia, “The Russian Avant-Garde Painting Palette: Documentary and Physicochemical Codification of Organic Colorants,” J. Cultural Heritage 9: 1-108 (2008).

[34] E. Mayr, W.J.Bock, , “Classification and Other Ordering Systems”, J. zool. Syst. Evol. Research, 40(4) 169-194 (2002).

[35] V. Zech-Matterne, L. Leconte, “ New Archaeobotanical Finds of Isatis Tinctoria L. (woad) from Iron Age Gaul and A Discussion of The Importance of Woad in Ancient Time,” J. Archaeobot. 19: 137–142 (2010).

[36] D. Corinne, “The Story of Dyes and Dyeing,” J. Chem. Ed., 26: 583-87(1979).

[37] J. Jacobs, “Ecology and Management of Dyer’s Woad (*Isatis tinctoria L.*)” 1th ed., Bozeman, Mt. U.S. Dept. of Agriculture, Natural Resources Conservation Service, USA. 165-180 (2007).

[38] C. Hall, “Celts’ Warpaint May be Weapon to Beat Cancer,” J. of Med. Science 14: 367-371(2006).

[39] M. Farnsworth, “Red madder dye”, J. Chem. Educ. 28: 72–78 (1951).

[40] R. Chenciner, “Madder Red: A History of Luxury and Trade”, 1th ed., Curzon, Richmond, 235-250 (2001)

[41] S. John, and W. Raymond, “The organic Chemistry of Museum Objects”, 2nd ed., Butterworth-Heinemann Ltd. 141-155 (1994).

[42] L. Fieser, “Alizarin”, J. Chem. Educ. 7: 2609–2611(1930).

[43] G. Schaefer, “Madder”, Ciba Rev., 5: 407-417(1941).

[44] J.H. Hofenk-de Graaff, “Natural Dyestuffs for Textile Materials: Origin, Chemical Constitution, Identification” ICOM Committee for Museum Laboratories, Brussels 3: 165-175 (1967).

---

[45] W.W. Robbins, T.E. Weier, et al., “Botany: Plant Science”, 3rd ed., Wiley International, New York, 215-237(1965).

[46] G.A. Fester, “Madder”, Isis 44: 13-17(1953).

[47] D.H. Abrahams, A.M. Edelstein, “A New Method for the Analysis of Ancient Dyed Textiles in Levey,” Archaeological Chemistry- a Symposium, Univ. Pennsylvania, Philadelphia 3: 15-27 (1967).

[48] S.B.E. Ferreira, A. Alison, N. Hulme, M.N. Hamish and A. Quye, “The Natural Constituents of Historical Textile Dyes”, Chem. Soc. Rev. 33: 329-336 (2004).

[49] B. Cox, “Henna”, the Analyst, RSC Journals Archive 63: 397 (1938).

[50] C. Bryan, “Ancient Egyptian Medicine,”2nd ed., The Papyrus Ebers Ares Publishers Inc. Chicago, 161-132 (1974).

[51] S. Kumar, Y.V. Singh, M. Singh, “Agro-History, Uses, Ecology and Distribution of Henna (*Lawsonia inermis L. syn. Alba Lam*) Henna Cultivation, Improvement and Trade”. Jodhpur, India: Central Arid Zone Research Institute, 11-17 (2005).

[52] I.Q. Al-Jawziyya, “Medicine of the Prophet, The Islamic Texts Society”1th ed., translation by P. Johnstone, Cambridge, UK. 71-86 (1998).

[53] P. K. Roy, M. Singh, P. Tewari, “Composition of Henna Powder, Quality Parameters and Changing Trends in its Usage Henna, Cultivation, Improvement and Trade”, Jodhpur, India, Central Arid Zone Research Institute, 39-42 (2005).

[54] The Encyclopedia of Plants and Flowers on Botany.com

[55] E. Mikropoulou, E. Tsatsaroni, V. Evangelia , “ Revival of Traditional European Dyeing Techniques Yellow and Red Colorants”, J. Cultural Heritage 10: 447-460 (2009)

[56] M. Singh, S. K. Jindal & D. Singh, “Natural Variability, Propagation, Phenology and Reproductive Biology of Henna, Cultivation, Improvement and Trade”, Jodhpur, India, Central Arid Zone Research Institute, 23-34 (2005).

[57] H. Rostkowska, M. J. Nowak, L. Lapinski and L. Adamowicz, “Molecular-Structure and Infrared-Spectra Of 2-Hydroxy-1,4-Naphthoquinone - Experimental Matrix-Isolation and Theoretical Hartree-Fock and Post-Hartree-Fock Study,” Spectrochim Acta A 54(8) 1091-1103 (1998).

[58] J.E. Simon, A.F. Chadwick and L.E. Craker, “Scientific Analysis on Henna Family,” in the scientific Literature on selected herbs, Aromatic and Medicinal plants of the Temperate Zone. Archon Books, Hamden, CT. Herbs, 770 (1984).

[59] A. Bosoglu, F. Birdane, H. Solmaz, “The Effect of Henna (Folium Lawsonia) Paste in Ringworm in Calves Department of Internal Medicine, Faculty of Veterinary Medicine, Selcuk University, Konya, Turkiye Indian Veterinary Journal 75: 1403-1412(1998).

[60] A.Verheckena, j.Wouters, “The Coccid Insect Dyes, Historical, Geographical and Technical Data”, Institute Royal du Pahimoine Artistique, Bulletin, 22: 207-239 (1988-1989).

[61] J. Wouters, A. Verhecwna, “The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarns’ Stud. Conserv. 34: 189-200(1989).

[62] O. Dimroth, W. Scheurer, “Kermes”, J. Analytical Chemistry 399: 43-61 (1913).

---

[63] H. Schweppe, R. Runge, “Carmine: Cochineal Carmine and Kermes”, in Feller, R. E. (ed.), Artists Pigments, Cambridge Univ. Press, New York, 225–283(1986).

[64] American Heritage Dictionary s.v. *Kermes*, Kluge.

[65] F.L.C. Baranyovits, “Cochineal Carmine: An Ancient Dye with A Modern Role,” Pergamen Press Ltd. Endeavor (N.S.) Great Britain 2: 85-92 (1978).

[66] B. Dahlgren, “La Grana Cochinilla”, UNAM, México. Historia verdadera de la conquista de la Nueva España. Editorial Promolibro, Madrid 4: 35-38 (1990).

[67] M. Koperska, T. Lojewski and J. Lojewska, “Vibrational Spectroscopy to Study Degradation of Natural Dyes. Assessment of Oxygen-Free Cassette for Safe Exposition of Artefacts,” J. Analytical and Bioanalytical Chemistry 399(9) 3271-3283 (2011).

[68] L.M. Dutton, “Cochineal: A Bright Red Animal Dye” M.A. Thesis for Baylor University,162-177 (2010).

[69] E.A. Gonzez, E.M. Garc, M.A. Nazareno, “Free Radical Scavenging Capacity and Antioxidant Activity of Cochineal (Dactylopius Coccus C.) extracts”, J. Food Chemistry 119: 358–362 (2010).

[70] P. Robbins, “Tropical Commodities and Their Markets”, TWIN, ASARECA research 102-109(2005).

[71] W. Elisabeth, “Artists' Pigments: A Handbook of Their History and Characteristics, Washington, DC: National Gallery of Art 3: 344-358 (1997).

[72] L. Meyer, “Dyeing Red”, West Kingdom (SCA) Arts and Sciences Tourney 11: 22-32 (2005).

[73] A. Butler, Greenfield, “A Perfect Red: Empire, Espionage, and the Quest for the Color of Desire”,1th ed., Harper Collins Publishers Inc., New York, 340-347 (2005).

[74] S. Iwasa, O.L.O. Schleichera, I.F. Hanum & L.J.G. van der Maesen, “Plant Resources of South-East Asia. Auxiliary Plants”. Prosea Foundation, Bogor, Indonesia, 11: 227-229 (1997).

[75] W. Xia, L. Jian-zhang, F. Yong-ming and J. Xiao-juan , “Present Research on the Composition and Application of Lac,” Beijing Forestry University, co-published with Springer-Verlag GmbH. 8(1) 302-310 (2006).

[76] P.E. McGovern, and R.H. Michel, “Royal Purple Dye: It’s Identification by Complementary Physicochemical Techniques”, Inorg. Chem. 3(1) 69-76 (1991).

[77] A. Tsatsarou-Michalaki, N. Hliopoulos, G. Priniotakis, Ch. Mpoussias” Natural Dyes-Unifying the Heritage of the Past for an Eco- Friendly Future,” Technological Education Institute of Piraeus, Department of Textiles, 38-44 (2002).

[78] J. Doumet, “ A Study on the Ancient Purple Color”, Imprimerie Catholique, Beirut, 42-33 (1980)

[79] M. Saltzman, “Identifying Dyes in Textiles”, Am. Sci. 80: 474-481(1992).

[80] M. Saltzman, A.M. Keay, J. Christiansen, “The Identification of Colorants in Ancient Textiles, Dyestuffs,” ”, J. Anal. Chem. 44: 241–251(1963).

[81] S. Bruni, V. Guglielmi and F. Pozzi, “Surface-enhanced Raman spectroscopy (SERS) on silver colloids for the identification of ancient textile dyes: Tyrian purple and madder”, journal of Raman spectroscopy, John Wiley & Sons, Ltd 42: 465-473 (2009).

[82] C. J. Cooksey, Tyrian Purple: 6,6′-Dibromoindigo and related compounds”, a review, Molecules 6: 736–739(2001).

---

[83] W. Nowik, R. Marcinowska, K. Kusyk, D. Cardon, M. Trojanowicz, "High Performance Liquid Chromatography of Slightly Soluble Brominated Indigoids from Tyrian purple," Journal of Chromatography A, 1218(9) 1244-52 (2011).

[84] L. Meijer, A.L. Skaltsounis, P. Magiatis, "GSK-3-Selective Inhibitors Derived from Tyrian Purple Indirubins", Chemistry & Biology 10: 1255–1266 (2003).

[85] A. Dalby, "Food in the Ancient World from A to Z," 1th ed., Routledge, London, UK. 56-72 (2003).

[86] M.S. Moghaddasi, "Saffron Chemicals and Medicine Usage," J. Medicinal Plants Research 4(6) 427-430 (2010).

[87] Darling "Saffron", Darling Biomedical Library (UCLA), (8) 92-105 (2002).

[88] A. Dalby, "Dangerous Tastes: The Story of Spices", University of California Press, 11: 55-72 (2002).

[89] R.J. Forbes," Studies in Ancient Technology", 2nd ed., E.J. Brill, Leiden, Netherlands, 56-90 (1964).

[90] P. Willard, "Secrets of Saffron, the Vagabond Life of the World's Most Seductive Spice", 2nd ed., Beacon Press, 233-239 (2002).

[91] L. Carl von, "Species Plantarum," Salvius, Austrian National Library, 2: 830-832(1753).

[92] J.C. Leffingwell, "Saffron "Leffingwell Reports 2(5)1-7 (2002).

[93] G.N. Andreen, B. Schrader, H. Schulz, "Non- Destructive NIR-FT-Raman Analyses in Practice. Part1. Analyses of Plants and Historic Textiles", Fresenius J. Anal Chem. 12(5)1015 (2001).

[94] J.L. Rios, M.C. Recio, R.M. Giner and S. Mhnez, "An Update Review of Saffron and its Active Constituents," Phytotherapy Research, 10: 189-193 (1996).

[95] R.S. Verma, D. Middha, "Analysis of Saffron (*Crocus sativus L.Stigma*) Components by LC–MS–MS," Chromatographia –Wiesbaden 71(1-2) 117-123 (2010).

[96] L. Yeonhee , L. Jihye , K. Youngsoo , Ch. Seokchan , W.H. Seung, K. Kang-Jin," Investigation of Natural Dyes and Ancient Textiles from Korea using TOF-SIMS," Applied Surface Science 255:1033–1036 (2008).

[97] L.i. Shiyou, W. Yuan, G. Deng, P. Wang, P. Yang and B.B. Aggarwa, "Chemical Composition and Product Quality Control of Turmeric (*Curcuma longa L)",* Pharmaceutical Crops, 2: 28-54 (2011).

[98] S. Sharma, SK. Kulkarni, J.N. Agrewala, K. Chopra, "Curcumin Attenuates Thermal Hyperalgesia in A Diabetic Mouse Model Of Neuropathic Pain", Eur J Pharmacol, 536(3) 256-61 (2006).

[99] I. Chattopadhyay1, K. Biswas1, U. Bandyopadhyay and R.K. Banerjee "Turmeric and Curcumin: Biological Actions and Medicinal Applications", Review Articles, Current Science 87(1) 45-53 (2004).

[100] G. Singh, I.P.S. Kapoor, P. Singh, C.S. de Heluani, M.P. de Lampasona, C.A.N. Catalan, "Comparative Study of Chemical Composition and Antioxidant Activity of Fresh and Dry Rhizomes of Turmeric (Curcuma Longa Linn.)", Food and Chemical Toxicology, 48: 1026–1031(2010).

[101] I.A. Bhatti , Sh. Adeel , M. AsgharJamal , M. Safdar , M. Abbas, " Influence of Gamma Radiation on The Colour Strength and Fastness Properties of Fabric using Turmeric(*Curcuma Longa L.*) As Natural Dye," Radiation Physics and Chemistry 79: 622–625 (2010).

[102] A. Amat, Ca. Clementi, C. Miliani, A. Romani, A. Sgamellottiab and S. Fantacci, " Complexation of Apigenin and Luteolin in Weld Lake: a DFT/TDDFT Investigation", journal of the Owner Societies 12: 6672-6684(2010).

---

[103] J. Kirby, “Dyes, Dyeing and Lake Pigments, Historical Background”, Organic colorants in ancient and contemporary art 2: 1-26 (2011).

[104] C.C. Mell, “A Brief Historical Account of Weld”, J. Textile Colorist 35, 33-51(1932).

[105] S. Subash, P. Subramanian, “Morin a Flavonoid Exerts Antioxidant Potential in Chronic Hyperammonemic Rats: A Biochemical and Histopathological Study”, J. Molecular and Cellular Biochemistry, 327(1-2) 153-161 (2009).

[106] S.K. Mannal, R.S. Aggarwal, “Morin (3,5,7,2′,4′-Pentahydroxyflavone) Abolishes Nuclear Factor-κB Activation Induced by Various Carcinogens and Inflammatory”, J. Anal Chem.,13(5) 1042-1049 (2007).

[107] M.S. Arayne, N. Sultana, S.S. Bahadur, “The Berberis Story: Berberis Vulgaris in Therapeutics”, Pak. J. Pharm. Sci., 20(1), 83-92(2007).

[108] J. Smith. “Medieval Dyes”, Spinning Madly, Revised Edition, 45-65(1995).

[109] P.S. Vankar, “Chemistry of Natural Dyes”, General Article, RESONANCE, 73-80(2000).

[110] F.A. Nagia, S.R. EL-Mohamedy, “Dyeing of Wool with Natural Anthraquinone Dyes from Fusarium Oxysporum”, J. Dyes and Pigments 75: 550-555 (2007).

[111] E.J.W. Barber,” Prehistoric Textiles”, 3rd ed., Princeton University Press, 237-255(1991).

[112] I. Joosten, M.R. van Bommel, “Critical Evaluation of Micro-Chemical Analysis of Archaeological Materials,” J. Microchim Acta 162: 433-446 (2008).

[113] D. Cristea, G. Vilarem, “Improving Light Fastness of Natural Dyes on Cotton Yarn”, J. Dyes and Pigments, 70: 238-245 (2006).

[114] I. Szabolcs, “A Review of Late Antique/Early Byzantine Textiles With Special Emphasis on Dyestuffs and Dyeing Methodology Used For So-Called Coptic Textiles”, J. Cultural Heritage 11: 63-86 (2005).

[115] A.K.R. Choudhury, “Textile Preparation and Dyeing,” 2nd ed., Science Publishers, USA 734-740 (2006).

CHAPTER 3

Pigments

3. Pigments

3.1. Introduction

The meaning of the word “color” varies in diverse fields of interest. In the behavioral sciences, for example, color refers to the physiological perception of the appearance of objects or light sources, in chemistry, refers to substances that have certain optical properties (to exhibit color) and in physics, color refers to a specific property of visible light[1].

Pigments are insoluble in most liquids, particularly water, and generally (not exclusively) are of inorganic origin[2].

The freshness and brightness of the colors of the old Egyptian tomb painting have often been commented upon, and it is sometimes assumed that the pigments employed were such as doing not exist at the present day. They are either naturally occurring, minerals, finely ground or they have been made from mineral substances, to which fact is primarily due their excellent state of preservation[3].

Within a composition according to the rules of Egyptian canonical art, each pigment is applied evenly across outlined surface, the artist aiming at polychromatic effect rather than coloristic shading. The emphasis of the palette thus falls on the pure and intense colors, with a consequent delimitation of the materials in use.

The use of textile as a painting support dates back to ancient Egyptian civilization. Painted textiles do not commonly survive at any period, but include mid Eighteenth-Dynasty shrouds bearing texts and vignettes from the Book of the Dead. The shroud of Resti, an Eighteenth-Dynasty noblewoman (BM EA73807) revealed the same selection of pigments as that found on contemporary funerary papyri with huntite for white, orpiment for yellow, Egyptian blue for blue and hematite for red[4].

Canvas as a painting ground has been referred to already in connection with the portraits of Roman date found by Petrie in the Fayum, some few of which are on this material. Other examples of painted canvas are the so-called “painted handkerchief” from Deir el Medineh , a number of small painted cloths of Eighteenth Dynasty date that were found at Deir el-Bahari[3]. Several surviving linen textiles, dating from the New kingdom onwards, were painted with designs of varying degrees of complexity.

Sometimes these textiles had secular uses, but on other occasions they seem to have been intended for funerary purposes. With regard to secular use, a length of painted cloth was found with a chariot in the tomb of Tutankhamon[5], the material has two simple blue lines painted on it and was placed between the floor of the chariot and the side wall of the frame. In this position the textile would have been subject to hard wear and it is likely that it was necessary to replace it frequently, hence, presumably, the simple method of decoration. There are numerous examples of textiles which have been elaborately painted in order to represent jewelers and such fake jewels were often placed around the wrists of mummies in imitation of bracelets. There are also less elaborately painted examples of cloth bearing the outline of a god, commonly Osiris, which were usually used as shrouds (e.g. the Osiris shroud of Nesitiset, dating to the New kingdom. The painted linen shrouds so well known from the Greco-Roman period, more elaborate painted shrouds were in use[4].

The earliest Known instance of painting on linen, which dates from the Predynastic period is that found at Gebelein and now in the Turin Museum[3].

3.2. Pigments and their chemical properties

Pigments differ with respect to their chemical properties due to the fact that they are comprised of a wide variety of chemical compounds. Gettens and Stout (1966) named some common inorganic coloring materials as oxides, sulphides, carbonates, sulphates, phosphates, and silicates of the heavy metals. There are few metallo-organic compounds which are form pigments like Emerald green as well as pigments comprised of pure elements such as carbon and gold. Ideally, pigments should be inert to strong acids, alkyds, and heat, and resistant to photochemical reactions when exposed to light.

3.2.1. Pigments and their physical properties

Physical properties are characteristics that are innate to a material. The most important physical property of pigment is its color; the color of pigment is produced by that material's interaction with light, and more specifically, the way in which it absorbs the component colors of white light. Pigments selectively absorb the visible light and reflect the remaining. If an object reflects the entire visible wavelength range, then it is white. If some regions of this light are absorbed and others reflected, then the object is colored, e.g. a blue pigment absorbs all wavelengths except blue, it appears blue because it reflects only blue light absorbing all others in the visible region. A black surface appears black because it absorbs everything in the visible region and reflects nothing in the visible region. Thus, the visible region consists of wavelengths that give us the perception of color. A material's color characteristic, such as hue and purity, rely not only on color absorption but also depends on the size, shape, and texture of pigment grains. There are also characteristics related to the shape and size of a pigment, for example, mineral pigments are often sharp and angular and traditionally larger in grain size. This sharp angularity is caused by the cleavage properties of minerals. Earth pigments are generally small and rounded; though vary greatly in size and shape. Pigments also have particular physical properties related to density and their ability to be dispersed and wet in media[6].

Most pigments of archaeological interest are minerals, although other material such as charcoal and burned bone can also be pigments[7]. Moreover, during the second half of the 19th century, synthetic organic colorants were gradually introduced into the market and started to replace traditional inorganic pigments. Hence, modern artists have in their possession a great variety of pigments and binding media, and often utilize an impressive number of them even in the same painting[8].

3.2.3. The principal pigments which used in ancient times

The principal pigments which used in ancient times may be summarized as three pairs: black and white, red and yellow, and blue and green, variants to this frame work include brown, grey, orange, pink and purple[4].

3.2.3.1. Black pigments

Black pigments as they were directly derived from the material source; have been easy prepareable for painting purposes, the black color was a symbolic and a basic color in the Egyptian painter palette. The black pigments of antiquity fall into one of two categories: mineral blacks and human-made vegetable and animal blacks. The most common mineral blacks are pyrolusite, graphite and magnetite.

3.2.3.1.A. Pyrolusite

Also known as manganese black (composed of manganese dioxide (MnO_2) has been widely used not only as a black pigment but also as a glass decolorize. Pyrolusite a common mineral, although difficult to distinguish from similar minerals, pyrolusite forms under oxidizing conditions and high pH. Mainly a mineral of lacustrine, shallow marine and bog deposits, it is also found in the oxidized zones of manganiferous ore deposits and as deposits formed by circulating meteoric water. Both colloidal processes and bacterial action are important in its Formation. The use of pyrolusite has been the same as magnetite[9].

3.2.3.1.B. Graphite

Graphite-named from the Greek verb γράφω “to write”, also known as Carbon Inorganic or plumbago, (C- a crystalline form). It is one of the most stable and refractory of all materials, although physically it is “flaky” and friable because of its layered crystal structure of sliding sheets of atoms, extremely stable at high temperatures and conducts electricity like the metals can be either black or dark gray. It is composed of elemental carbon, as it is one of the two naturally occurring mineral allotropes of this element.

3.2.3.1.C. Magnetite

Fe_3O_4, small grains of magnetite occur in almost all igneous rocks and metamorphic rocks. Magnetite also occurs in many sedimentary rocks, including banded iron formations. Magnetite is sometimes found in large quantities in beach sand. It reacts with oxygen to produce hematite[10]. Magnetite was used as a black pigment in ancient Egypt after it was well grinded and mixed with paint medium.

3.2.3.1.D. Carbon "Organic"

(C- Amorphous form)[11], artificial, human-made black pigments have been derived mostly from either vegetable or animal matter.

Animal blacks are made by charring (partly burning) either bone or ivory. To prepare bone black, bones are burned in an oven or closed pit in which there is a reducing atmosphere, that is, a restricted supply of air and therefore a dearth of oxygen.

Black pigments of vegetable origin have generally been made from various kinds of charred plant matter, mostly wood "coal", but also leaves or seeds[12].

Charcoal is the blackish residue consisting of impure carbon. It is soft, brittle, lightweight, black and porous material, resembles coal and is 85% to 98% carbon with the remainder consisting of volatile chemicals and ash[13].

Carbon black was largely used as a pigment and ink ingredient since antiquity. A standard in Mediaeval and post Byzantine icon painting, the inexpensive material is encountered in most modernist palettes, complementing more sophisticated options, such as rich genuine ivory black, or ferrous minerals[14].

3.2.3.2. White Pigments

The use of white pigment for mural painting is known from the Predynastic period. White pigments in ancient Egypt have been all of inorganic origin (carbonates, oxides and sulfates). Chalk has been the first used white pigment at all. In Egypt three kinds of white have been in use[3].

3.2.3.2.A. Gypsum

$CaSO_4.2H_2O$ (Calcium sulfate dihydrate) Terra Alba, Gesso, Alabaster, from the Greek word (γύψos) (the mineral), the most used material as a white pigment has been gypsum; the beginning of its use was in the 5th dynasty[15].

The pigment material has been also used in the phase of non hydrated calcium sulfate (anhydrite $CaSO_4$), and in the phase of semi-hydrated calcium sulfate "Plaster of Paris"[16].

3.2.3.2.B. Limestone powder (Calcite)

$CaCO_3$, this pigment material has been used all over the historical periods in ancient Egypt, it has used as un-burnt limestone not as burnt lime, it has been mixed sometimes with gypsum for more hiding power, some quarries of snow white limestone structures have been known and used in Egypt.

The Max-Planck project recorded both calcium carbonate and calcium sulphate from the Fifth Dynasty to the Roman period but they found the latter (usually comprising gypsum and anhydrite to be the more common. In addition, their analyses of white pigments from Theban tomb-chapels of the Twelfth dynasty and Eighteenth to Twentieth Dynasties revealed magnesium calcite, chosen for its intensity as a first layer under main pigment on tomb-chapel walls**.**

3.2.3.2.C. Huntite

Calcium magnesium carbonate"$CaCO_3.3MgCO_3$"or "$CaMg_3(CO_3)_4$. Huntite forms compact fibrous chalky masses[17,18]. It is found in caverns in magnesium rocks, was used as a white pigment material since the new kingdom because of its advantages above the previous mentioned two pigment materials[19].

The Egyptian painter noticed these characteristics by time and practice; so this material became very wide used since the late period[20].

Blom-Boer also notes huntite as a pigment comparable to orpiment in terms of its quality and brightness[21].

Huntite would have been desirable as a painting material not only on account of its color, but also for its adhesiveness, its small particle size and its very fine grain, which would also have ensured a smooth painted surface. it is attested in the Persian Gulf and occurs both in salt lakes and on the margins of magnesium-rich strata conditions that can also be found in Egypt the nearest published north African source known to us is far to the west in Tunisia[22].

Huntite was also identified as a pigment or pigment component in the analyses of samples of pigments from the walls and from the painting equipment of two mid-Eighteenth-Dynasty Theban tomb-chapels. Wagenaar identified a white as powdered shell or cuttlefish bone: this has not been corroborated. Another papyrus of the Third Intermediate Period bore an unidentified white which contained calcium, phosphorus and low levels of magnesium according to the SEM (EDX) analysis[4].

3.2.3.2.D. White lead pigment

The Greeks contribution to painting was the manufacture of white lead pigment, which remained the most used white pigment available to artists until the 19th century. It is still regarded as the whitest of the white pigments. It is a complex chemical compound, containing both a carbonate and a hydroxide portion basic lead ($2Pb(CO_3)_2 .Pb(OH)_2$) and is, of course, toxic, like cinnabar, it was used as a cosmetic by Greco-Roman ladies who used it as face powder with predictable effects on their health and that of the men who kissed them. It continued in use as a cosmetic into the middle ages and beyond in Europe. White lead was made by stacking lead strips in porous jars with vinegar and burying the jars in animal manure which generated the heat necessary to speed up the reaction. With a few refinements, this process continued to be used until the 1960. The physical structure of white lead and its reaction with the oil give a very flexible, quick drying and permanent paint film, particularly important in oil painting[23,24].

3.2.3.3. Red Pigments

The best known and most widely used ancient red pigments were hematite, red ocher and the vermilion.

3.2.3.3.A. The ocher and sienna

Also known by their more general name natural earths, are a group of mixtures of clay, silica, and iron oxides. Their color which may vary from yellow or light brown to dark brown and even to orange and red is due mainly to iron oxides that occur as hematite.

Often the natural earths also contain small amounts of black pyrolusite which makes them darker and/or calcium and barium carbonates which make them lighter. There is no sharp compositional difference between ochers and siennas, in either iron content or color; it is customary, however, to classify natural earths of lighter color and lower iron oxide content as ochers and those of darker color and slightly higher iron oxide content as sienna. The intense red of red ocher, for example, is due mainly to a relatively high proportion of hematite (which is red) in the mixture. Deposits of red ocher abound in many places on the surface of the earth; only a few, however, are considered red enough and suitable for use as pigments. Red ocher has excellent hiding and staining powers and it probably was one of the preferred red pigments of antiquity.

3.2.3.3.B. Hematite

Composed of anhydrous ferric oxide (Fe_2O_3), Hematite is a very common mineral, colored black to steel or silver-grey, brown to reddish brown or red. It is mined as the main ore of iron. Hematite is harder than pure iron but much more brittle, the name of hematite is derived from the Greek word “αίμα” for blood, since hematite is almost red, the pigment has been used since the prehistoric ages in caves wall paintings.

The pigment in ancient Egypt has been used in a thick layer upon the gypsum white wash to have a good hiding power because the metal is very hard to be well grinded or to be good mixed with paint medium[25,26,27].

Red and yellow ochres were among the first pigments used for painting. It seems likely, therefore, that these might have been tried out and used very early for the dyeing of yarns and woven linen fabrics. Jan Wouters, Luc Maes and Renate Germer, detected red ochre on linen from 12th dynasty from red mummy wrappings found in one of several tombs of prin- cesses, excavated by de Morgan during 1894-95, thus representing one of the earliest known uses of this pigment for the dyeing of linen[28].

In Egypt there were two kinds of Hematite: the first one has been derived from Aswan “hematite of Aswan”, it has a brownish red color and has been used in the ancient Egyptian wall paintings as a brown color and in the statues has been usually used to paint the men bodies, the second one is derived from Sinai “Hematite of Sinai” and it has a red color but by effect of the deterioration factors it changes into the dark red color or the brownish red color and couldn’t be distinguished from the previous type.

The Max-Planck project identified most visually red samples as red ochre from the Fifth Dynasty to the Roman, they noted only a few instances in which hematite appeared to be used (ranging in date from the Sixth Dynasty to the First Intermediate Period and Eighteenth Dynasty) and they defined these simply as particularly rich in iron oxide.

The analysis of one red pigment from the Eighteenth-Dynasty Workmen's Village at Amarna also indicated the use of hematite[4].

3.2.3.3.C. Vermilion and cinnabar

Are two bright red, toxic minerals that share an identical composition (they are both composed of mercury sulfide HgS) but have different crystal structures. Two kinds of vermilion are known: one of natural origin and another made artificially. Finely ground natural vermilion may vary in hue from red to liver-brown and even to black.

Artificial vermilion was made from mercury and sulfur, the method of preparation seems to have been developed by the Chinese and was introduced into Europe only during the eighth century[29]. It is made by crushing, washing and heating the mineral cinnabar or mercuric sulphide to give a strong red pigment. Alternatively it was made by mixing mercury with molten sulphur and heating the mixture to produce the compound[30].

Cinnabar was mined at Almaden in Spain to provide the Romans with the pigment. It was extensively used in wall decorations in the houses of the wealthy in Pompeii, gladiators and statues were painted with it and it was used by Roman women as lipstick. Its strength of color meant that it was still being used in the 19th century and is present in Turner’s paint boxes which remain and are held in various museum and gallery collections[31].

Due to its unique physical and chemical properties, mercury has been used in many products such as thermometers, medicines, batteries, electrical switches and pesticides[32].

Samples of pigments from a wall-painting of a house of the first Pompeian style (400 B.C-168 B.C) found in Pella, Greece, were analyzed by the non-destructive methods of X-ray fluorescence and X-ray diffraction**.** The results of this study extend our investigation of ancient Greek pigments chronologically up to the second century B.C. The iron oxide pigments, such as hematite, goethite or the mixture of both, were widely used during this period as red and yellow coloring materials. Cinnabar was also used as a red pigment (identified by the authors on the wall-paintings of the neighbouring Virginia tombs[33].

Cinnabar was used in antiquity as a pigment but was very expensive and rarely recovered in archaeological materials. Possible sources of the cinnabar were Spain, from where Romans acquired the mineral or Ephesus in Western Anatolia[34].

3.2.3.3.D. Red lead

The Greeks also developed the use of red lead which was used for priming metal in construction until it was banned in the 1990. Red lead is a form of lead oxide (Pb_3O_4 - tetra oxide of lead) and is found as the mineral minimum after the River Minius in northwest Spain. It is also manufactured by heating litharge (PbO) in air[23]. It has a good hiding power, Moderate permanence and stability. Initially orange-red in color it is photo oxidized to a light pink in the sun or a brownish red depending upon the environmental influences. Browning has more notably occurred when it has been applied in water color or tempera medium. Red lead is favored because it has a good hiding power and a thick texture[35].

3.2.3.4. Yellow Pigments

Three main types of natural yellow pigments were known to the ancients**:** yellow ocher (Goethite), Orpiment and Jarosite.

3.2.3.4.A. Orpiment

A highly poisonous, soft, lemon-yellow mineral composed of sulphide of arsenic (As_2S_3). Orpiment was identified in Egyptian paintings at Tell-Amarna, in Egypt and it is mentioned in the writings of the Roman writers Vitruvius and Pliny.

In the past orpiment was used not only as a pigment but also for the removal of hair from animal hides before the tanning processes.

Orpiment was used for bright yellow or gold and realgar or red sulphide of arsenic for bright reds. These pigments were used as long ago as the 16th century B.C. and continued in use until the 19th century[36]. It was also identified as the yellow pigment on early Eighteenth-Dynasty linen shrouds (BMEA 73806-7) papyri of the Nineteenth Dynasty (BMEA 9949 and 9968), Twentieth Dynasty (BMEA 10472, third Intermediate Period (BMEA 9919 and 10029), thirtieth Dynasty or early Ptolemaic (BMEA 9944.) and late Ptolemaic period (BMEA 9916)[4].

Orpiment is also known as “King's Yellow”, “Chinese Yellow” and “Yellow Orpiment”; it has been mixed with goethite for a bright yellow color.

Arsenic sulphide is found in volcanic and geothermal regions, although it is also found with limestone and dolomite. The colors are not permanent and fade on exposure to light[16].

3.2.3.4.B. Yellow ocher

The word ‘‘ochre’’ comes from the Greek word Ochros, meaning yellow, so the name yellow ochre is tautologies. The chemical responsible for the color is hydrated iron oxide FeO (OH), familiar to everyone as rust, and it is found mixed with silica and clay, grinding and washing produces the pigment which is essentially yellow clay. Red ochre is produced by heating the yellow ochre to drive off the water and produce anhydrous ferric oxide. By controlling the heating it is possible to produce a range of warm yellows to bright red. Red ochre occurs naturally in volcanic regions where thermal activity has caused the dehydration. The color has excellent permanence and the abundance of raw material means that ochres remain among the cheapest artists colors available[23].

The Max-Planck project identified the yellow pigments as yellow ochre on samples from Fifth Dynasty to the Roman period but they found orpiment in pure form only on eighteenth- and Nineteenth-Dynasty sarcophagi of kings and on the walls of the tomb of Thutmose IV (KV43). One of the major findings of the project was the mixture of orpiment and yellow ochre applied to New kingdom temple and tomb walls.

Blom-Boer (1994) reports layering of first yellow ochre, then orpiment and finally yellow ochre again on the walls of tombs and temples in the New Kingdom, thus giving the ochre the greater intensity of color characteristic of orpiment[4].

The yellow pigment has been used in the tomb of Kha’ Em Het (TT57), new kingdom is identified as a mixture of orpiment and goethite according to the SEM-EDS and XRD analysis. That mix has been used to get a shiny yellow color[37].

3.2.3.4.C. Jarosite

Potassium ferric sulphate hydroxide $KFe_3(SO_4)_2(OH)_6$, was used to produce a pale yellow. Jarosite is named after the Jaroso Ravine in Sierra Almagrera, Spain, where it is found and it is formed as a result of weathering of volcanic rocks.

Jarosite is not a common mineral, colored dark yellow to yellowish-brown. It can sometimes be confused with limonite or goethite, the pigment has been found on pottery jars from the 11th dynasty[16,38] and also as a pigment in wall paintings of the Amen Em Hab tomb (TT 278**)** New kingdom by SEM-EDS and XRD analysis[37].

Jarosite is an ancient and exotic pigment used seldom in the painting of Egyptian and Roman's artworks. It is a member of the alunite group, having the formula $\mathbf{X}Fe_3(SO_4)_2(OH)_6$. The X is usually a large monovalent cation, such as Na^+ and K^+, but Pb^+, Ag^+, $NH4^+$ and H_3O^+ may also be observed. Jarosite has previously been identified as an ancient Egyptian pigment, Schiegl et al. (1992) suggested that the jarosite found in Egyptian contexts was never used as a pigment in its own right but is rather a degradation product of an iron-rich glass applied as a pigment. Greco–Roman artists used goethite (yellow ochre) as a yellow pigment and rarely, jarosite as a yellow or yellow-brown pigment[39]. Also it is found in "Saint-George with scenes from his life", in the form of jarosite or natrojarosite[40].

The presence of Jarosite and natrojarosite on the planet Mars has recently been invoked as evidence for water limited chemical weathering of the surface[3,41].

3.2.3.5. Blue Pigments

Mountain blue "azurite" and glaucophane were the most widely used natural ancient blue pigments.

3.2.3.5.A. Azurite

Mountain blue is made by crushing and reducing to the bright blue powder. It is Derived from the mineral "Azurite" (composed of a basic carbonate of copper $2CuCO_3.Cu(OH)_2$ that occurs in only a few regions of the world from where it was and still is exported in the form of massive rocks**,** found in Sinai and the Eastern desert was[42].

Spurrell (1895) in the following examples a shell used as a palette in a Fourth-Dynasty context at Meidum, a cloth over the face of a Fifth-Dynasty mummy also at Meidum and a number of Eighteenth- Dynasty "paintings", presumably wall-paintings. There is, however, no more recent corroboration of Spurrell's finding.

The Max-Planck project (covering the Fifth Dynasty to the Roman period) reported no instances of azurite and it has been concluded that identifications of blue pigment as natural azurite are not secure.

Blom-Boer suggests that the apparent absence of azurite from the Egyptian's palette was perhaps a result of its poor quality and impermanence as a pigment[4].

Azurite is liable to undergo slow deterioration with loss of carbon dioxide and conversion to malachite and in some circumstances, it can transform to a black tenorite “CuO”. Further examples of its use may be found in future studies, although given the comparative rarity of azurite, Egyptian blue was always the most commonly used blue[43].

3.2.3.5.B. Glaucophane

A blue mineral (composed of sodium magnesium aluminum hydrosilicate ($Na_2Mg_3Al_2(Si_8O_{22}(OH)_2)$) was used by the Greeks as a blue pigment as early as the seventeenth century B.C. It is named from its typical blue color (in Greek *glaucophane* means “blue appearing”).

3.2.3.5.C. Lapis lazuli

The name may reflect the strong blueness of the pigment, meaning that its color was bluer than that of the sea, although it has been interpreted as meaning coming “across the seas” or imported. It was made by grinding the semi-precious mineral lapis lazuli, a rock containing the mineral lazulite and was used in Afghanistan in the sixth century A.D.

Lazulite is complex sulphur-containing aluminium silicate ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), also known as Ultramarin. During the renaissance, the color blue was associated with purity and ultramarine was used to striking effect in paintings of the Virgin Mary when she was almost invariably depicted wearing ultramarine blue garments. The high price of the pigment also meant that its use was appropriate in the case of a noble subject such as the mother of Christ.

This color therefore best characterizes the paintings of that time. The lapis lazuli stone was ground, then mixed with wax and kneaded in a lye bath to separate the impurities from the lazulite crystals. The pigment produced from these pure crystals was light-fast. The combination of the price of the semi-precious stones and the cost of the process meant that ultramarine was more expensive than gold[30]. There is no evidence that lapis lazuli was used as a pigment in ancient Egypt[4], but it was used in Egypt as early as the Predynastic Period for beads, inlay, amulets, cylinder seals, small vessels, and scarabs. Although Egyptian texts indicate that lapis was purchased from trading stations in western Asia and from Meroe and Punt to the south of Egypt, all of the lapis in ancient Egypt is thought to have originated from the quarries in Afghanistan. At present, there is no evidence for the use of lapis originating from areas other than from Afghanistan. The use of natural ultramarine from the 18th Dynasty is the earliest recorded use of this material as a pigment in the world[41].

3.2.3.5.D. Egyptian blue

Egyptian blue was the first synthetic pigment ever produced by man, it is considered a great technology development in ancient Egypt from the 4th dynasty (c.2613-2494 B.C.) till the Roman times, this pigment is appeared in Egypt during the 3rd millennium B.C.[6,44].

Egyptian blue should not be confused with another, also blue or greenish-blue, Egyptian faience, which is made from much the same raw materials. Egyptian blue remains one of the most stable and easily made synthetic blue pigments, it is calcium copper silicate ($CaCuSi_4O_{10}$) made by first preparing a mixture of quartz sand, natron, copper filings and an alkali such as potash or natron (sodium sesquicarbonate $Na_2CO_3.NaHCO_3.2H_2O$, and then heating the mixture to about 850°C. The raw materials melt at this temperature, reacting with each other to form a definite chemical compound calcium copper silicate. As the melt cools, it does not crystallize but solidifies into a frit, which is then powdered[41,45].

Texture and hue hardness, texture and resultant color of Egyptian blue when used as a pigment depend on the initial components, the microstructure of the sintered product and final particle size after grinding to produce a pigment. Tite, Bimson and Cowell (1987) categorize Egyptian blue as dark blue or diluted light blue. The dark blue is low in alkali, with a microstructure showing coarse crystals of cuprorivaite ($CaCuSi_4O_{10}$) crystals are smaller and intimately mixed with the other components. The diluted light blue is high in alkali, and as a result contains a large proportion of glass, this results in a paler blue material which is also harder than the low alkali products[46].

Egyptian blue was often thickly applied, with coarse particles up to 50 μm across. In general a higher degree of grinding will produce smaller particles, which appear paler than if they were coarsely ground. Some paler blue samples were found to contain white, generally calcite or gypsum.

Spurrell, Laurie and Smith report Egyptian blue on objects as early as the Fourth Dynasty and the Ma-Planck project identified it as the blue pigment in all samples analyzed, from the Fifth Dynasty to the Roman period, apart from the grey-blue pigments in the First Intermediate Period tomb-chapels of the local governors Ankhtifi and Setka in el-Mo'alla and Aswan respectively[4].

The blue on the famous Eighteenth-Dynasty head of Queen Nefertiti (Berlin, AM 21300) has also been identified as Egyptian blue. All blue samples in the British Museum conservation Project were likewise found to be Egyptian blue, and no tin was detected in these despite their date “New Kingdom to Roman period”[47].

In ancient Egypt two kinds of man-made blue pigments were used. One of these was the ‘‘Egyptian blue’’ which was already synthesized in c. 3000 B.C. and had been used during all the Egyptian ages. The other kind of pigment was the “Amarna blue”, believed to be used only in the 18th and 19th Dynasty “1500 B.C-1200 B.C.” whose chemical compositions was a mixture of $CaSO_4$ and $CaO.Al_2O_4$. The Archaeological Mission of Waseda University to Egypt has excavated numerous fragments decorated with Amarna blue in those 300 years from (1) the Malqata South Kom El-Samak constructed in the 18th Dynasty (1400 B.C.) (2) The 18th Dynasty tomb located at the site of Dahshur and (3) the site of Abu Sir used during the Old and New Kingdoms[48].

It was already mentioned that the use of Egyptian Blue had spread all over the Mediterranean area by the first millennium B.C. and was employed by many civilizations. Egyptian Blue of high quality was obtained at this time and as long as no compact bodies had to be produced, the physical and chemical conditions for the synthesis were relatively easy to attain.

Even before the collapse of the Egyptian Empire, Egyptian Blue reached the ancient Greek and Roman civilizations. Egyptian Blue was also widely used in Mesopotamia and in the area of today’s Iran. Concurrently it became a commodity for the Romans[49].

3.2.3.6. Green Pigments

Green pigments have been usually one of the most interesting pigments for the man as he started from the beginning to watch the green colored objects (trees, grace, some animals……etc). The human dream to simulate those objects in his drawings some times to avoid there evil or to get there benefit, encouraged him to collect similar colored materials from the nature to use them as pigments, by time and by the progress of the human civilizations he noticed that naturals materials are not stable against ageing factors, so he started to create new, stable and durable pigment materials[50].

A variety of mineral ores, mostly copper minerals such as malachite and chrysocolla, were probably the most used green pigments in the past. Various green minerals derived from metals other than copper, such as green earth was used in confined regions.

3.2.3.6.A. Malachite

Malachite is a bright green natural mineral (composed of basic copper carbonate ($CuCO_3Cu(OH)_2$), , which is widely distributed in nature. The consolidated form of the mineral has also been appreciated since antiquity as a semiprecious gemstone.

The Egyptians converted malachite mineral to pigment by crushing and washing. Powdered malachite was used as a pigment by the ancient Egyptians from Predynastic times. Egyptian women also used malachite to paint their eyelids.

It is also used by the Romans in illuminated manuscripts, and by the Chinese in paintings from the ninth century. Malachite pigment appeared in European paintings from the 15th and 16th centuries[30].

3.2.3.6.B. Chrysocolla

Also a copper mineral (composed of hydrated silicate of copper $CuSiO_3\ nH_2O$), may range in color from bright green to bright blue. It is often found naturally mixed with other minerals of copper, such as malachite and azurite[12].

The green on a Nineteenth-Dynasty papyrus at the University of Philadelphia Museum was identified by XRF and wet chemical analysis as Egyptian blue mixed with orpiment[51].

This might account for the arsenic sulphide identified from a green pigment from the royal Tomb at Amarna, although the recorded XRD data have been found to be more consistent with copper compound[52].

From the late Ptolemaic or Roman period, the British Museum conservation project found that the green color on a funerary papyrus (BMEA 916) consisted of Egyptian blue with orpiment. This rare and presumably more expensive, mixture of blue and yellow to produce a green seems to follow those New Kingdom antecedents[4].

3.2.3.6.C. Egyptian Green

$(CaCu)_3(Si_3O_9)$, the ancient Egyptians employed for the green color a synthetic material which is often termed “green frit”. It is made in reducing conditions by mixing similar ingredients as for Egyptian blue, but with higher lime, and lower copper content.

The research of (Pagès-Camagna and Colinart, 2003) proved that the process in which Egyptian green is synthesized is a sintering reaction in a liquid phase involving three steps, and that the synthesis cannot be explained by a solid-state diffusion. The first step is the creation of an eutectic, through the reaction of the silica and the soda flux. The second, corresponding to the appearance of the color, is the diffusion of the copper ions and the last is the increase in the calcium concentration in the amorphous colored phase which leads to the formation of parawollastonite. Egyptian green probably owes its turquoise color to the copper-bearing amorphous phase. The degree of the produced color depends mainly on the amount of copper and the high amount of flux material and silica will give rich glass phase and high amount of copper will give deep degree of green color[6].

3.2.3.6.D. Atacamite

Basic copper paratacamite or atacamite ($Cu_2(OH)_3Cl$), is found in analyses of green pigment samples from surfaces as late as the end of 12th dynasty, but recent investigations led to the conclusion that atacamite may be a degradation product of artificial copper pigments, and that only a few examples of green earlier than the new kingdom were applied as green, the remainder being applied as light blue. According to previous authors[53,54], copper chloride pigments were not intentionally produced before the new kingdom, the apparent Old and Middle kingdom greens were in fact the product of degradation of the multi-phase synthetic pigment Egyptian blue, natural features as plant stems and tree tops were originally painted light blue. Weathering of the alkali-rich glass can result in the formation of chlorides and/or malachite, causing the pigment to become paler, spongy and friable[55].

3.2.3.7. Brown Pigments

Brown pigment in most of the ancient Egyptian wall paintings has been some kind of hematite which has a dark color, in some rare cases the ancient Egyptians mixed the black pigments with the red ones to get the brown color.

Lucas states that iron oxide or ochre was used for the color brown, citing analyses of samples dating to the Fourth Dynasty, Amarna period and Late Period. He also notes the late nineteenth-century identification by Spurrell of Fourth-Dynasty brown samples as red painted over black[56].

Winlock recorded that the models from the late Eleventh or early Twelfth-Dynasty tomb of Meketra at Deir el-Bahari included brown pigment obtained by varnishing over deep yellow ochre. The Max-Planck project identified ochre (generally red, but sometimes brown or yellow) as the material used for brown from the Fifth Dynasty to the Roman period throughout Egypt. Lucas records the Dakhla Oasis as a provenance for good ochre.

The British Museum conservation project found that the brown pigment on one early Eighteenth-Dynasty papyrus (BMEA 10477) was a mixture of hematite with orpiment and carbon black. The brown pigment on a Twenty-first or early Twenty-second Dynasty papyrus (BMEA 10029) was found to contain hematite and carbon black. It should be noted that a green sample containing orpiment yellow and Egyptian blue had turned brown at the edges on one papyrus of the late Ptolemaic or early Roman period (BMEA 9916), perhaps from sulphurous emissions in the photochemical degradation of the orpiment component of the green.

A red-brown on a Nineteenth-Dynasty papyrus at the University of Philadelphia Museum was identified by XRF and wet chemical analysis as realgar with iron oxide[4].

The Max-Planck project found that a rare beige hue in samples ranging from the Fifth Dynasty to the Ramesside period, within Upper Egypt, consisted of a mixture of yellow ochre and white pigments, it should be stressed that the hue intended by the artist at application is not always clear from these analyses[17].

The collected brown sample from the Temple of Madinet Habu in Al Qurna identified as a brown ferric chromate (chromite, $FeCrO_4$) by the µ-XRF and SEM-EDS analysis. The presence of chromites in the sample may refer to one of the rarest samples of that kind from the Egyptian wall paintings or the first sample of that kind from that period[37].

3.2.3.8. Grey Pigments

Lucas reports that a number of Fourth-Dynasty and Fifth- Dynasty samples incorporated a grey obtained by mixing gypsum white with carbon black. Reisner had asserted that the grey color used to paint pottery at the Upper Nubian site of Kerma was obtained from a sandy stone but this is yet to be confirmed[3].

Blom-Boer (1994: 74) reports carbon black or combination of gypsum with carbon black, from the Fifth to the Twentieth Dynasties but notes as with other mixed colors, the difficulty in distinguishing contaminated samples and establishing the original hue intended by the artist at application .On one of several Ptolemaic and Roman period papyrus fragments from Elephantine, Ashmunein and the Fayum, a grey pigment was identified by XRD as kaolinite mixed with quartz[4].

3.2.3.9. Orange pigments

Lucas (1962) refers to analyses of orange which identify the color as red painted over yellow, or else as a mixture of red and yellow, but he does not identify which red or yellow pigments nor does he mention realgar or orpiment .The Max-Planck project found orange in samples from the Sixth Dynasty to the Roman period throughout Egypt to be red ochre with or without white pigments. In the British Museum conservation project the orange color used on an early Eighteenth-Dynasty papyrus (BMEA 10477) was found to be orpiment or pararealgar with red iron oxide, the orange colors in one Ramesside and one thirtieth-Dynasty or early Ptolemaic papyrus was identified as Pararealgar and that in a late Ptolemaic papyrus (BMEA 9916) was found to be similar to realgar. In at least eighteenth- dynasty funerary papyrus (BMEA 9968) realgar has been identified as the substance used for a red orange ink in a rubric that has now turned into yellow ink in a rubric that has now turned into yellow pararealgar[4].

3.2.3.10. Pink pigments

Pink color in paintings on the plaster in tombs from the Greco-Roman period was identified as consisting of madder dye on a gypsum base[12]. Lucas (1962) refers to the following identifications of pink Pigments.

Spurrell identified the pink paint used in the Old and New Kingdoms as a mixture of red ochre and gypsum white. While Borchardt (1923) reached the same conclusion concerning the pink paint used on the Nefertiti head from Amarna (Berlin). For the Hellenistic and Roman periods, Russell (1893-1995) identified the pink color in a tomb-painting (presumably on a wall or ceiling) as madder painted over gypsum white. Wagenaar identified a late pink as finely powdered shell, but this has not been corroborated. The Max-Planck project found pink on samples from the Fifth to the Twentieth Dynasties to be invariably red ochre with or without white pigment. The unusual bright pink on the Third Intermediate Period papyrus BMEA 9919 was found to consist of an organic substance over a gypsum ground and it is possible that this might be an early example of the use of madder, Consistent with the results of Russell[3]. The change in palette from the Ptolemaic Period included a greater use of pink with new inorganic as well as the above-cited organic materials, thus the pink-red on a funerary papyrus of the late Ptolemaic or early Roman period was found to be vermilion (HgS) (BMEA 9916)[4].

3.2.3.11. Purple Pigments

True purple seems not to have been used in Egyptian painting, and the color is not mentioned by Lucas except with reference to Predynastic pottery. True purple is not to be confused with the dark red background color on the inside walls of early Twenty-second- Dynasty anthropoid coffins from Thebes, this appears to be a mixture of yellow and red ochre, judging from the analysis of the paint on two such coffins in the British Museum[4].

The most common technique of painting used since antiquity, entails the application usually with a brush but also with a swab, a stick, or the fingers of a coating of fluid paint to a surface[12].

The cakes of pigments probably were made by mixing finely ground pigment with gum such as Arabic gum and water and drying, and they were used in the same manner as modern watercolor painting, namely, by dipping the brush in water and rubbing it on the pigment[3].

3.3. Arabic Gum

Gum is obtained at the present day largely from various species of acacia that grow in the Sudan but as the acacia also grows in Egypt, where it was more plentiful formerly than now, the greater part of the ancient Egyptian gum may have been obtained locally. Pliny states that in his day the best gum was obtained from Egypt, which, however, may mean from the Sudan through Egypt[3].

Gum Arabic is mainly used as a binder in antiquity for water color painting; it is also a common constituent of inks, because it dissolves easily in water. Pigment of any color is suspended within the gum Arabic in varying amounts, resulting in watercolor paint. Water acts as a vehicle or a diluent to thin the watercolor paint and helps to transfer the paint to a surface such as paper, papyrus, walls and textiles. When all moisture evaporates, the gum Arabic binds the pigment to the support surface[57].

According to Herodotus, gum was employed to fasten together the linen bandages which mummies were warped after embalming; with reference he states that the Egyptians mostly used it instead of glue. Gum has been identified on mummy bandages in two instances (undated) by Reutter and in four instances (all Twentieth Dynasty) by L. Alfred, and Elliot Smith states that a sheet of cloth saturated with some gum-like substance was placed in front of the face of mummy of Amenhotpe 111 (Eighteenth Dynasty) and he also mentions gum saturated bandages. Spurrell found gum which he states was gum acacia, used as an adhesive for paint in the Fourth Dynasty and also in the eighteenth dynasty. This he says had decayed and left the pigment pulverulent and loose. He also states that several pots of paint were found to have a thick layer of gum overlying the color which had settled out at the bottom, these had not been exposed and the gum answered all the usual tests. Gum was also used for the painting of Akhenaton and the little princesses. It was used also on parts of the painted pavement. Laurie found gum in Nineteenth Dynasty date. Winlock reports the use of a water-soluble gum as a varnish on certain parts of the models from the tomb of Meketre (Eleventh Dynasty). Another probable use of gum was for binding together the powdered pigments to make the cakes that are found on the scribe's palettes[3].

Gum Arabic (Gum *acacia Senegal*) is defined as the dried exudates obtained from the stems and branches of Acacia Senegal, Fig.19.1 native to eastern Africa, or the related species of Acacia. It consists mainly of high molecular weight polysaccharides and their calcium, magnesium and potassium salts which on hydrolysis yield arabinose, galactose, rhamnose, glucuronic and galacturonic acids[58,58]

A damage tree will give a larger yield of gum. Thus, the natives will cut and strip the bark from a tree and return later to remove the tears of gum that form in the wounds or scars.

***Fig.19.1**. Gum acacia Senegal*

Within 3-8 weeks the gum will start to collect in the wound, but this depends on the weather conditions. Gum droplets are about 0.75-3.0 inches in diameter and they gradually dry and harden on exposure to the atmosphere. A young tree will yield 4.00-7.000g annually. Gum droplets when are grounded, the pieces are paler and have a glassy appearance**.**

Gum Arabic *(A. seyal)* is more brittle than the hard tears of gum Arabic *(A. Senegal)*. It is also available commercially in the form of white to yellowish-white flakes, granules, powder, roller dried, or spray-dried material. Gum Arabic is highly nutritious. It is related that the Bushman Hottentots have been known in times of scarcity to support themselves on it for days. In many cases of diseases, it is considered that a solution of Gum Arabic may for a time constitute the exclusive drink and food of the patients[59].

A film made of gum Arabic and formed by the evaporation of water is rigid and brittle. It is also acidic due to the presence of the glucuronic and galacturonic acids in the polymer. It has remarkably good adhesion properties. Swelling and shrinkage on absorption and desorption of water is common with thick films made of plant gums. This may cause wave-like distortions in unsized textiles in an environment with fluctuating relative humidity. Owing to their polysaccharide natural, plant gums are sensitive to photo-oxidation and undergo yellowing, accompanied by increasing acidity. The acidity of gum Arabic may cause the acid hydrolysis of silk and any paper or other cellulosic material it is in contact with. This results in discoloration to yellow or brown and embrittlement of the substrate material.

Fungi and bacteria easily colonize plant gum films under humid condition, due to the readily accessible source of sugars and sugar oligomers[60].

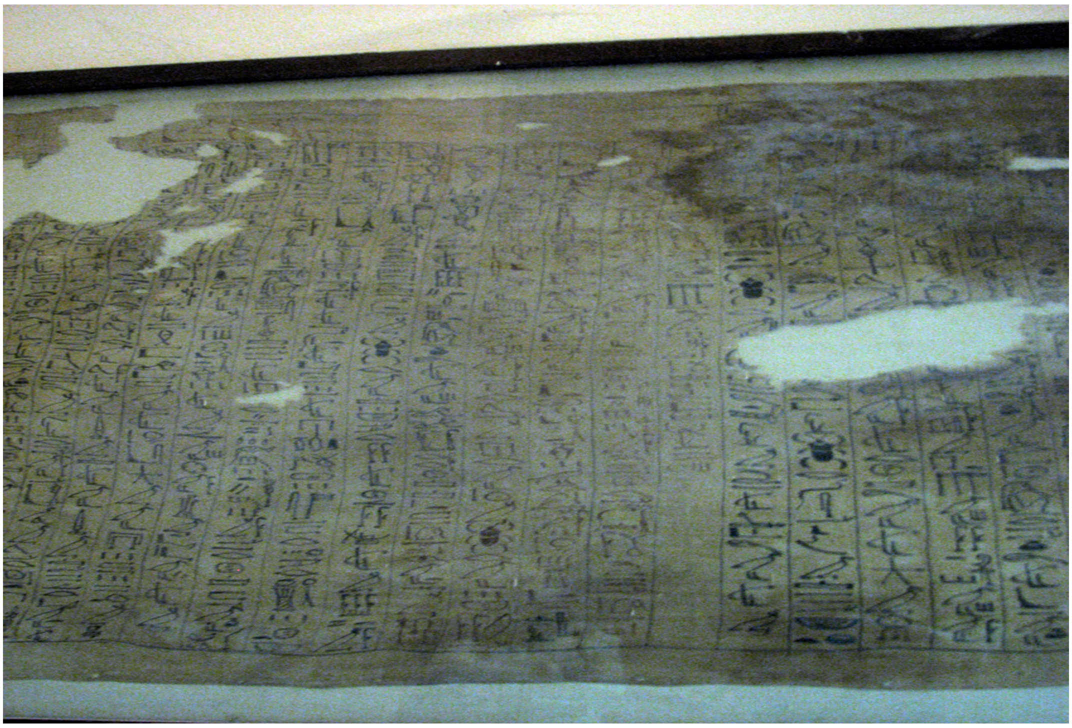


Fig.20.1. *Painted linen textiles with texts from the Book of the Dead, JE 36043, Egyptian museum, 18th dynasty*

Fig.20.2. *Painted Linen mummy-wrapping, gallery 62, British Museum. London.*

.

Fig.20.3. *Votive cloth, painted linen, New Kingdom, 19th dynasty, JE 43983, Egyptian museum, Cairo.*

Fig.20.4. *Fragment of painted linen "The funerary meal", late period, Egyptian museum, Cairo.*

Fig.20.5. *Painted Linen shroud, JE. 42999, late period, Egyptian museum, Cairo.*

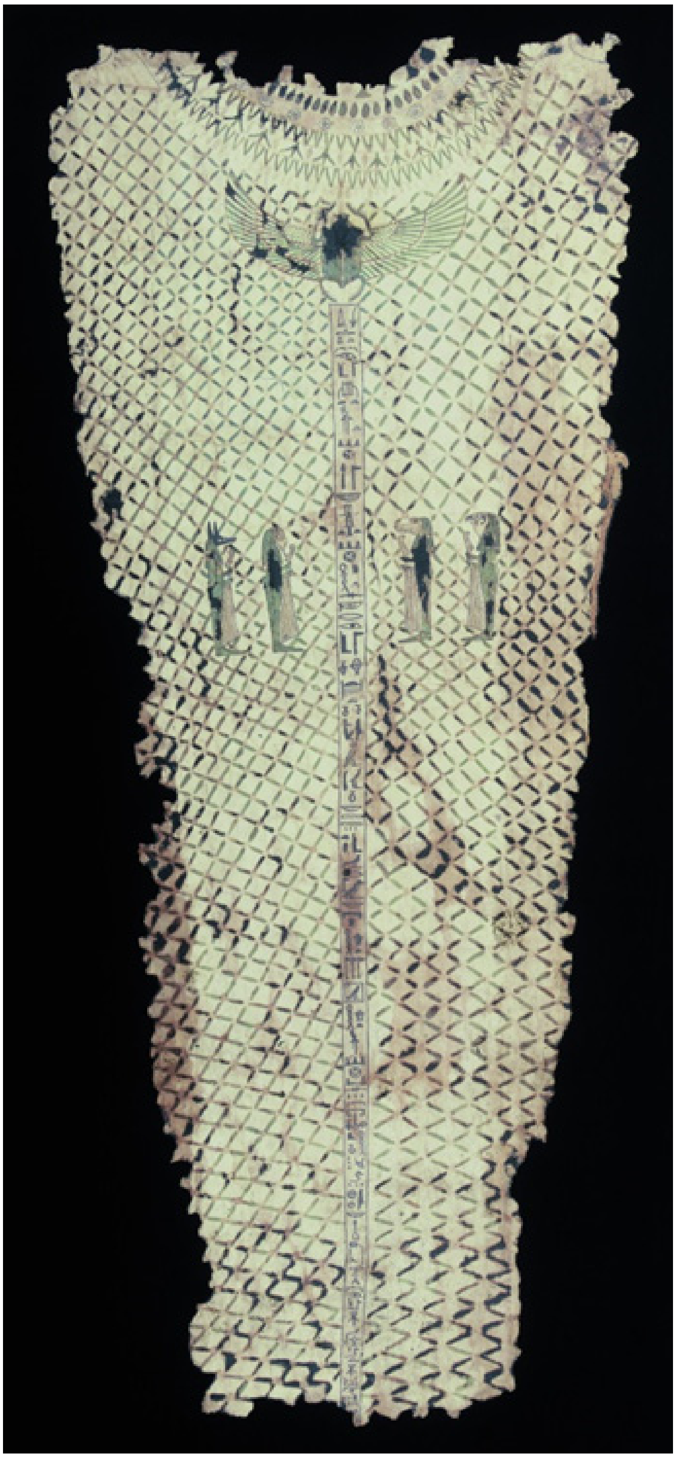


Fig.20.6. *Mummy cover, painted linen, late period, 26th dynasty, TR 11/3/25/1, Egyptian museum, Cairo.*

Fig.20.7. *Fragment of painted shroud, JE 99315, Ptolemaic period, Sheikh Abd el-Qurna, Egyptian museum, Cairo.*

Fig.20.8. *Funerary shroud, painted Linen, CG.33282, Greek-Roman period, Egyptian museum, Cairo.*

Fig.20.9. *Funerary shroud, painted Linen, JE. 41099, Roman period, Egyptian museum, Cairo.*

Fig.20.10. *Funerary shroud, Painted linen, TR 9.12.95.1, Roman period "Saqqara", Egyptian museum, Cairo.*

3.4. References

---

[1] M.V. Orna, "The Molecular Basis of Form and Color", J. Chem. Educ. 53: 638-645 (1976).

[2] K. Mclaren, "The Colour Science of Dyes and Pigments," 2nd ed., Adam Hilger Limited, 285-297 (1986).

[3] A. Lucas, "Ancient Egyptian Materials and Industries," 4th ed., Edward Arnold & Co.London 339-366 (1962).

[4] P.T. Nicholson and I. Shaw, "Ancient Egyptian Materials and Technology", 1th ed., Cambridge University Press 475-494 (2000).

[5] M.A. Littauer, J.H. Crouwel, "Chariots and related equipment from the Tomb of Tut'ankhamun". Oxford: Griffith Institute, part 2:14-18 (1985).

[6] H.H. Mahmoud, "Study of the Chromatic Changes of the Ancient Pigments in Some Wall Painting in Egypt, the Procedures of Conservation", Ph Thesis, Aristotle's University of Thaloniki, 14-28 (2009).

[7] T.D. Price, J.H. Burton, "An Introduction to Archaeological Chemistry", 3rd ed., Springer Science Business Media, LLC. 6-24 (2011).

[8] P.Z. Eirini, K.S. Andrikopoulos, V. Evangelia, "Study of the Stability of A Series of Synthetic Colorants Applied With Styrene-Acrylic Copolymer, Widely Used In Contemporary Paintings, Concerning The Effects Of Accelerated Ageing", Journal of Cultural Heritage 11: 381-931 (2010).

[9] T. Kohler, , T. Armbruster, , E. Libowitzky, "Hydrogen Bonding and Jahn- Teller Distortion in Groutite, α MnOOH, and Manganite, γ-MnOOH, and their Relations to the Manganese Dioxides Ramsdellite and Pyrolusite", Journal of Solid State Chemistry 133(2) 347-356 (1997).

[10] C.I. Pearce, C.M.B. Henderson, R.A.D. Pattrick, G. Laan, D.J. Vaughan, "Direct Determination of Cation Site Occupancies in Natural Ferrite Spinals by L 2,3 X-Ray Absorption," American Mineralogist 91: 880–93(2006).

[11] J. Winter, "The Characterization of Pigments Based on Carbon", J. Studies in Conservation, 28(2) 49-66(1983).

[12] Z. Goffer, "Archaeological Chemistry", 2nd ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 62-74 (2007),

[13] R. Oberndorf, P. Durst &etc. "Simple Technologies for Charcoal Making, Using Charcoal Efficiently," FAO Corporate Document Repository 10: 35-50 (2010).

[14] E. Kampasakali, V. Evangelia, A. Arella, "The Russian Avant-Garde Painting Palette: Documentary and Physicochemical Codification of Organic Colorants," Journal of Cultural Heritage 9:77-88(2008).

[15] A. El Goresy, H. Jaksch, W. Seipel, K.L. Weiner, "Ancient Pigments in Wall Painting of Egyptian Tombs and Temples", J. Archaeometry 12: 1–45 (1986).

---

[16] W. Noll, “Mineralogie und Technik der Bemalten Keramiken Altagyptens, Neues Jahrbuchfiir. Mineralogie, Abhndlungen, 133(13) 227–290 (1978).

[17] A. El Goresy, “Polychromatic Wall Painting Decorations in Monuments of Pharaonic Egypt: Compositions, Chronology and Painting Techniques. In: Sherratt, S. (Ed.), Proceedings of the First International Symposium: “The Wall Paintings of Thera”, Petros M. Nomikos and Thera Foundation, Piraeus, Athens, Hellas, 1: 25-36 (2000).

[18] D.J.J. Kinsman, “Huntite from a Carbonate Evaporate Environment, in the American Mineralogist, 52: 1332–40 (1967).

[19] M. Barbieri, G. Calderoni, “Huntite: a Mineral used in Antiquity”, in Archaeometry, 16: 219-228 (1974).

[20] J. Riederer, “Recently Identified Egyptian pigments”, Research notes and Application Report, J. Archaeometry 16: 211-220 (1974).

[21] I. Blom Boer, “Zusammenselzung altagyptischer Farbpigmente und ihre Herkunftslagerstitten in Zeit und Raum,” OMRO. 74: 55-107 (1994).

[22] I. Perthuisot, S. Castanier and A. Maurin, “La Huntite de la Seblcha el-Melah (Zarzis, Tunisie): un exemple de microbiodiagen Pse carbonatogene”. Bulletin de la SociCt Cgologique de France, 8-17 (1990).

[23] J.R. Barnetta, S. Millerb, E. Pearce, “Colour and art: A brief history of pigments”, Article in press, ELSEVIER, 21: 547-555(2005).

[24] R. J. Gettens, H. Kuhn, and W. T. Chase, “Identification of the materials of paintings, Lead white”, Stud. Conserv. 12(4) 125-139 (1967).

[25] R.M. Cornell, U. Schwertmann, “The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, Wiley-VCH, Weinheim, 251-225 (2003).

[26] G.K.h. Rozenberg, L.S. Dubrovinsky, M.P. Pasternak, O. Naaman, , T. LeBihan, , R. Ahuja, “High-Pressure Structural Studies of Hematite (Fe_2O_3)”, in Physical Review B. 65: 165-173(2002).

[27] M.Z. Dang, , D.G. Rancourt, J.E. Dutrizac, , G. Lamarche, R. Provencher, “Interplay of Surface Conditions, Particle Size, Stoichiometry, Cell Parameters and Magnetism in Synthetic Hematite-like Materials”, Hyperfine Interactions 117(1-4) 271- 319(1998).

[28] J. Wouters, L. Maes and R. Germer, “The Identification of Hematite as A red Colorant on an Egyptian Textile from the Second Millenium B.C.”, Studies in Conservation 35: 89-92 (1990).

[29] R. J. Gettens, R. L. Feller, and W. T. Chase, “Vermilion and Cinnabar”, Studies in Conservation 17: 45-69 (1972).

[30] J.R. Barnetta, S. Miller, E. Pearce, “Colour and Art: A Brief History of Pigments”, J. Optics & Laser Technology 38: 445-453 (2006).

[31] V. Finlay, “Colour: Travels Through the Paint Box Hodder and Stoughton; in Architectural Colour in the Professional Palette,” 1th ed., Hodder & Stoughton 323-344 (2003).

---

[32] Y. Jin , X. Wang, J. Lu, C. Zhang , Q. Duan , " Effects of modern and ancient human activities on mercury in the environment in Xi'an area, Shannxi Province, P.R. China", Atmospheric Environment, 42(36) 8382-8883 (2008).

[33] M. Calamiotou, M. Siganidou, S. E. Filippakis, "X-Ray Analysis of Pigments from Pella, Greece", International Institute for Conservation of Historic and Artistic, Studies in conservation 28(3) 117-121 (1983).

[34] M.E. Malainey, "A Consumer's Guide to Archaeological Science, Manuals in Archaeological Method, Theory and Technique", 1th ed., Springer Science+Business Media, LLC. 361-365 (2011).

[35] J. Jakubko, E. Cernoskova, "Differential Thermal Analysis of the Mixtures of Silicon and Red Lead", Journal of Thermal Analysis 50(3) 511-515(1997).

[36] M.E. Madden, R.J. Bodnar, J.D. Rimstidt, "Jarosite as an Indicator of Water-Limited Chemical Weathering on Mars Nature in Sedimentary Geology at Meridiani Planum, Mars", Gulf Professional Publishing 431(7010) 821-3 (2004).

[37] A.B. Moussa, "Assessing The Decay Agents Of Wall Paintings in AL Qurna And Wadi EL Natrun Regions-Egypt", Phd.Thesis, Aristotle University of Thessaloniki, Faculty of Sciences, School of Geology, 222-228, (2007).

[38] H. Jaksch, " Farbpigments aus Wandmaleraien altagyptischer Graber und Tempel: Technologien der Herstellang und Mögliche Herkunftsbeziehungen", Dissertation, Univ. Heidelberg, 241-249 (1985)

[39] N. Buzgar, A. Buzatu, A.I. Apopei, D. A□tefanei, F. Topoleanu, "Raman Study of The Brownish-Yellow Pigment from a Roman Basilica (Dobrogea, Romania, 4th–6th century A.D.)", Analele Stiintifice ale Universitatii "Al. I. Cuza" din Iasi Seria Geologie, 57(2) 15–18 (2011).

[40] S. Lahlil , E. Martin, "Characterisation of 18 Melkite Icons Dating from the 17th to the 19th c. AD", Journal of Cultural Heritage 13: 332–338 (2012).

[41] B. Roger, J.R. Herbert, "Properties of Goethite and Jarosite Precipitated From Acidic Groundwater, Dalarna, Sweden", J. Clays and Clay Minerals 45(2) 261 273(1997).

[42] W. Rostoker, B. Bronson, "Pre-Industrial Iron: Its Technology and Ethnology", Review in Journal of the economic and social history of the Orient (Leiden) 36: 304-308 (1993).

[43] D.A. Scott, "Ancient Egyptian Pigments: The Examination of Some Coffins from the San Diego Museum of Man," MRS Bulletin- Materials Research Society 35(5) 390-396 (2010).

[44] G. Robins, "The art of ancient Egypt", 2nd ed., Harvard University Press, 156-171(2000).

[45] M.S. Tite, , "Egyptian Blue, faience and related materials", in Jones, R. E. and H. W. Catling (eds.), Science in Archaeology, British School of Athens, London 2:30-39 (1986).

[46] M. Bimson, M.S. Tite, M. Cowell, "Technological Examination of Egyptian blue. In: Lambert, J.B. (Ed.)", Archaeological Chemistry III, American Chemical Society, Advances in Chemistry Series, 215–242 (1984).

---

[47] H. Wiedemann, G. Bayer, “The bust of Nefertiti the analytical approach”, J. Analytical Chemistry 54, 619- 628 (1982).

[48] M. Uda, , M. Nakamura, , S. Yoshimura, J. Kondo, , M. Saito, Y. Shirai, & etc. ‘‘Amarna blue, Painted on Ancient Egyptian Pottery”, Nuclear Instruments and Methods in Physics Research B. 189, 382–386 (2002).

[49] H. Berke, “Chemistry in Ancient Times: The Development of Blue and Purple Pigments,” Angewandte Chemie International Edition, 41(14) 2483-87(2002).

[50] C.S. Hurlbut, C. Klein, “Manual of Mineralogy”, 3rd ed., Durrie & Peck 375-391 (2006).

[51] D. Evans, D. Hamburg, M. Mickelsan, “A Papyrus Treatment: Bringing the Book of the Dead to Life”. In Art Conservation Training Programs Conference, Newark, University of Delaware, 109-113 (1980).

[52] F. Weatherhead, “Two Studies on Amarna Pigments” in Amarna Reports, London: EES. 6: 391-396 (1995).

[53] Y. Seto, S. Ohi, N. Shimobayashi, M. Kitamura, A. Miyake, Y. Hiroi, , G.H. Grantham,. “Clinopyroxene Exsolution in Wollastonite from Namaqualand Granulite, South Africa”, in American Mineralogist, 91: 446-450 (2006).

[54] L. Lee, S. Quirke, “Painting Materials, in Ancient Egyptian Materials and Technology”, (Shaw, I., Ed.,) 1st ed., Cambridge University Press, London, UK. 104-120 (2001).

[55] S. Schiegl, “Diversity of Newly Discovered Deterioration Patterns in Ancient Egyptian Pigments”, Materials Research Society, 831-858 (1992).

[56] C. Smitt, J. Cox, P. Davies, “Salt Transport in the Bremer Hills, Interpretation of Spatial Datasets for Salt Distribution, Fourth Report for NAP South Australian Salt Mapping and Management, in Sciro Land and Water”, Australia, 49: 654-662 (2003).

[57] K. Wenite, “The Materials and Techniques of Painting”, 4th ed., Prentice Hall, New York, 44-56 (2001).

[58] C. Cozic, L. Picton, M.R. Garda, F. Marlhoux, D. Cerf, “Analysis of Arabic gum: Study of Degradation and Water Desorption Processes”, Food Hydrocolloid 23: 1930–1934 (2009).

[59] O.S. Azeez, “Decolourization of Gum Arabic using Activated Charcoal”, Leonardo Journal of Sciences, 7: 23-32 (2005).

[60] A. Timar-Balazy, D. Eastop, “Chemical Principles of Textile Conservation”, 1th ed., Butterworth-Heinemann, London, 123-124 (1998).

CHAPTER 4

Experimental work

4. Experimental

The aim of this study is to evaluate the physicochemical properties of Egyptian linen textiles coloring with a variety of inorganic pigments and organic natural dyes used in coloring linen textiles in ancient times after thermally aged to get linen samples which are similar as possible to the ancient linen textiles.

Furthermore, illustrate whether, pigments and natural dyes playing a role in protecting the fiber from the thermal deterioration or even reduce the exposure of the fibers to the damage.

The evaluations were based on Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) configured with an EDS microanalysis detector, X-ray powder diffraction (XRD) tensile strength and elongation measurments.

The results of this study may explain why archaeologists discovered colored textiles in great quantities in comparison with the analogous uncolored ones. Furthermore, the latter are far more deteriorated. Moreover, changes in the properties of linen textiles which may occur as a result of coloring processes after thermal ageing are deliberated. Evaluation and comparison of different methods and techniques of exposition of textiles and paintings will be discussed in terms of analytical techniques.

In this study some laboratory new coloured linen samples with some of pigments and natural dyes were prepared with techniques as close as possible to the ancient ones.

4.1. Materials and methods

4.1.1. Fabric

Scoured, unbleached Egyptian plain linen fabrics were supplied by Egylan Co. at the Second Industrial Zone, Alexandria, Egypt. Warp and weft threads are 20 and 18 per cm respectively. The fabrics were further purified in the laboratory (scouring) by boiling in water for 1 hour[1] and then boiling in a solution containing 2.0 g/L of sodium carbonate at a temperature of 60°C for 1- 1½ hour in order to remove natural wax and other impurities. Samples were thoroughly washed with tap water and dried at ambient conditions[2]. After that the linen samples were cut into 5× 20 cm (width × length) warp test specimens. The warp strips were produced by ravelling away yarns on each side forming 4.5 cm wide strips with a 2.5 mm fringe down each side[3].

4.1.2. Colour materials

Commerical inorganic natural and synthetic pigments from Kremer (pertinent information included in parentheses has been provided by 'Kremer pigmente GmbH &Co".

Hematite (Fe_2O_3) (N.48600), Egyptian blue ($CaCuSi_4O_{10}$), (N.10060), Malachite ($CuCO_3.Cu(OH)_2$), (N.10300), Gypsum ($CaSO_4$ $2H_2O$), (N.58300), Yellow Ochre ($FeO(OH)$), (N.48000), Vermillion (HgS), (N.42000) and Charcoal (C), (N.10350). The choice of the pigments was done based on some of the most common pigments which used in painting in different period in ancient Egypt while we excluded others based on orpiment and lead due to their toxicity.

Arabic Gum was used as a binding media of the pigments, supplied by Elatar shop, Egypt. Arabic Gum was extensively used in ancient Egypt as a binding media for water colors techniques[4] promoted by the fact that it is also a common constituent of ink. According to Herodotus, Arabic gum was utilized to fasten together the linen bandages which mummies were warped after embalming. Accordingly, gum has been identified on mummy bandages in two instances (undated) by Reutter, and in four instances (Twentieth Dynasty)[5].

4.1.3. Natural Dyes

Commercial organic natural dyes were kindly provided by Department of Organic Chemistry, Aristotle University of Thessaloniki: Indigo, Madder, Turmeric, Cochineal, Henna, Safflower and Saffron. The details of the tested dyes are mentioned previously in chapter 2. The choice of the dyes was done based on the some of the most important natural dyes which used in dyeing in different period in ancient times.

4.2. Preparation of painted samples

The linen samples were painted directly by utilizing the brush on the linen samples without a ground layer because this technique is the most common used in painting textiles in ancient Egypt[6]. The procedure followed involved dissolving 15.0 g of Arabic gum in 300 mL of hot water, stirred it thoroughly and left overnight until it was completely dissolved[7]. The cakes of pigments were made by mixing finely 5.0 g of each pigment with 10 mL of Arabic gum solution and let them to dry. They were used in the same manner as modern watercolor painting, namely, by dipping the brush in water and rubbing it on the pigment and then paint the samples[5]. The samples were left to dry completly in ambient temperatures.

4.3. Preparation of dyed samples

4.3.1. Mordanting procedure

Alum (potassium aluminum sulphate ($KAl(SO_4)_2 12H_2O$) was the most important mordant for dyeing with natural dyes in ancient times and was also used in this study. The linen samples were treated with the mordant solution. The alum (8.0 g) was first well dissolved in a small quantity of water and then added to 1 L of hot water (40°C). 30.0 g of linen fibers were entered into the mordant solution and then slowly heated to 90°C, turned the linen occasionally to ensure that it takes up the mordant evenly. Left the mordant solution for 1 h at this temperature and let the linen fibers cool in this solution at room temperature (RT). The linen samples were removed, squeezed and air dried, until it was dyed[8].

4.3.2. Dye bath and dyeing process

The linen samples were dyed separately with natural dyestuffs according to published procedures[8]. 3.0 g of pulverized madder roots or 2.7 g of turmeric powder or 15.0 g of henna powder or 1.8 g of cochineal or 6.0 g of safflower or 1.5 g of saffron were wrapped loosely in a cotton cloth and the bundle was soaked in 180 ml of deionized water for 12 hours at RT. The temperature of the dye bath was increased very slowly to 80- 90°C and the solutions of all dyestuffs were boiled for ½-1 h, except of madder and cochineal dye bath were boiled for only10-15 min, "because the dyeing time must not be too long, this would impair the brilliance of the red, and the result would be brown-red". The bundles containing the dyes powder were pressed frequently with a spoon to help the dye to dissolve. After cooling, the bundle with the dyestuffs was removed from the bath and pressed as much dye as possible out of the bundle. Then the dyebath was diluted with water to 180 mL. About 6.0 g of alum-mordanted linen was then rinsed with water and was immersed in a dye bath at 40°C heated to boiling point for ½-1 h. After cooling the dye bath, the linen was removed, rinsed with deionised water and dried in the dark.

For the indigo a different process was followed. 3.0 g of indigo powder was stirred with 15 mL of warm deionized water in a glass beaker until a paste is formed. 6.0 g of sodium carbonate (Na_2CO_3) in 24 mL of distilled water was added to the indigo paste and the mixture was stirred. 6.0 g of sodium dithionite ($Na_2S_2O_4$) was added to the mixture and 200 mL of deionized water was added. The mixture was heated to 55°C resulted in a yellowish solution. After 20 min the color turned to yellow-green. 6.0 g of the scoured, unmordanted linen was wetted in warm water and then was immersed in the dye bath of indigo at 55°C for some minutes, so that no oxygen can enter into the vat "dyebath". Then the linen fibre was taken out of the vat and squeezed the liquor out thoroughly. When the linen fibers came out of the vat, they had a green-yellow colour, which turned to blue in 20 min, when the material was exposed to the air. Finally, it was dried completely and rinsed thoroughly with deionised water. In order to obtain a deeper shade, dip the linen into the liquor again and take them out after 15-20 min. Repeated dipping and airing makes the dyed shade deeper and deeper[8].

4.4. Acidity measurements

Cellulose is most stable in a neutral condition. Both acid and alkaline cause damage[9], Linen is resistant to dilute acids, but it is damaged by diluted hot and cold concentrated acid[10]. High acidity carries out acid hydrolysis of the cellulose polymer. The product of acid hydrolysis is called "hydrocellulose", which is a rigid, brittle and mechanically weak material which may turn to powder. Alkaline attack the glycosidic ether bonds between two anhydroglucose units of cellulose. Extreme swelling of cellulose may occur in strong alkaline solution. Under this extreme condition, cellulose may swell enormously but will not dissolve[11].

The acidity of the dyebath solutions was measured during the dyeing process with pH-indicator strips (non-bleeding) (Merck KGaA, Germany) and was found to be from neutral to mild alkaline (pH = 7-8).

4.5. Accelerate Thermal Ageing (TA)

Ageing is the processes of changing over time, the term ageing as applied to museum objects, generally combines degradation and deterioration. Ageing may be defined as irreversible changes that occur slowly over time[12] .

Thermal degradation aimed at the production of artificially aged model of linen fabrics similar as possible to the archaeological ones, taking into account that the thermal degradation increases with increasing the temperature degree and the duration of ageing[11].

Painted and dyed linen samples were hanged separatly in a temperature-controled electronic oven and thermally aged at a constant temperature of 140°C for 72 h, according to Kerr et al(1989)[13] and Feller (1994)[14]. This is estimated to be equivalent to about 100-200 years of ageing under normal conditions. Although this is a good approximation for natural ageing. it lacks the presence of moisture, which severely affects the phenomenon. On the other hand, the environmental conditions in which the ancient Egyptian linen textile was manufactured and kept were not so humid. Finally, electronic oven was turned of and left to cool until it reached room temperature, thenThe samples were removed and settled at ambient conditions for 24 h[15]. The standard uncolored linen sample was let without ageing.

Standard unpainted, unaged linen

unpainted,thermally aged linen

painted linen with Egyptian blue

painted linen with Malachite

painted linen with Hematite

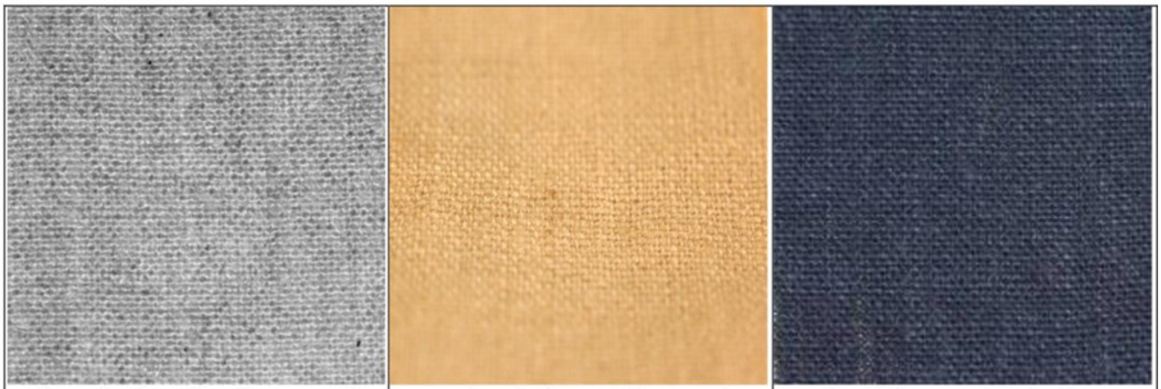
painted linen with Vermillion

painted linen with Yellow ochre

painted linen with Charcoal

painted linen with Gypsum

Fig.21.1. *Standard and painted linen samples.*


Standard undyed, unaged linen

undyed, thermally aged linen

dyed linen with Indigo


dyed linen with Madder

dyed linen with Turmeric

dyed linen with Cochineal


dyed linen with Henna

dyed linen with Safflower

dyed linen with Saffron

Fig.21.2. *Standard and dyed linen samples*

4.6. Scientific Techniques Used in the Analysis of Tested Painted, Dyed Linen Fibres and Archaeological Samples

4.6.1. Introduction

The materials (organic and inorganic) used by the artist are an important object of study for the analytical chemist and conservators. Nowadays, all important museums throughout the world have teams of scientists to help with the work of conservation. Similarly, any plan for conservation treatment on works of historical and artistic importance has to consider the historical, stylistic-aesthetic, scientific and technical aspects.

The analytical information obtained is given to the conservator-restorer of the work of art to provide a scientific diagnosis on the conservation conditions and sufficient information on the chemical characteristics of the materials which may be subjected to treatment. Among other analytical problems certain constraints on the sampling and preliminary treatments have to be resolved which are due to the characteristics of the objects in the study as works of great cultural and historical value whose loss would be irreparable because they are unique. The main analytical problem involves identification of organic and inorganic components in works of art.

Other analytical studies aim to clarify the influence of the environmental agents (e.g. light, temperature, and relative humidity), biological agents and atmospheric pollution on the degradation process of these types of materials. These studies should be carried out prior to designing preventive conservation treatment. In these treatment programs the identification and quantification of the above alteration agents are essential. The analytical chemist is also needed when restoration treatment is decided on, to help chose the products used in each step (cleaning agents, protective agents, solvents, etc.) and the most effective application method[16].

The analysis of the materials used in textile dyeing may be a valuable tool to understand how an object originally looked, where it comes from and how old it is. The identification of the colorants used on ancient textiles provides a historical pathway to the understanding of the processes associated with one of the oldest of chemical technologies, namely textile dyeing and discover the development and technological advancement of textile dyeing through various archaeological periods[17]. Also the identification of archeological textile dyes and pigments is of great interest as it can provide information regarding the commercial transactions possibly allowing the usage of a certain dye far from its geographical source[18], furthermore, to understand the techniques of color preparation and application. In addition, through the study of pigments, it is possible to discover the lines of communication and trade exchange[19].

Moreover, the identification of the coloring materials can help the restorers to choose the proper cleaning conditions as well as to understand the degradation processes taking place on selected areas of the textiles. Organic dyes are among the most labile components of a work of art, due to their poor light fastness. Over the last few decades, analytical chemistry has developed useful procedures to identify organic dyes in works of art, but the analysis of historical samples is still a challenging task. The analyst has to deal with four major problems: the relatively small amount of samples available, the low concentration of dye molecules in the original material, the presence of possible degradation products, and the lack of information on the original recipes[20].

Lahanier et al. (1985) [21] reported that the ideal method for analyzing objects of artistic, historic, or archaeological nature should be:

(a) *Non-destructive, i.e.* respecting the physical integrity of the material/object. Often valuable objects can only be investigated when the analysis does not result in any (visible) damage, usually this completely eliminates sampling or limits it to very small amounts or in situ analysis to avoid any sampling or loss of the archeological artifact.

(b) *Fast*, so that large numbers of similar objects may be analyzed or a single object investigated at various positions on its surface, this property is very valuable since this is the only way of being able to discern between general trends in the data and outlying objects or data points.

(c) *Universal*, so that by means of a single instrument, many materials and objects of various shapes and dimensions may be analyzed with minimal sample pretreatment, allowing with the same technique average compositional information to be obtained, but also local information of small areas (e.g. millimeters to micrometer-sized) from heterogeneous materials.

(d) *Sensitive*, so that object grouping and other types of provenance analysis can be done not only by means of major elements but also by means of trace-element fingerprints.

(e) *Multi-elemental*, so that in a single measurement, information on many elements is obtained simultaneously and more importantly, so that also information is obtained on elements which were not initially thought to be relevant to the investigation[21] .

4.6.2. Methods of Analysis

4.6.2.1. X-ray Diffraction Analysis (XRD)

It is considered the most famous method used in the identification of crystalline compounds by their diffraction pattern. X-ray diffraction plays an important role in the study of works of art and museum objects, also it helps in answering questions related to degradation processes[22].

One of the most important applications of XRD to textiles is the study of fibres texture, i.e. the degree of molecular orientation, the size and shape of the crystallites and the degree of crystallinity, for these factors control the physical and physico–chemical properties to a large degree. The crystalline nuclei give a fibre brittle strength, while the amorphous regions give resilience and some plasticity. The term crystalline and amorphous as used in connection order, but they should not be taken too literally, since the same long chain molecule may run through several crystalline regions and pass through all intermediate state from perfect order to complete disorder[23,24].

X-rays are electromagnetic radiations with typical photon energies in the range of 100 eV–100 keV. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials, the energetic X-rays can penetrate deep into the materials and provide information about the bulk structure[25]. Powder X-ray diffraction is perhaps the most widely used X-ray diffraction technique for characterizing materials such as:

- Characterization of crystalline materials.
- Identification of fine-grained minerals such as clays and mixed layer clays.
- Measurement of sample purity.

As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The term "powder" really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various *d* spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. Powder diffraction data can be collected using either transmission or reflection geometry, because the particles in the powder sample are randomly oriented, these two methods will yield the same data.

Powder diffraction files: the task of building up a collection of known patterns was initiated by Hanawalt, Rinn, and Fevel at the Dow Chemical Company (1930). They obtained and classified diffraction data on some 1.000 substances. After this point, several societies like ASTM (1941–1969) and the JCPS began to take part (1969–1978). In 1978, it was renamed the International Center for Diffraction Data (ICDD) with 3.00 scientists worldwide. In 1995, the powder diffraction file (PDF) contained nearly 62.000 different diffraction patterns[26], in 2012, the powder diffraction file (PDF) contains nearly 760.019[27].

Samples: X-ray powder diffraction techniques usually require some sample preparation. This may involve crushing the sample to fit inside a glass capillary tube, or packing it into a sample holder. The ideal specimen is a statistically infinite amount of randomly oriented powder with crystallite size less than 10 μm, the most easily prepared, and most commonly used specimen mounting is the 'smear' on a glass plate[26].

In this study X-ray diffraction patterns were carried out for studying the size, shape of the crystallites and the degree of crystallinity of textiles samples. Moreover, identiffication of three ancient inorganic pigments, by using a Bruker AXS D8 Advance diffractometer in Bragg–Brentano geometry equipped with a Cu sealed-tube radiation source (λ = 1.54178 Å) and a secondary beam graphite monochromator, Fig.22.1. The textile samples were investigated by XRD in a small piece without crushing them to powder.

Figure.22.1. *X-ray diffraction chamber, School of physics, Ioannina University.*

4.6.2.2. X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence (XRF) spectrometry has been used for the investigation of archaeological and historical materials for some fifty years, though, a great variety of spectrometers has been successfully employed[28].

The main advantages of XRF techniques are their rapidly, enabling multi-component analysis, and providing simple spectra, accuracy and reproducibility. Applications of this technique to the analysis of artwork have been related to the identification and determination of major, minor, and trace elements composing inorganic materials such as pigments, metal, stone, ceramics, glass, surface coatings and deposits of adventitious materials on the surface, etc[29].

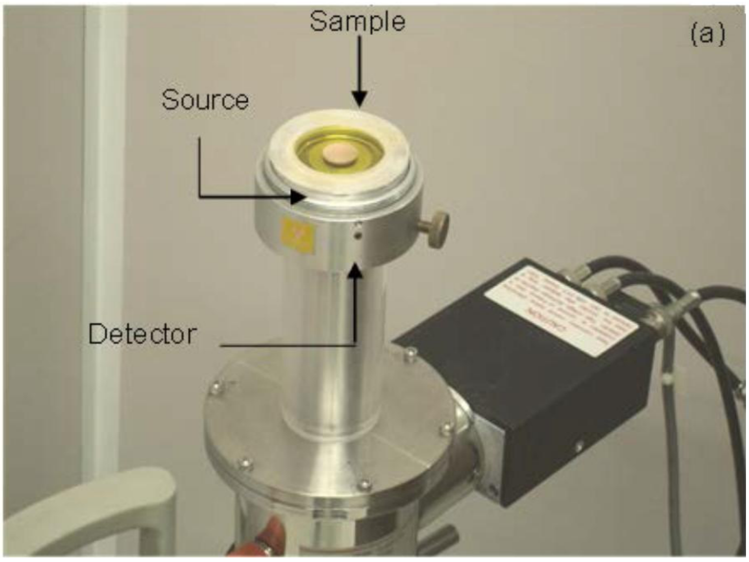
All XRF techniques are working without consuming the samples and give range from 100% down to some ng/g[30]. X-ray fluorescence analysis is both a qualitative and quantitative analytical method, it can be applied to the identification of practically all elements with atomic number $Z > 11$ [31],[32].

However, many light elements are quite difficult to measure and require advanced instrumentation. Even in that case, the detection of the characteristic radiation of the elements with an atomic number between 11 and 16 (Na–S) is difficult[33]. Basic principle of this method is that an inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis).

A typical XRF spectroscopy arrangement includes a source of primary radiation (usually a radioisotope or an X-ray tube) and equipment for detecting the secondary X-rays[34].

In this study X-Ray Fluorescence (XRF) Spectroscopy was done to obtain on Elemental compositions of the three ancient inorganic pigments (red, yellow, and green).

Sample excitation was performed with an annular ^{109}Cd radio-isotopic source. The source has a radius of 14.5 mm and is housed in a cylindrical container, fixed coaxially above a CANBERRA SL80175 Si(Li) detector (5 mm crystal thickness, 80 mm2 area), with a 25 µm-thick Be window and an energy resolution of 171 eV for the 5.9 keV Mn Kα line. Data acquisition was performed using a PCI card, controlled by the ORTEC MAESTRO-32 emulator and spectral analysis was carried out using the WinQxas software package (IAEA 1997-2002). Samples were measured in the form of thin pellets, 12 mm in diameter, prepared by mixing 10.0 mg of sample with cellulose. Elemental compositions were assessed with reference to standard pellets prepared using $FeCl_2 \times 4H_2O$, $CuCl_2$, $CaCl_2 \times 2H_2O$ and JLs_{-1} standard limestone.



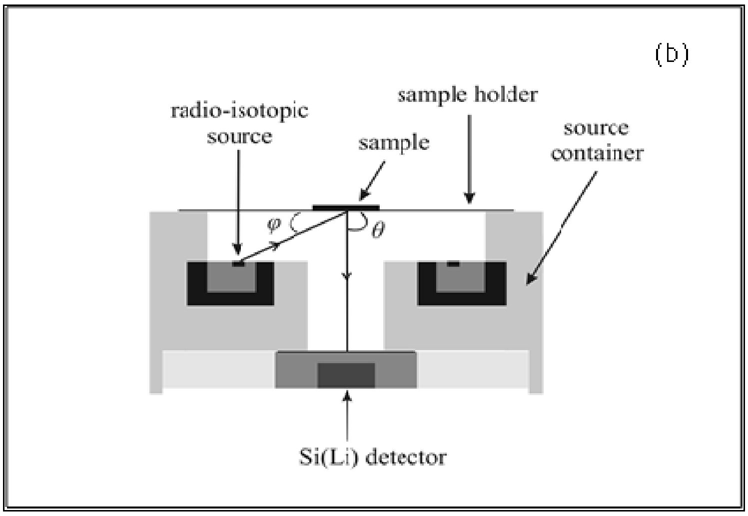


Figure.22.2. *(a) Illustration of the XRF setup used for sample analysis. (b) Schematic diagram of the excitation-detection geometry: φ is the angle of incidence on the sample for the exciting radiation, while θ is the angle of emergence from the sample for the fluorescence radiation, School of physic, Ioannina University.*

4.6.2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

It is an analytical technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic, also it is considered a powerful tool for the study of the deterioration processes.

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FT-IR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FT-IR spectral pattern is then analyzed and matched with known signatures of identified materials in the FT-IR library. The FT-IR technique offers a quick analysis of micro samples (less than 0.5 mg)[35], and can be used to identify an unknown sample especially when compared to known spectra[36].

In particular, the greatly improved sensitivity and spatial resolution achieved by coupling a microscope to the FT-IR spectrophotometer revealed new and interesting spectral features-certainly not evident in the well-known transmission spectra- which should be taken into account when carrying on the identification of pigments[37].

KBr method

To measure an infrared spectrum of a powder sample by a transmission method, the KBr disc method is usually used. Since a particle diameter is too large when we use a powder sample as it is, incident light is irregularly reflected and, as a result, we cannot obtain a good spectrum. Therefore, it is necessary to crush the sample into pieces each having a diameter of 1–2 pm in advance. When using the KBr method, crush and mix 1–2 mg of a sample and approximately 100 mg of KBr powder in an agate mortar, introduce the mixture into a tabletting equipment, and tablet. If the sample is not sufficiently crushed, the tablets produced will become opaque or the quantity of transmitted light will decrease (due to light scattering). Hence, the crushing must be sufficient. When the amount of the sample is small, micro-tabletting can be used which allows one to make a tablet having a diameter of 1 mm[38].

In this study FTIR spectra were recorded on a Perkin–Elmer Spectrum GX FTIR system Fig.22.3. in the 4000 to 370 cm^{-1} range, with 4 cm^{-1}signal resolution. All spectra were taken with an average of 32 scans. Samples were prepared as KBr pellets by pressing the ground material at 1 % concentration[39]. The collected spectra have been expressed by absorbance units and baseline has been corrected. The IR results were performed over the normalized spectra.

Fig.22.3. *The Perkin-Elmer Spectrum GX FT-IR spectrometer used in the study Laboratory of Inorganic and analytical Chemistry, Ioannina University.*

4.6.2.4. Scanning Electron Microscopy (SEM-EDS)

Scanning Electron Microscopy has been extensively used for the material characterization of objects of artistic and archaeological importance, especially in combination with energy dispersive X-ray microanalysis (SEM/EDS). Moreover SEM have been widely used for studying the texture of materials, the alteration and biodeterioration of materials, and for monitoring consolidation and cleaning treatments on textiles, stone, ceramics, paintings, sculpture, archaeological, and ethnographical objects[40].

Furthermore, scanning electron microscopy offers powerful means of characterizing materials by utilizing the wide range of signals resulting from the interaction of solid samples with a scanning beam of energetic electrons.

In this way, a wide range of topographic (e.g., detailed fracture surface shapes), micro structural (e.g., the size and shape distributions of phases) and micro chemical (e.g., segregation profiles) information can be retrieved, often with sub-micron spatial resolutions. An obvious attraction of SEM techniques is the ability to form readily-accessible visual images from the various signals emanating from the sample, for example, surface topography and shape (secondary electron imaging), the determination of local crystallographic orientation using selected area channeling patterns and the determination of local chemical composition (including the detection of light elements down to carbon) using energy dispersive X-ray analysis (EDS) techniques[41].

Scanning Electron Microscopy uses electrons instead of light and magnetic lenses focuses the electron beam which is irradiated on a sample placed in a vacuum chamber. From the interaction between the electrons and the sample surface photons and various electron signals are emitted. Detectors collects these signals such secondary electron and X-ray detectors which are extensively used in conservation.

Samples must be prepared with a conductive coating, most often carbon. Gold or palladium coatings may be more desirable for pure imaging due to their greater conductivity. Cross-sections may be examined using SEM but this requires a highly polished sample. SEM is often used in combination with EDS, which identifies the elemental composition of a sample, heavier than boron. This technique measures emitted X-rays and generates fluorescence from atoms in its path. EDS output is in the form of a peaked spectra or X-ray mapping[21].

In this study textile samples were examined by SEM (Secondary Electron) in a Jeol JSM 5600 system configured with an energy dispersive X-ray spectroscopy (EDX) detector , Fig.22.4. operating at 20-kV accelerating voltage and 20-mm working distance. The surface morphology of textile samples was measured on small pieces coated with a thin film of gold for 90 seconds, using POLARON SC 7620 SPUTTER COATER to increase their conductivity and to avoid charging effects[42]. The EDX data were compiled for analysis using the Link ISIS system (Oxford Instruments, UK).

Fig.22.4. *SEM, Jeol JSM 5600 system configured with an EDX detector [Oxford Instruments, UK) used in the study, Laboratory of Inorganic and analytical Chemistry, Ioannina University.*

4.6.2.5. Tensile strength and elongation measurements

Tensile strength is the breaking strength of the fibre. It is expressed as a force per unit of cross sectional area. Elongation characterizes is the stretching properties of a fibre or yarn when subjected to a force. It is expressed as a percentage of the original fibre or yarn length relative to the length of the stretched fibre. It can be measured either as an elongation under a particular load or (more commonly) as the elongation reached when the fibre breaks. The tensile strength and elongation properties of fibres are dependent on the temperature and relative humidity of the atmosphere[43,44].

Equipment: The most common testing machine used in tensile testing is the universal testing machine. This type of machine has two *crossheads*; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen. The machine must have the proper capabilities for the test specimen being tested. There are three main parameters: force capacity, speed and precision and accuracy. Force capacity refers to the fact that the machine must be able to generate enough force to fracture the specimen. The machine must be able to apply the force quickly or slowly enough to properly mimic the actual application. Finally, the machine must be able to accurately and precisely measure the gauge length and forces applied, for instance, a large machine that is designed to measure long elongations may not work with a brittle material that experiences short elongations prior to fracturing.

Alignment of the test specimen in the testing machine is critical, because if the specimen is misaligned, either at an angle or offset to one side, the machine will exert a bending force on the specimen. This is especially bad for brittle materials, because it will dramatically skew the results. This situation can be minimized by using spherical seats or U-joints between the grips and the test machine. A misalignment is indicated when running the test if the initial portion of the stress-strain curve is curved and not linear. Newer test machines have digital time, force, and elongation measurement systems consisting of electronic sensors connected to a data collection device (often a computer) and software to manipulate and output the data.

Process: The test process involves placing the test specimen in the testing machine and applying tension to it until it fractures. During the application of tension, the elongation of the section is recorded against the applied force[45].

In this study tensile strength and elongation percentage at break of colored (painted and dyed) and standard uncolored, unaged linen samples with dimension 4 × 4 cm, before and after TA were measured using Tensile Testing Machine Type INSTRON 3344, Model 2519 106, Fig.22.5. These tests were done according to ASTM (2000) D 5035-95[46], the initial jaw spacing was 50 mm and the test speed was 25 mm/ min, temperature was 23°C, and R.H. 65%. Five samples of each standard and colored sample were replicated for each test and the results were expressed as average values.

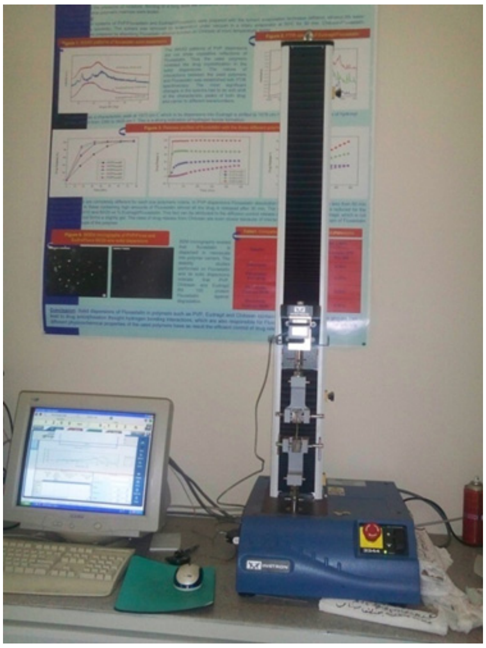


Fig.22.5. *Tensile Testing Machine Type INSTRON 3344, Model 2519 106 used in the study, National Research Centre, Cairo, Egypt.*

4.7. Refrences

---

[1] H. Wickens, “Natural Dyes for Spinners and Weavers”, 1th ed., B.T.Batsford Limited.London, 27-75(1983).

[2] M.N. Micheal, F.M.Tera and E. M.Othman, “Degradation Measurements of Linen Fabrics” J. Polymer-Plastics Technology and Engineering, 43: 1377-1386 (2005).

[3] O.M.A. Abdel-Kareem, “The Long-Term Effect of Selected Conservation Materials Used in The Treatment of Museum Artifacts on Some Properties of Textiles,” Polymer Degradation and Stability 87: 121-130 (2005).

[4] V. Gillian, E .Wood, “Textiles”, in Ancient Egyptian Materials and Technology”, 1th ed., Cambridge, University press, U.K. 475-494 (2000).

[5] A. Lucas, “Ancient Egyptian Materials and Industries”, 4th ed., London, 5-7 (1962).

[6] M. Taro, A. To., “Genuine of False Investigation of Metal-Printed Textiles Dated to the 11-15th Centuries”, 10th Triennial Meeting Washington, D.C, ICOM Committee for Conservation, Allen Press, 325-380 (1993).

[7] A. Neuburger, “The Technical Arts and Sciences of The Ancients”, translated by Henryl Brose, Barnes & Noble Co.LTD, London, 420-433(1969).

[8] H. Schweppe, “Practical Hints on Dyeing with Natural Dyes”, 1th ed., Smithsonian Institution, Washington DC USA, 1-61 (1986).

[9] T. Padfield, “The Deterioration of Cellulose”, in “Problems of Conservation in Museums”, International Council of Museums, Eyrolles, Paris, 8: 119-164 (1969).

[10] A. Naik, “Characterization of Natural Fibers: Experimental Method”, Euro Mediterranean Post- Graduate Advanced School, Italy, 122-136 (2001).

[11] E. May, M. Jones, “Conservation Science Heritage Materials”, In” Analytical Archaeometry, The Royal Society of Chemistry, Cambridge, UK. 23-45 (2006).

[12] A. Harby, “Development of Biotechnological Process for Restoration of Historical Textiles”, PHD Thesis, School of chemical engineering (NTUA) 52-55 (2009).

[13] N. Kerr, T. Jenning, E. Methe, “The Long-Term Stability of Cellulosic Textiles, Effect of Alkaline Deacidifying Agents on Naturally Aged Cellulosic Textiles”, in: S.H. Zeronian, H.L.Needles, Eds., Historic Textile and Paper Materials II (American Chemical Society, USA, 233-287(1989).

[14] R.L. Feller, “Accelerated Aging: Photochemical and Thermal Aspects”. 2nd ed., The J. Paul Getty Trust, USA, 143-194 (1994).

[15] O.M. Abdel-Kareem, Y. Zidan, N. Lokma & H. El-Gaoudy, “Conservation of a Rare Painted Ancient Egyptian Textile Object from The Egyptian Museum in Cairo Conservation of Ancient Egyptian Textile,” Preservation Science, 5: 9-16 (2008).

---

[16] M.T. Domenech Carbo, F. Bosch Reig, J.V. Gimeno Adelantado, V. Periz Martinez, “Fourier Transform Infrared Spectroscopy and the Analytical Study of Works of Art for Purposes of Diagnosis and Conservation”, Journal of Molecular Structure (56) 559-563 (1997).

[17] I. Petroviciu , F. Albu & A. Medvedovici, “LC/MS and LC/MS/MS Based Protocol For Identification of Dyes in Historic Textiles,” , J. Microchemical 95(2) 247-254(2010) .

[18] S. Bruni, V. Guglielmi, F. Pozzi, “Surface-Enhanced Raman Spectroscopy (SERS) on Silver Colloids for the Identification of Ancient Textile Dyes: Tyrian Purple and Madder”, Journal of Raman Spectroscopy, 41(2) 175-180 (2010).

[19] G.A. Mazzocchin, F. Agnoli, S. Mazzocchin, I. Colpo, “Analysis of Pigments from Roman Wall Paintings Found in Vicenza,” Talanta 61: 565-572 (2003).

[20] I. Degano, J. Łucejko & M.P. Colombini, “The Unprecedented Identification of Safflower Dyestuff in A 16th Century Tapestry Through the Application of A New Reliable Diagnostic Procedure,” Journal of Cultural Heritage, 30: 288-297(2011).

[21] Ch. Lahanier, G. Amsel, Ch. Heitz, M. Menu, H.H. Andersen, “Proceedings of the International Workshop on Ion-Beam Analysis in the Arts and Archaeology”, Pont-A-Mousson, Abbaye des Premontrés, France, February, 18–20 (1985).

[22] M.C. Corbeil, “Applications of X-ray Diffraction in Conservation Science and Archaeometry”. JCPDS-International Centre for Diffraction Data. Advances in X-ray Analysis, 47: 18–29(2004).

[23] R. Meredith, “X=Rays in Relation to Textiles”, Journal of the textile institute proceedings, 39(4) 132-140 (1948).

[24] S. Chang, W. Jong, J. Han, L. Kihoon & H. Young, “The Effect of Residual Silk Sericin on The Structure and Mechanical Property of Regenerated Silk Filament” , International Journal of Biological Macromolecules, 41: 346-353(2007).

[25] J.R. Connolly, “Introduction to X-ray Powder Diffraction”, J. X-Ray Spectrum, 11:1-9 (2007).

[26] J. Zussman, “Physical Methods in Determinative Mineralogy”, Academic Press, London, 2nded, 392–421 (1977).

[27] ICDD. “The International Centre for Diffraction Data”, http://www.icdd.com.

[28] S. Fitzgerald, “Non–Destructive Micro Analysis of Art and Archaeological Objects Using Micro-XRF”, Archeometriai Műhely 3: 75-80 (2008).

[29] Ch. Streli, P. Wobrauschek, P. Kregsamer, “X-ray Florescence Spectrometry Applications”,2thed., Springer-Verlag Berlin Heidelberg, 687-700(1999).

[30] A. Bohlen, “Total Reflection X-ray Fluorescence Spectroscopy: A Versatile Tool Ultra-Micro Analysis of Objects of Cultural Heritage”, Preservation Science 1: 23-34 (2004).

[31] M. Mantler, M. Schreiner, “X-Ray Fluorescence Spectrometry in Art and Archaeology”, X-Ray Spectrum, 29: 3-17 (2000).

[32] S. Pessanha, A. Guilherme, M. Manso, M.L. De Carvalho, “X-ray Fluorescence Applications to Art and Cultural Heritage: Study of Japanese Print”, Spectros. Europe 20(6) 516-525(2008).

---

[33] M. Schreiner, B. Frühmann, D. Jembrih-Simbürger, R. Linke, "X–Rays in Art and Archaeology: An Overview", Powder Diffr. 19(1) 335-342 (2004).

[34] V. Desnica, M. Schreiner, "A Lab View-Controlled Portable X-ray Fluorescence Spectrometer for the Analysis of Art Objects", X-Ray Spectrum 35: 280-286 (2006).

[35] G. Bitossi, Giorgi, R. Mauro, M. Salvadori, B. D. Dei, "Spectroscopic Techniques in Cultural Heritage Conservation: A Survey", Applied Spectroscopy Reviews 40: 187-228 (2005).

[36] C.L. Silva, "A Technical Study of the Mural Paintings on the Interior Dome of the Capilla De La Virgen Del Rosario, IGLESIA SAN JOSÉ, SAN JUAN, PUERTORICO", Mater.Sci, University of Pennsylvania, USA, 45-52 (2006).

[37] S. Bruni, F. Cariati, F. Casadio & L. Toniolo, "Spectrochemical Characterization by Micro-FTIR Spectroscopy of Blue Pigments in Different Polychrome Works of Art", Vibrational Spectroscopy (20)15–25 (1999).

[38] A.A. Christy, Y. Ozaki, V.G. Gregoriou, "Modern Fourier Infrared Spectroscopy," In: Barcelo, D. (Ed.), Comprehensive Analytical Chemistry, (35)131-194 (2001).

[39] F. Ferrero, F. Testore, G. Malucelli, C. J. Tonin, "Thermal Degradation of Linen Textiles: The Effects of Ageing and Cleaning," Text. Inst. 89(1) 562-569 (1998).

[40] M. Schreiner, M. Melcher & K. Uhlir, "Scanning Electron Microscopy and Energy Dispersive Analysis: Applications in the Field of Cultural Heritage", Anal. Bioanal.Chem. 387(3) 737–747 (2006).

[41] T.F. Page, B.A. Shaw, "Scanning Electron Acoustic Microscopy (SEAM): A Technique for the Detection of Contact-Induced Surface & Sub-Surface Cracks", J. Mater.Sci. 39: 6791–6805 (2004).

[42] I. Joosten, M.R. Bommel, R.H.D. Keijzer, H. Reschreiter, "Dyestuff and Element Analysis of Textiles from the Prehistoric Salt-Mines of Hallstatt," Microchim. Acta. 45(5) 155- 169 (2006).

[43] A. Timar-Balazy, D. Eastop, "Chemical Principles of Textile Conservation", 1thed., Butterworth-Heinemann, London, 19-55 (1998).

[44] N. Reddy, Y. Yang, "Properties and Potential Applications of Natural Cellulose Fibers from Cornhusks," journal of The Royal Society of Chemistry, 190-195 (2005).

[45] D. R. Joseph, "Tensile testing," 2nd ed., ASTM International, 245-258 (2004).

[46] American Society for Testing and Materials, Annual Book of ASTM Standards, Pennsylvania, USA. 7(2) (2000).

CHAPTER 5

Results and Discussion of painted linen samples with pigments

5.1. FTIR spectroscopy

Characteristic infrared bands of all samples are shown in Table 1.3 and in Fig. 23.1, 23.2, 23.3, 23.4, 23.5, 23.6, 23.7, 23.8, and 23.9.

The strong broad band centered at 3370 and 3406 cm^{-1} of unaged and aged linen, respectively, indicates the presence of hydroxyl groups and is assigned to the stretching v(OH) vibrations. These bands are indicative of inter and intramolecular hydrogen bonds. Flax cellulose exhibits strong inter and intramolecular bonding interactions between adjacent cellulose chains, involving the hydroxyl groups. The band of unaged and aged linen at 2900 cm^{-1} is assigned to stretching vibrations of methyl and ethyl groups $v(CH_3)$ and $v(CH_2)$ (cellulose compounds). The broad band at 1639 cm^{-1} is assigned to vibrations of v(C=C) (lignin compounds), δ(OH), and v(CO) bonds (derived from carbonyl, or aldehydic, or carboxyl groups). The bands at 1431 and 1373 cm^{-1} are assigned to bending vibrations of methyl and ethyl groups $v(CH_3)$ and $v(CH_2)$ (cellulose compounds).

The two bands at 1112 and 1060 cm^{-1} are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (β-glycoside linkages, cellulose compounds)[1,2]

The spectrum of Egyptian blue pigment exhibits a broad strong band at 3427 cm^{-1} attributable water of hydration v(OH). The spectral pattern of Egyptian blue exhibits bands at 1223, 1161 cm^{-1} and two very strong bands at 1054 and 1003 cm^{-1}. These four bands are attributed to antisymmetrical Si–O–Si stretching vibrations, while the bands at 755, 663, 594 cm^{-1} are assigned to the symmetrical Si–O–Si stretching vibrations[3]. The bands at 522, 482, 422, and 409 are assigned to O–Si–O, Si–O–Cu, and Cu–O stretching vibrations[4,5] The bands of Egyptian blue at 1054 and 1003 cm^{-1} are shifted to higher frequency at 1058 and 1010 cm^{-1}, respectively.

The spectrum of malachite exhibits two sharp strong bands at 3404 and 3314 attributable to v(OH). The spectral pattern of malachite exhibits bands at 1495*vs*, 1390*vs*, 1047*vs*, 875*s*, 821*s*, 749*s*, 573*s*, 524*s*, 506*sh*, and at 428*s* cm^{-1}. The bands at 1495 and at 1047 cm^{-1}are assigned to *vasym* and *vsym* stretching vibrations of carbonate group (CO3). The bands at 573s, 524s, 506*sh* are attributed to v(Cu–O–Cu) and the band at 428s at v(Cu–O) stretching vibrations[6,7]. The bands of malachite at 1495 and 1390 cm^{-1} are shifted to lower frequency at 1490 and 1386 cm^{-1}, respectively, and the band at 573 cm^{-1} is shifted at 570 cm^{-1}.

The spectrum of hematite exhibits bands at 3402 cm^{-1} attributable to ν(OH), at 1706 cm^{-1}, 1655 attributable to δ(OH), and at 1638, 1438, 1155 cm^{-1}. Two very strong bands at 559 and 458 cm^{-1} are assigned to ν(Fe–O–Fe) and ν(Fe–O) stretching vibrations[8]. Previous studies on the infrared spectrum of standard powdered hematite report two major bands at ca. 540 and 470 cm^{-1}, which can be attributed to lattice vibrations, published values for the exact position of these two bands differ by up to 30 cm^{-1}. Several reasons for these variations have been suggested in the literature, but it is generally accepted that variations among the spectra are most often caused by differences in the size and more importantly, in the shape of hematite crystals[9]. The bands of aged linen attributable to lignin compounds and cellulose compounds exhibited a slight shift to ∼1 cm^{-1}. The bands of hematite at 559 and 458 cm^{-1} are shifted at 552 and 472 cm^{-1}, respectively.

The spectral profile of the aged linen painted by vermilion shows differences compared to the spectrum of aged linen and vermilion. The band at 1639 cm^{-1} of aged linen has been shifted to lower frequency at 1628 cm^{-1} ν(C=C) and ν(CO), lignin compounds). The band at 1431 cm^{-1} has been shifted at 1429 cm^{-1} (cellulose compounds) and the band at 1114 and 1061 cm^{-1} have moved to lower frequency at 1113 and 1058 cm^{-1} (glycosidic linkage, cellulose compounds).

From these data, it is concluded that the vermilion (HgS) exhibits an interaction to cellulose compounds. It was not possible to identify vermilion (HgS) as the characteristic bands of ν(Hg–S) appear below 400 cm^{-1} [10,11].

The spectrum of yellow ochre exhibits a strong band at 3128 cm^{-1} attributable to ν(OH) probably due to intra and intermolecular hydrogen bonding. The spectral pattern of yellow ochre exhibits strong characteristic bands at 903, 798, 623, and 407 cm^{-1}. The bands at 623 and 407 cm^{-1} are assigned to ν(Fe–O–Fe) and ν(Fe–O) stretching vibrations[2].

The spectral profile of the aged linen painted by yellow ochre shows some differences, the bands of aged linen attributable to lignin compounds and cellulose compounds exhibited a slight shift to ∼1 cm^{-1}. The bands of yellow ochre at 623 and 407 cm^{-1} are shifted to lower frequency, the former one at 616 cm^{-1} and the latter one is appeared below 400 cm^{-1}.

The spectrum of charcoal exhibits a broad strong band at 3424 cm^{-1} attributable to ν(OH). The spectral pattern of charcoal exhibits bands at 1701, 1580, 1432, 1221, and 874 cm^{-1}. The bands at 1580 and 874 cm^{-1} are assigned to stretching and bending vibrations of C=C bonds. The spectral profile of the aged linen colored by charcoal shows slight differences compared to the spectrum of aged linen. The bands at 1114 and 1061 cm^{-1} have shifted at 1115 and 1059 cm^{-1}, respectively (glycosidic linkage, cellulose compounds). Charcoal does not exhibit characteristic bands below 870 cm^{-1}.

From all these data, it is concluded that spectral profile of the aged linen colored with these pigments shows the spectral pattern of pigments superimposed a lot of bands of the aged linen. Furthermore, the pigments seem to interact to cellulose and lignin compounds of the aged linen and the environment while the strength of the bonds of Si(IV)–O, Cu(II)–O, Fe(III)–O has been changed.

The infrared spectrum of gypsum exhibits bands at 1153, 1095 cm^{-1} and at 660, 601 cm^{-1} corresponding to the stretching ν(S–O) and bending δ(S–O) vibrations of the sulfato group. The lattice water of gypsum exhibits two sharp bands an antisymmetric and a symmetric stretching vibration ν(OH) at 3611 and 3558 cm^{-1}, respectively, and a bending vibration δ(OH) at 1621 cm^{-1}. The spectral profile of the aged linen painted by gypsum shows many differences compared to the spectrum of aged linen and gypsum. The bands of gypsum are overlapped by the bands of aged linen. The bands of the lattice water of gypsum have disappeared. The band at 1639 cm^{-1} of aged linen has been shifted to lower frequency at 1628 cm^{-1} (ν(C=C) and ν(CO), lignin compounds). The band at 1431 cm^{-1} has been shifted at 1483 cm^{-1} (ν(CH) cellulose compounds) and the bands at 1114 and 1061 cm^{-1} have moved to higher frequency at 1126 and 1074 cm^{-1} (C–O–C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the gypsum after dehydration bind strong to lignin and cellulose compounds resulting in possible degradation of them[10,12].

Table.1.3. *Characteristic infrared band of the standard and painted samples in cm^{-1}*

Sample	**Wave numbers (cm^{-1})**
Unaged linen	3370, 2900, 1639, 1431, 1373, 1112, 1062, 668, 615, 560
Aged linen	3406, 2900, 1639, 1431, 1373, 1112, 1060, 668, 615, 560
Egyptian blue	3427, 1223, 1161, 1054, 1003, 755, 663, 595, 522, 482, 422, 409
Aged linen painted by Egyptian blue	3423, 1638, 1431, 1375, 1162, 1058, 1100, 754, 663, 595, 521, 483, 423, 408
Malachite	3404, 3314, 1495, 1390, 1047, 875, 821, 749, 573, 524, 506, 428
Aged linen painted by malachite	3404, 3319, 2900, 1638, 1490, 1424, 1386, 1048, 879, 821, 570, 523, 428
Hematite	3402, 1706, 1655, 1638, 1438, 1155, 559, 458
Aged linen painted by hematite	3394, 2900, 1638, 1431, 1374, 1160, 1115, 1060, 552, 472
Yellow ochre	3128, 903, 798, 623, 460, 407
Aged linen painted by yellow ochre	3409, 2901, 1639, 1438, 1374, 1115, 1060, 902, 798, 616, 457
Vermilion	3437, 1711, 1630, 1426, 1363, 1222, 605, 531
Aged linen painted by vermilion	3404, 2900, 1638, 1429, 1373, 1113, 1058, 668, 612, 561
Charcoal	3424, 1701, 1580, 1432, 1221, 874
Aged linen painted by charcoal	3424, 2901, 1638, 1432, 1372, 1156, 1115, 1059
Gypsum	3611, 3554, 1621, 1153, 1095, 660, 601
Aged linen painted by gypsum	3275, 2902, 1628, 1483, 1461, 1318, 1172, 1126, 1074, 700, 667, 615, 562

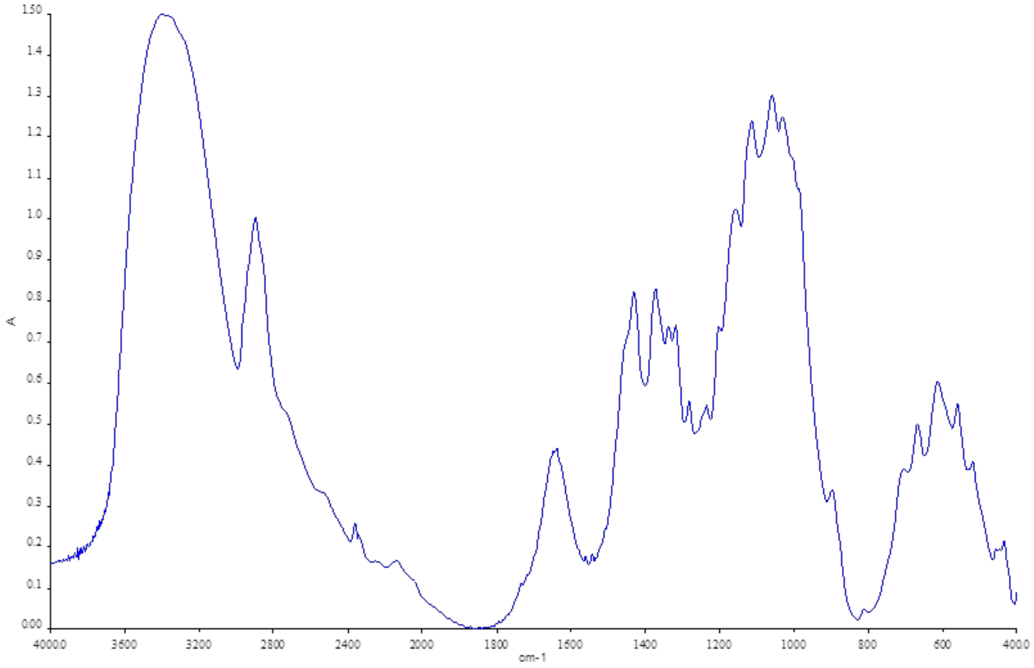


Fig.23.1. FTIR spectra of standard uncolored and unaged linen sample.

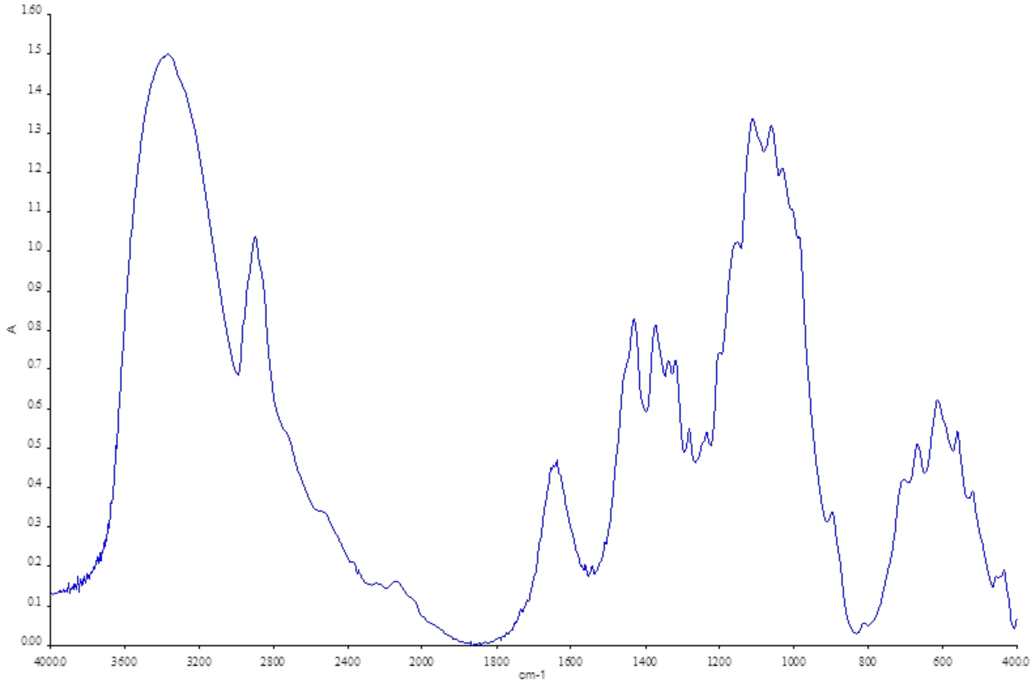


Fig.23.2. FTIR spectra of uncolored linen sample after thermal ageing.

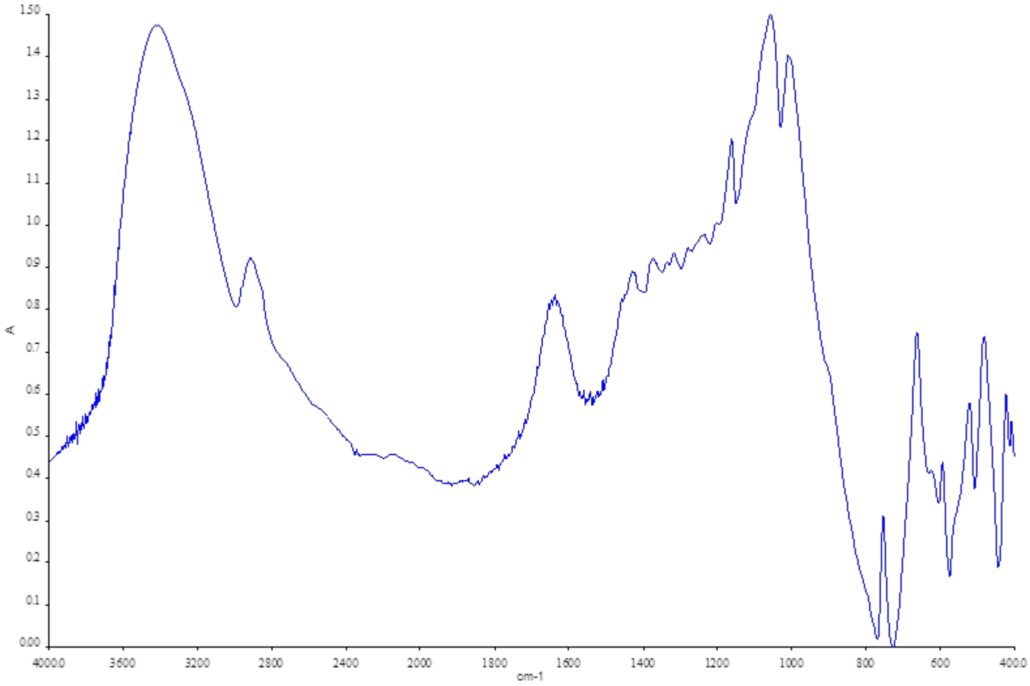


Fig.23.3. *FTIR spectra of painted Linen sample with Egyptian blue after TA.*

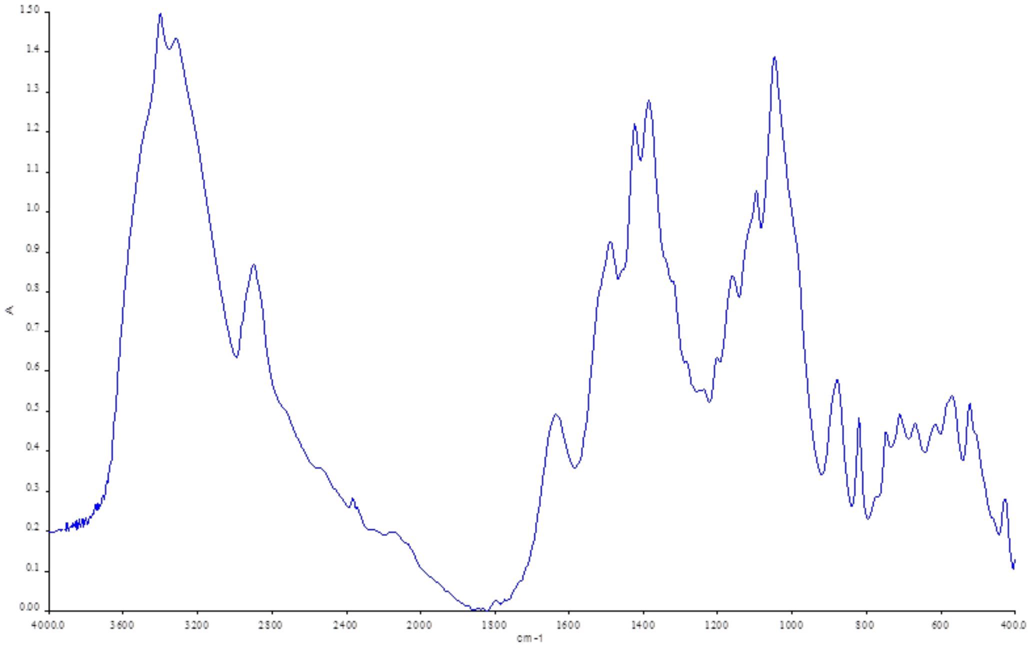


Fig.23.4. *FTIR spectra of painted Linen sample with Malachite after TA.*

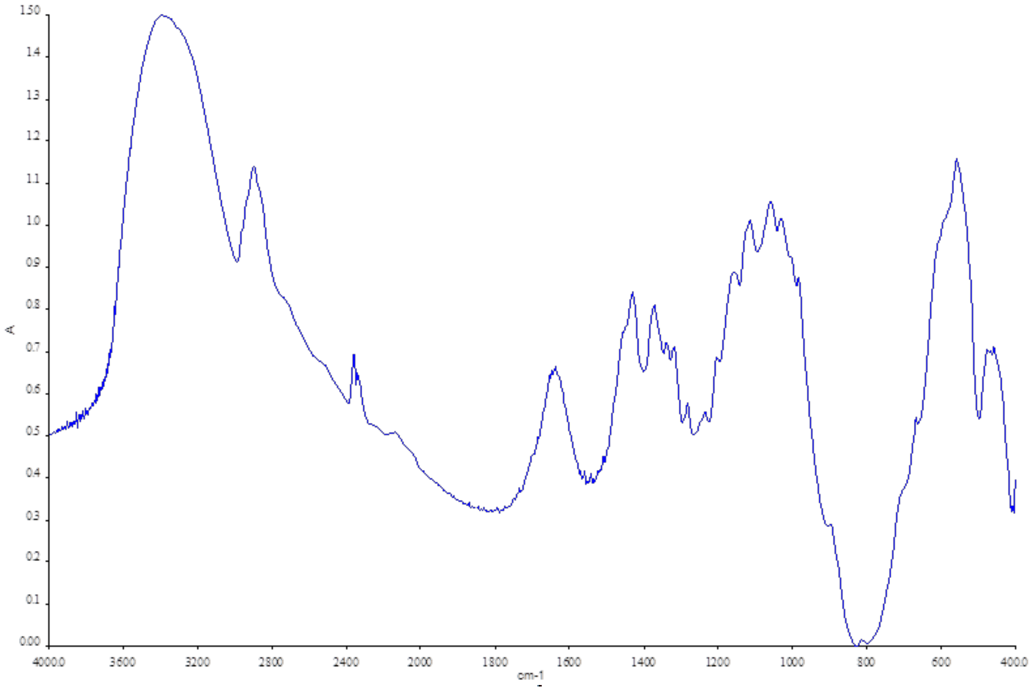


Fig.23.5. *FTIR spectra of painted Linen sample with Hematite after TA.*

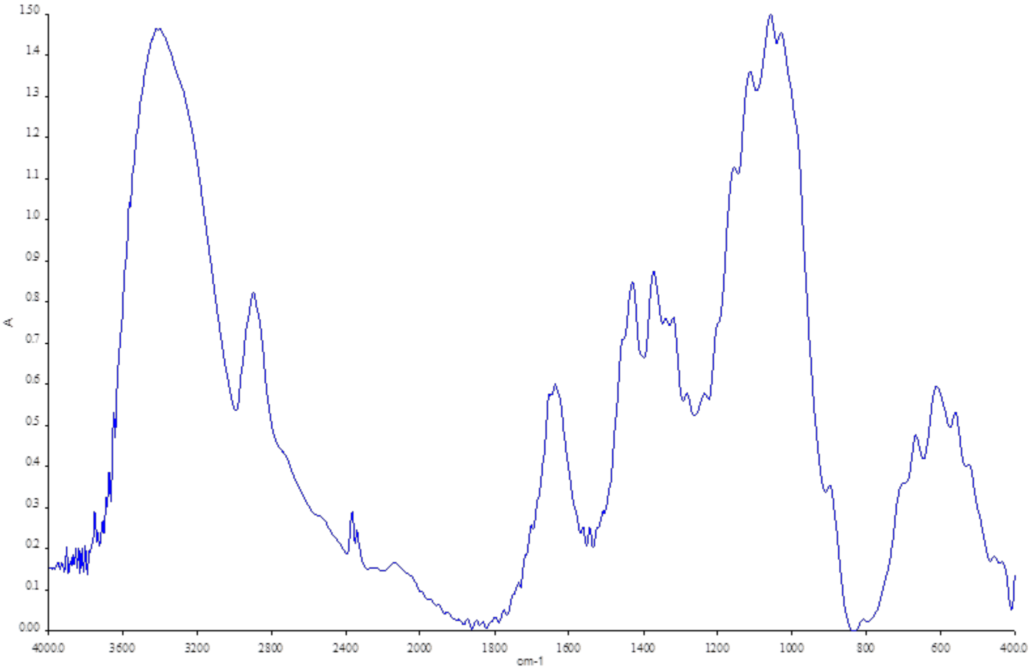


Fig.23.6. *FTIR spectra of painted Linen sample with Vermillion after TA.*

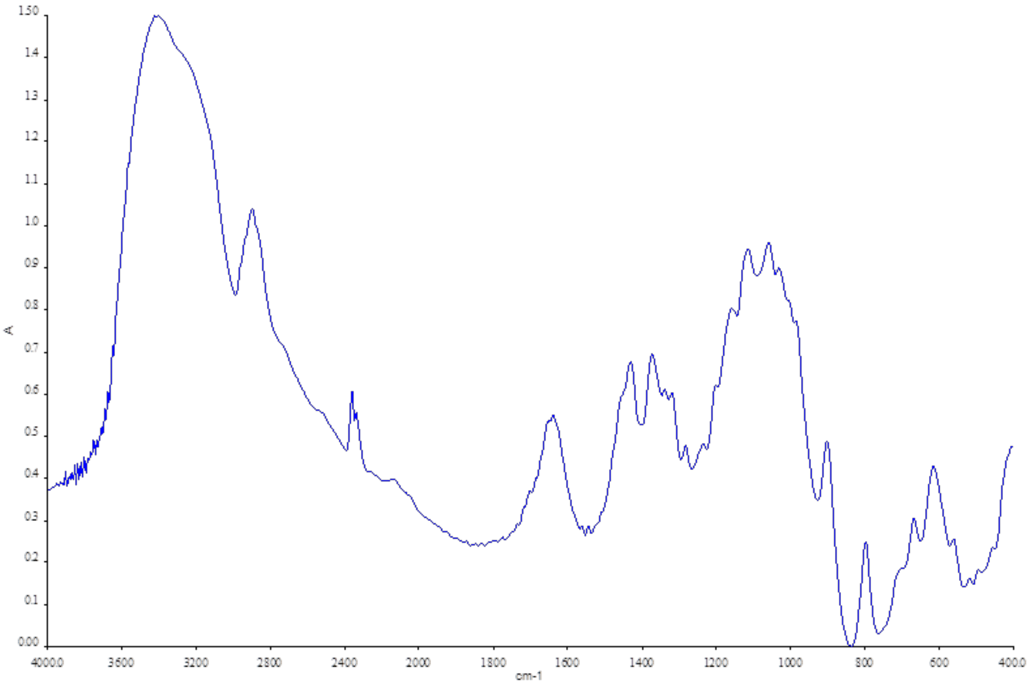


Fig.23.7. *FTIR spectra of painted Linen sample with Yellow ochre after TA.*

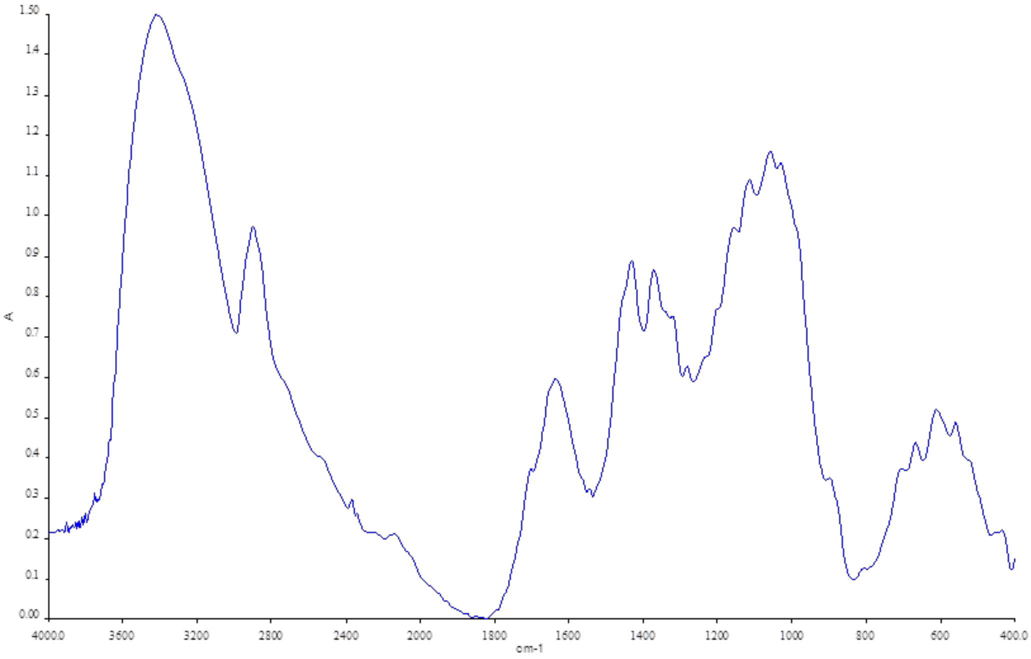


Fig.23.8*. FTIR spectra of painted Linen sample with Charcoal after TA.*

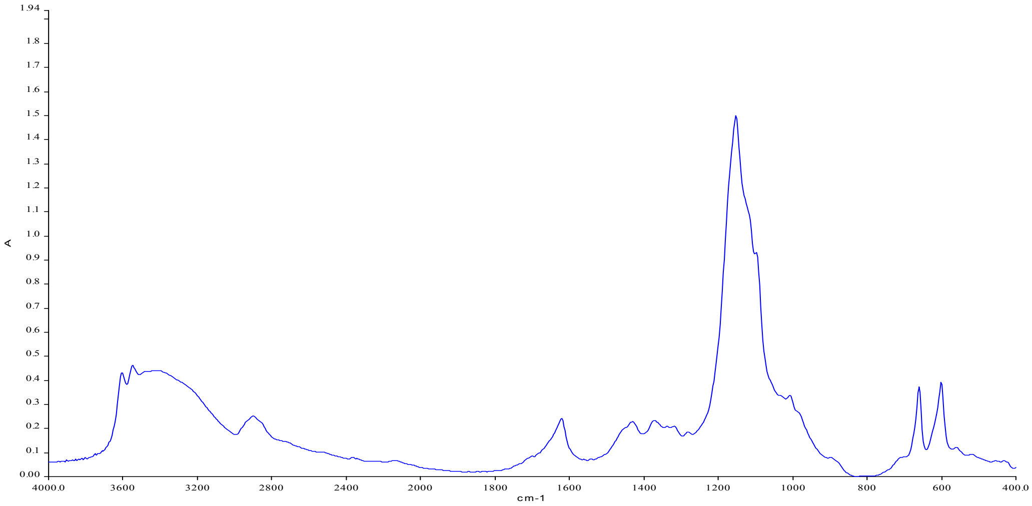


Fig.23.9. *FTIR spectra of painted Linen sample with Gypsum after TA.*

5.2. Scanning Electron Microscope (SEM-EDS)

SEM photos of the standard unpainted and unaged linen sample in fig.24.1 show the typical morphology of the linen fiber. The nodes structure is clearly observed in the fibers and the weave pattern of the linen textile sample is plain weave 1/1. Thermal ageing at 140ºC for 72 h, does not cause significant changes to neither of the fibers morphology nor of the weave structure as depicted in figure 24.1(c,d,e). Nevertheless, some fibers are damaged as breaking, tearing and the other fiber with a brush –like fracture. This degradation occurs as a result of rupture of the glycosidic bond between the units of the cellulose fibers and from the oxidation of hydroxyl groups which may be initially formed during thermal oxidation and subsequently cause scission on the molecular chains of the cellulose polymer. Yet, ageing at this degree does not modify appreciably the morphology of the linen fiber. However, in general, the thermal degradation increase with increasing the temperature degree and the duration of ageing[13,14].

On the contrary after painting linen fibers with all pigments, the SEM analysis confirmed that the fiber morphology is completely masked by the pigment layers and the pigment particles were deposited on and between the fibers surfaces, without any destructive effect on the linen fibers. As an exception, SEM measurements of painted fibers with hematite in Fig.24.4 show some broken fibers with transverse cracking and longitudinal splitting characterized by small scratches on the fibers surfaces, this particular sample's degradation may be due to presence of Fe ions since metal catalyzed polymer oxidation is possible for pigments based on transition metals[15].

In general, however, the results indicate that the pigments play a protective role for the deterioration of the fibers caused by thermal ageing. The results of EDX analysis for all painted samples are compatible with presence and composition of the respective pigments as shown in table1.3.

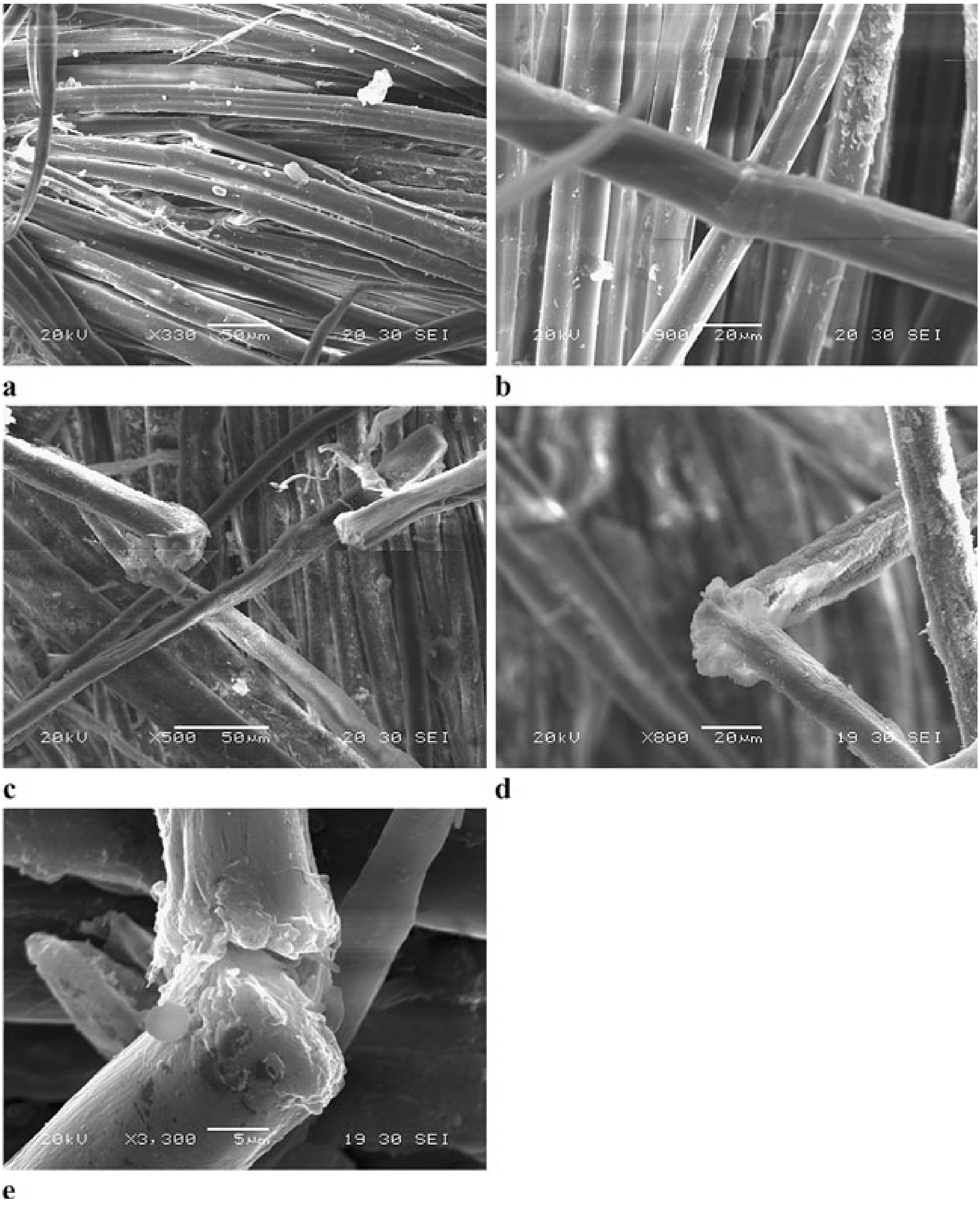


Fig.24.1. *SEM microphotographs of standard, unpainted and unaged linen sample (a, b). SEM microphotographs of unpainted linen sample after TA (c, d, e)*

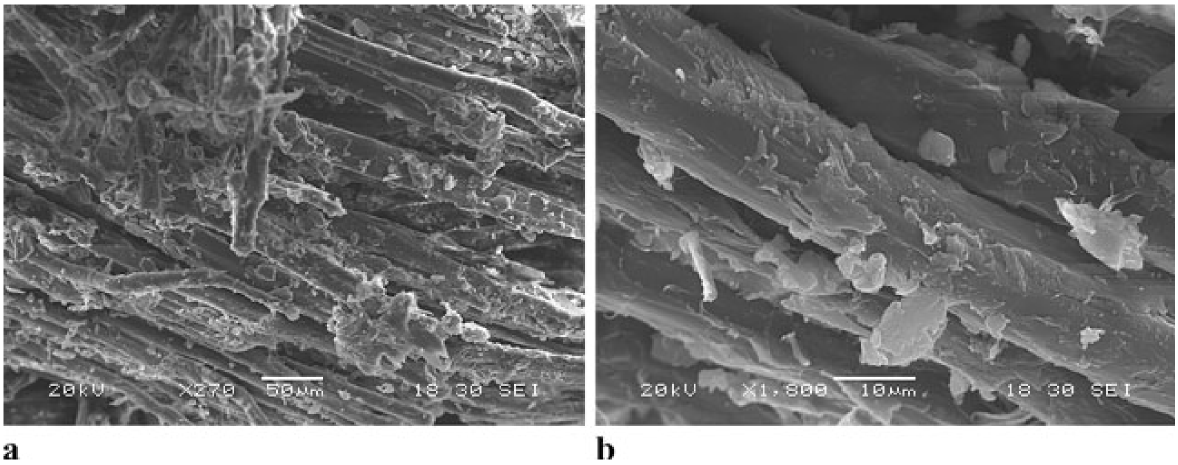


Fig.24.2. SEM microphotographs of painted linen sample with Egyptian blue after TA.

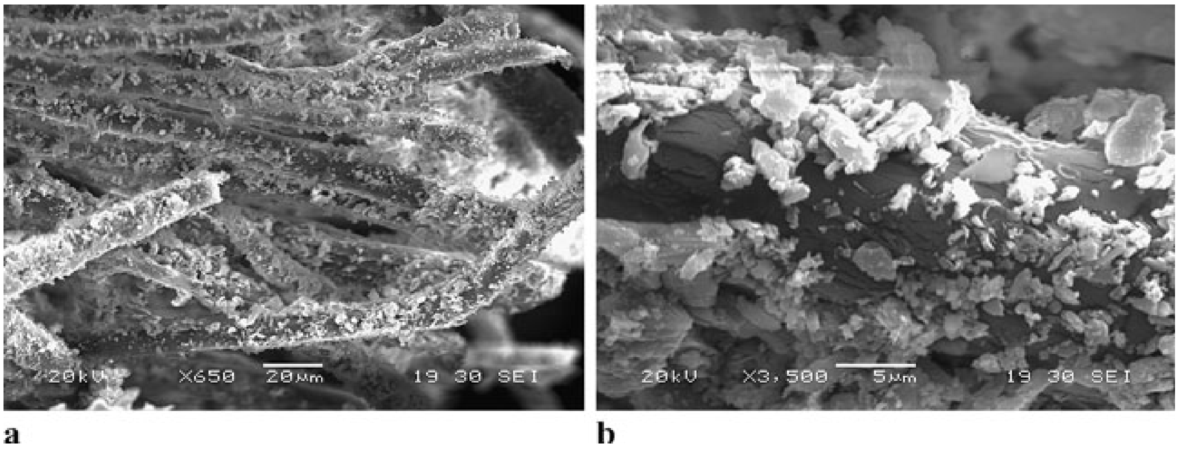


Fig.24.3. SEM microphotographs of painted linen sample with Malachite after TA.

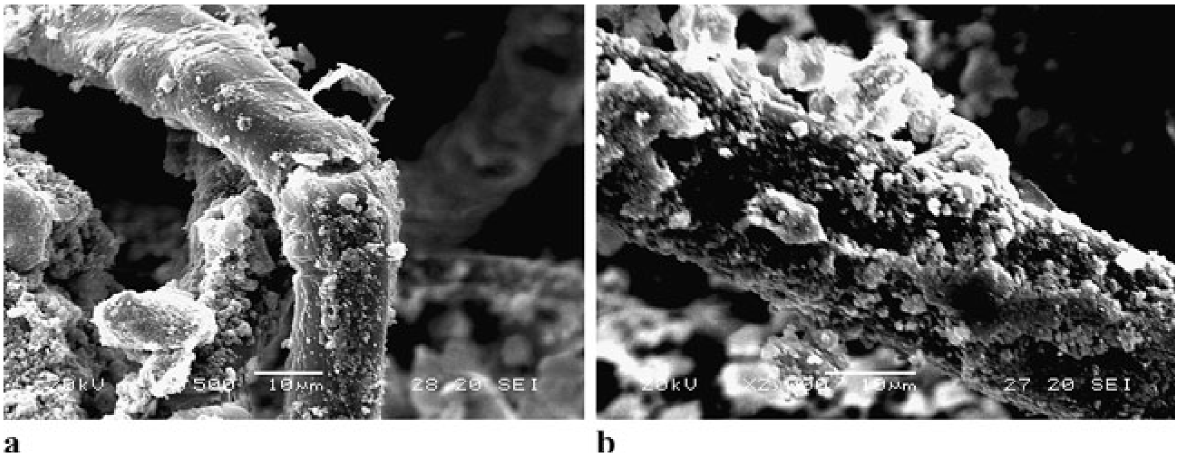


Fig.24.4. SEM microphotographs of painted linen sample with Hematite after TA.

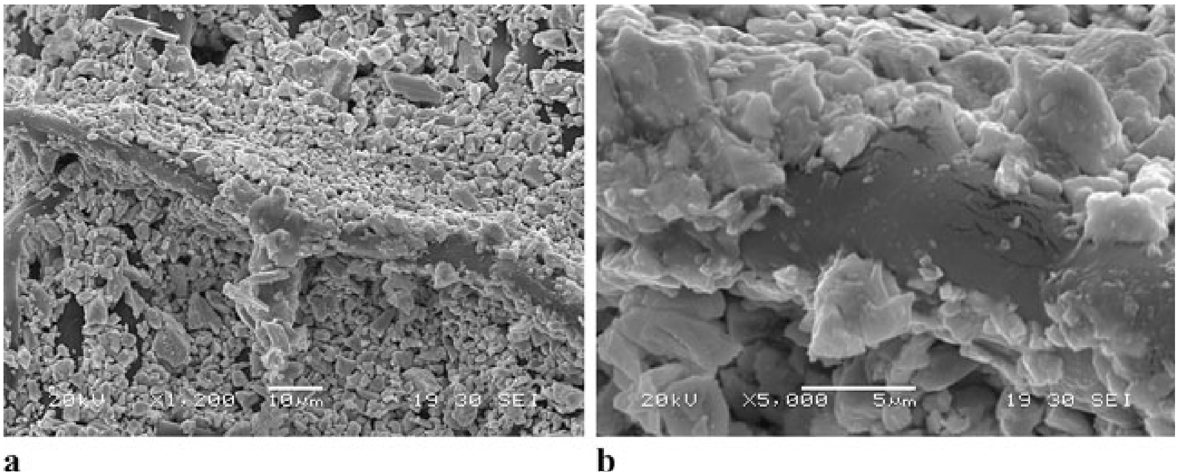


Fig.24.5. SEM microphotographs of painted linen sample with Vermillion after TA.

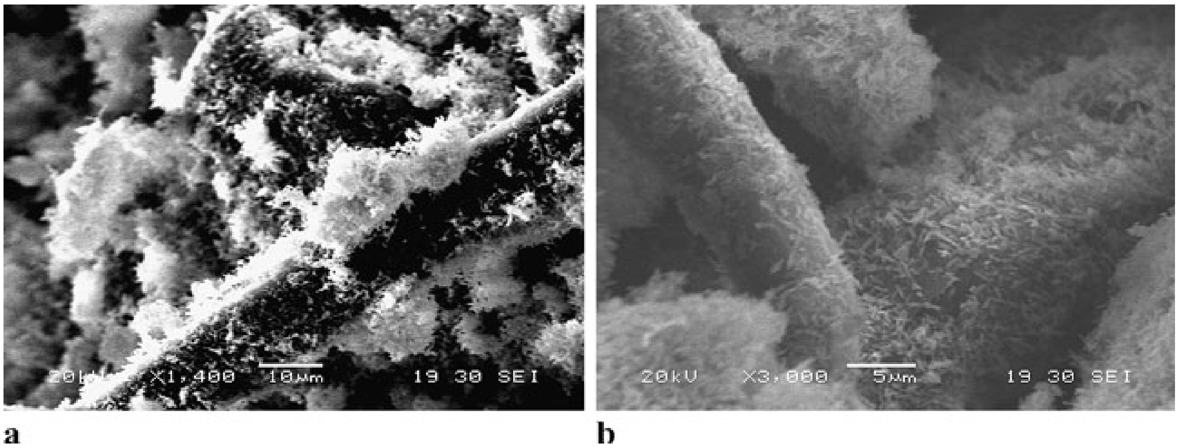


Fig.24.6. SEM microphotographs of painted linen sample with Yellow ochre pigment after TA.

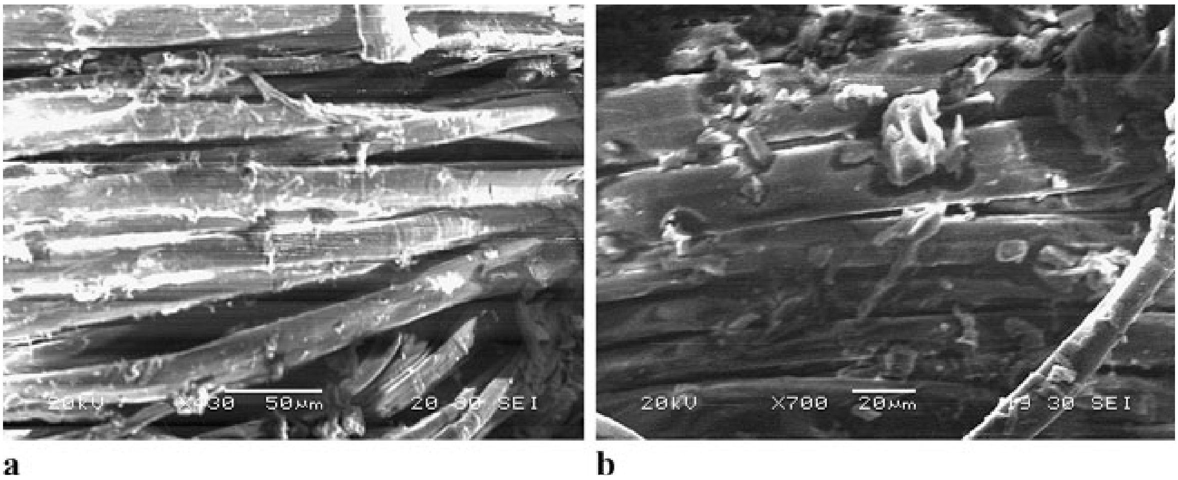


Fig.24.7. *SEM microphotographs of painted linen sample with charcoal pigment after TA.*

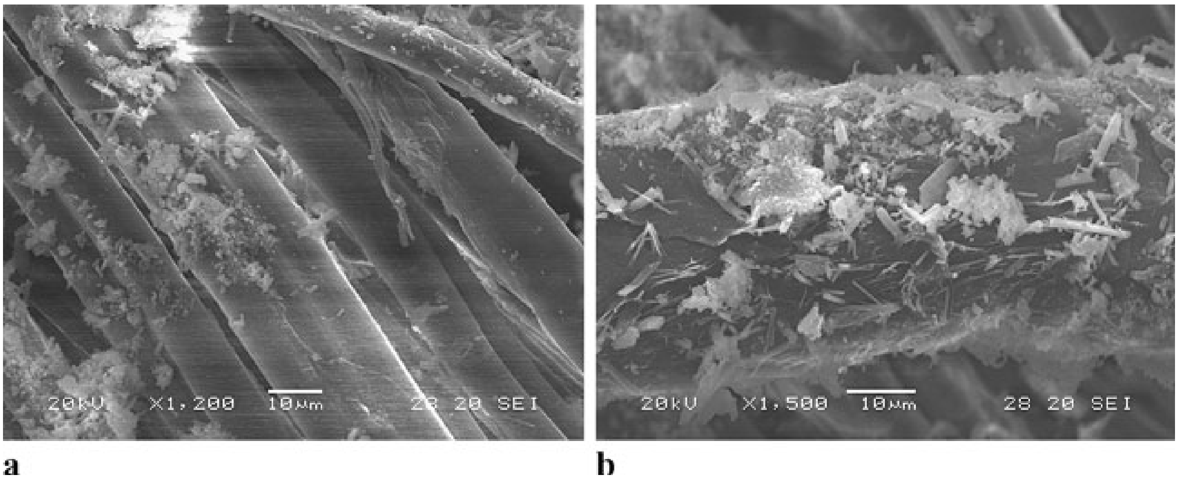


Fig.24.8. *SEM microphotographs of painted linen sample with Gypsum pigment after TA.*

5.3. X-ray diffraction

Cellulose is partly crystalline and partly amorphous since the order of the macromolecules in a fiber is not uniform. Cellulose adopts different crystal forms depending on the source and physicochemical treatment, differing in unit cell dimensions and chain polarity. Both intra- and intermolecular hydrogen bonding occurs within the crystalline (ordered) regions of cellulose chains which do not form such bonds in the amorphous (disordered) areas. Intervention of the hydroxy moieties present at these areas and on the surface of the cellulose fibers is possible after treatment resulting in changes in swelling and crystallinity.

Native cellulose, cellulose I, consists of two different crystal structures, Iα and Iβ[16], which are interconverted by bending during microfibril formation and metastable cellulose Iα converts to cellulose Iβ on annealing[17]. Still, the monoclinic crystal cell proposed by Meyer et al.[18] is still in use by most researchers. The latter exhibits three principal planes of reflection (101), $(10\bar{1})$, (002) with peaks at 2θ = 14.9°, 16.6° and 22.8°, respectively Fig.25.1. The characteristic (101) and $(10\bar{1})$ peaks found in linen are severely overlapped forming a broader doublet region. Reduced crystallite size as well as other impurities can contribute to this effect[19]. The lower intensity of these peaks is attributed to the relative orientation of the crystals within the fibers[20]. On the other hand, the (002) reflection is the most intense peak and corresponds to the crystallographic planes of the charged glycosidic moieties[21].

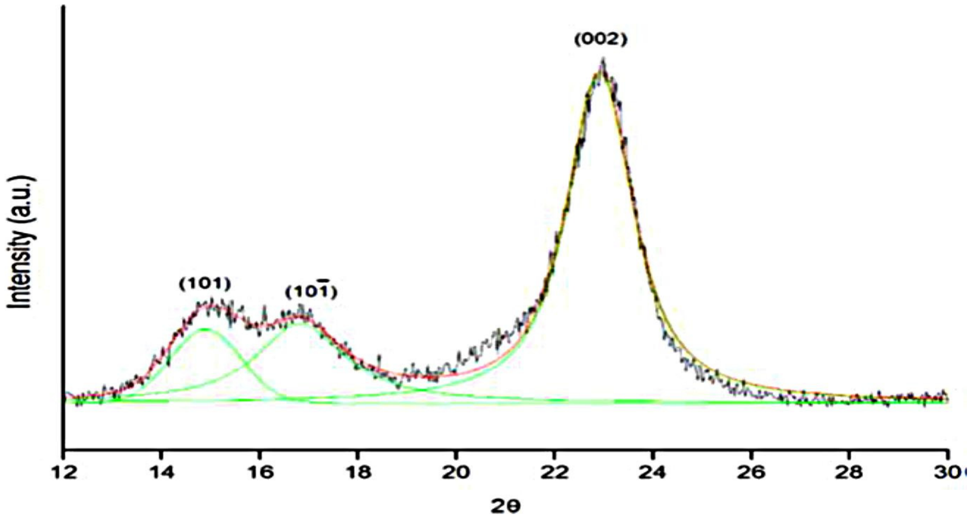


Fig.25.1. *Resolution of X-ray diffraction curves of standard linen featuring cellulose I peaks.*

The degree of crystallinity (or the crystallinity index, CI) was evaluated according to the Segal method by using the empirical equation[22].

$$\mathrm{CI} = 100[(I00_2 - Iam) / I00_2]$$

where $I00_2$ is the intensity of the cellulose peak attributed to the (002) plane and Iam is the intensity of the amorphous part usually measured at Bragg angle $2\theta=18^{o}$.

The assessment of the crystallite size of cellulose has been done using the Scherrer equation[23] which calculates the mean sizes of the crystals from the half-maximum (FWHM) of the hkl reflection measured in 2θ of the corresponding Bragg angle. To increase the confidence of the prediction, line profile analysis was performed using the pseudo-Voigt fitting approximation[24].

Thermal ageing at 140^{o}C for 72h, does not significantly alter the crystalline properties of the samples. Aged and normal linen have effectively the same diffractograms with the exception of the different intensity (less for thermally aged). Nevertheless, thermal ageing only slightly affects the crystalline properties of linen which is manifested as a minor peak broadening. This may be due to the fragmentation of some crystallites and possible microstrain, and therefore SEM findings are further supported that this process does not alter significantly the initial polymer. Taking into account that the decreasing in the crystalline properties of the linen fibre increase with increasing the temperature degree and the duration of ageing.

The crystallinity index was found to be approximately 94% for the standard, unpainted and unaged linen sample and for the unpainted linen sample after thermal ageing. The crystallite size perpendicular to (002) is 4.8±0.2 nm while the average size from all three peaks is 5.1 nm albeit having increased standard deviation due to poor resolution of the peaks corresponding to lower interplanar spacing (d).

The diffraction diagrams of painted linen samples after thermal ageing are dominated by the presence of the natural pigments as these are found in the ICDD-PDF database[25]. All pigments but charcoal, exhibit well defined peaks that completely mask the weak diffraction signals of cellulose I.

The most intense peaks at 2θ= 27.10°, 29.78°, 26.53°, 23.51°, 27.93°, 29.25°, 34.72°, 11.69°, 39.77°, 34.11°, 24.36° and 38.84° are attributed to Egyptian blue. The most intense peaks at 2θ= 31.70°, 24.50°, 36.04°, 15.34°, 18.20°, 21.81°, 32.77° and 39.85° are attributed to malachite. The most intense peaks at 2θ= 33.44°, 35.87° and 24.33° are attributed to hematite. The most intense peaks at 2θ= 26.61°, 31.33°, 28.32° and 38.03° are attributed to vermillion. The most intense peaks at 2θ=21.23°, 36.65°, 33.24°, 34.68°, 17.79°, 36.04°, 26.33° and 39.97° are attributed to yellow ochre (goethite). The most intense peaks at 2θ=14.66°, 29.57°, 25.53°, 31.97° and 32.86° are attributed to anhydrite (calcium sulfate) pigment, while the peaks at 11.69°, 29.16° and 20.78° are attributed to gypsum pigment , this result confirmed that the most of gypsum pigment converted to anhydrite resulting of dehydration after thermal ageing and this result is compatible with the result of FTIR.

The sample treated with charcoal has the same diffraction pattern, with decreased peaks intensity, with linen due to the amorphous nature of the pigment and the absence of charcoal peaks in the selected 2θ region.

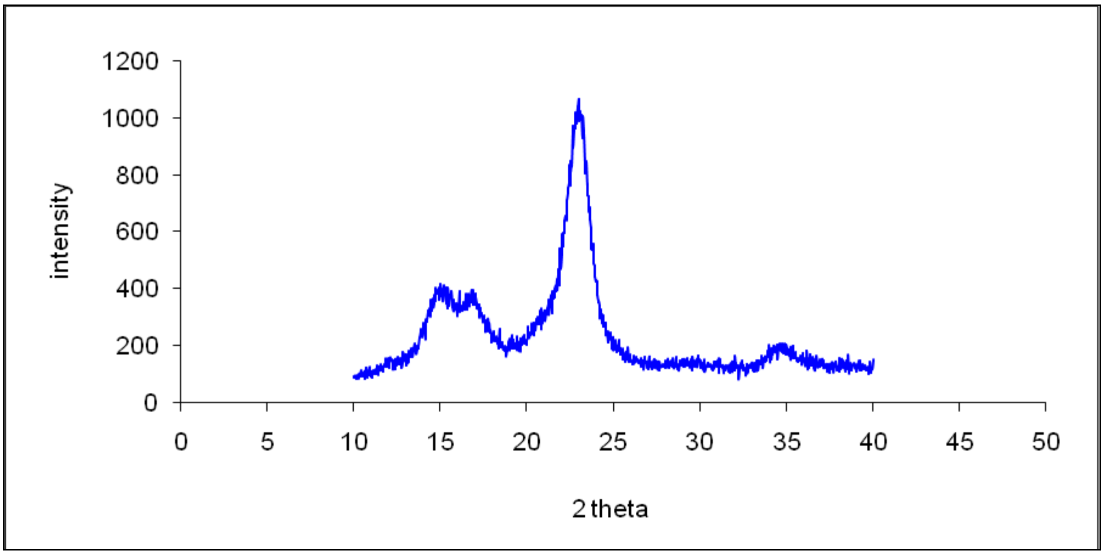


Fig.25.2. *X-ray diffractograms of standard unpainted and unaged linen sample.*

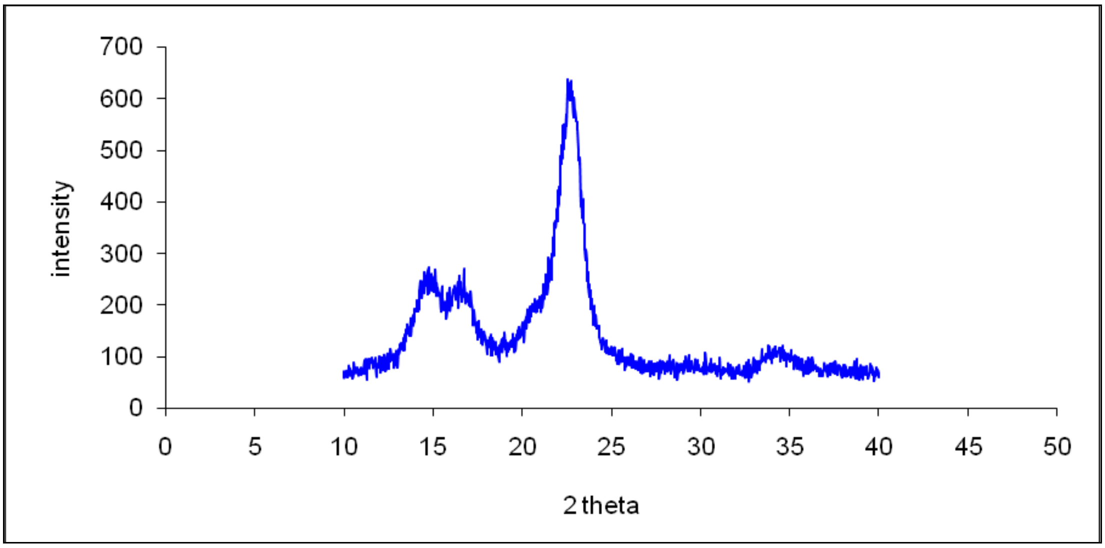


Fig.25.3. *X-ray diffractograms of standard unpainted linen sample after TA.*

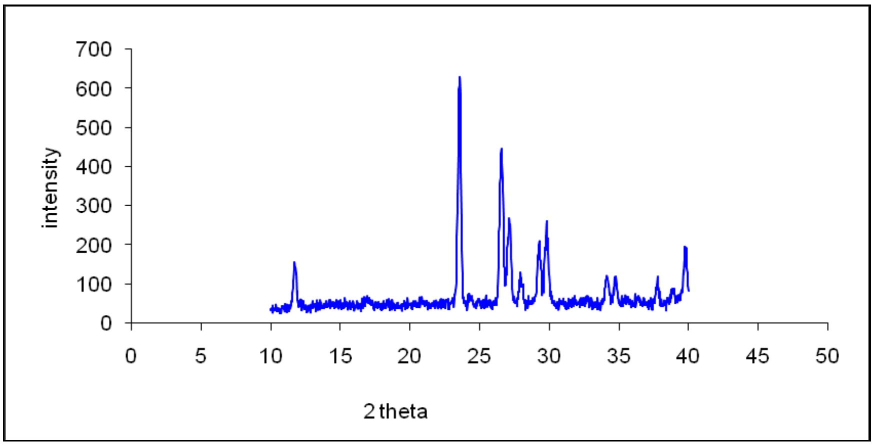


Fig.25.4. *X-ray diffractograms of painted linen with Egyptian blue after TA.*

PDF #04-007-8625 ($CaCuSi_4O_{10}$; egyptian blue, syn)

2 Theta	d (A)	I	h	k	L
27,106	3,28695	999	2	0	2
29,7849	2,99714	961	2	1	2
26,5325	3,35669	802	1	0	4
23,5159	3,78	677	0	0	4
27,9363	3,19112	445	2	1	1
29,2596	3,04973	395	1	1	4
34,729	2,58094	283	2	2	0
11,6959	7,56	267	0	0	2
39,7717	2,26455	253	1	1	6
49,9309	1,825	246	4	0	0
34,1187	2,6257	226	2	0	4
51,1367	1,78476	186	3	2	4
53,8106	1,70221	170	3	1	6
49,7947	1,82967	149	1	0	8
24,3661	3,65	134	2	0	0
38,8468	2,31631	129	3	0	2
57,7324	1,59556	120	4	2	2
56,3141	1,63233	106	4	2	0
51,9568	1,7585	100	4	1	1
66,9295	1,39689	95	2	0	10
68,0181	1,37716	91	5	1	3
57,4258	1,60335	90	4	1	4
46,0309	1,97013	85	3	1	4
17,164	5,16188	84	1	1	0
45,1443	2,00674	84	3	2	1
67,7706	1,38159	84	3	2	8
37,7333	2,38206	83	1	0	6
38,9842	2,30846	76	3	1	0
70,5208	1,3343	71	5	2	2
49,6426	1,83492	68	3	1	5
39,4545	2,28202	64	3	1	1
45,4288	1,99483	61	2	1	6
65,0055	1,43351	53	5	0	2

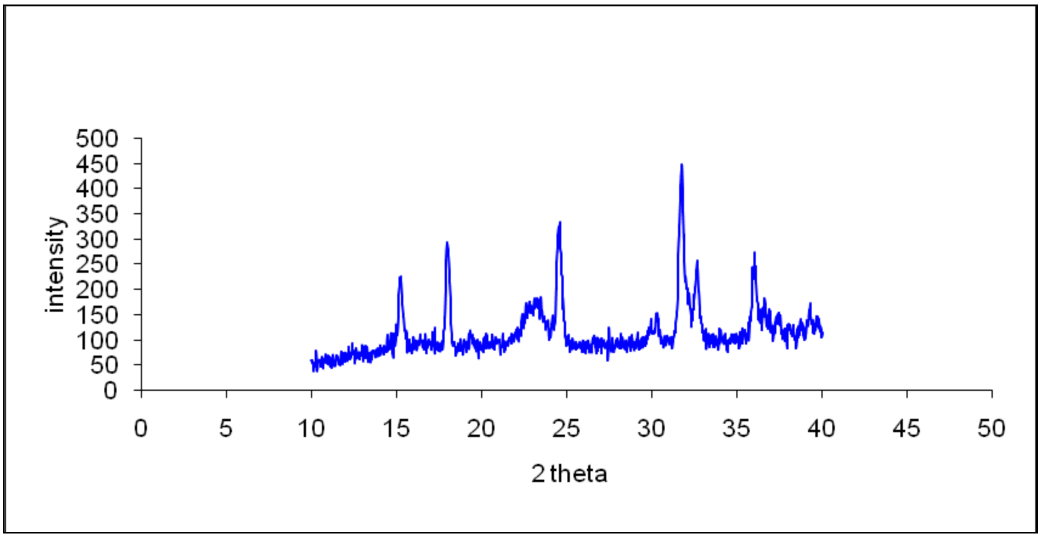


Fig.25.5. *X-ray diffractograms of painted linen with malachite after TA.*

PDF #00-002-0806 ($CuCO_3 \cdot Cu(OH)_2$; Malachite)

2 Theta	d (A)	I	h	k	L
31,7035	2,82	100	0	2	1
24,5024	3,63	80	1	3	0
36,0401	2,49	80	0	3	1
15,3435	5,77	60			
18,2012	4,87	60			
55,2942	1,66	60	1	6	1
63,6854	1,46	60	-1	3	2
56,4018	1,63	50	3	5	1
61,3437	1,51	50	1	2	2
65,7011	1,42	50	-3	1	2
21,819	4,07	40			
28,5865	3,12	40	3	0	0
32,7776	2,73	40	-1	2	1
39,8551	2,26	40			
41,7844	2,16	40	3	4	0
43,253	2,09	40	-3	2	1
44,599	2,03	40	4	3	0

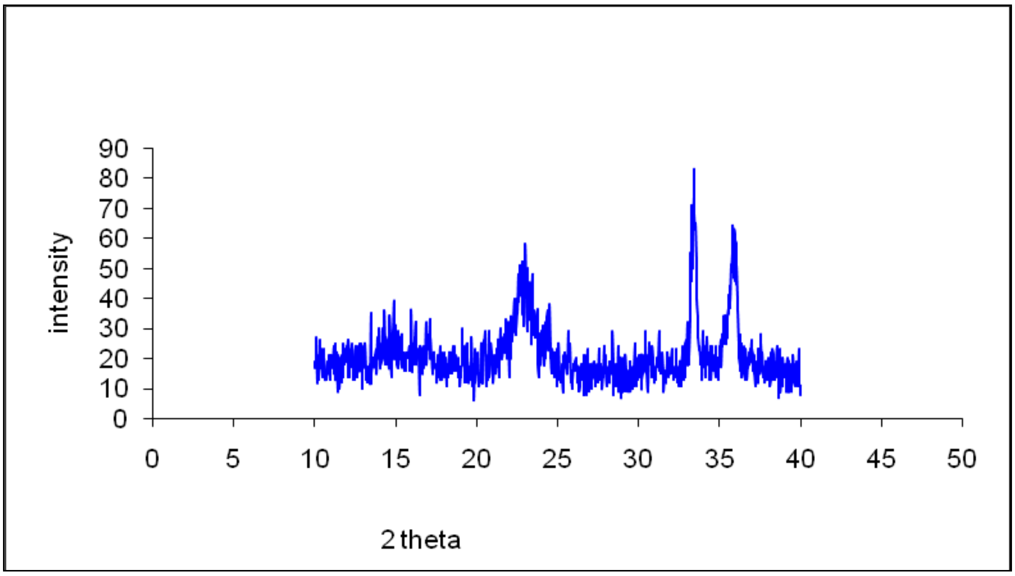


Fig.25.6. *X-ray diffractograms of painted linen with hematite afterTA.*

PDF #04-008-7627 (Fe_2O_3; hematite, syn)

2 Theta	d(A)	I	h	K	l
33,4452	2,67702	999	1	0	4
35,8762	2,501	700	1	1	0
54,5494	1,68089	406	1	1	6
49,8567	1,82754	328	0	2	4
24,3318	3,65507	295	0	1	2
64,4784	1,44395	256	3	0	0
62,936	1,47557	251	2	1	4
41,1738	2,19061	196	1	1	3
72,7175	1,29931	83	1	0	10

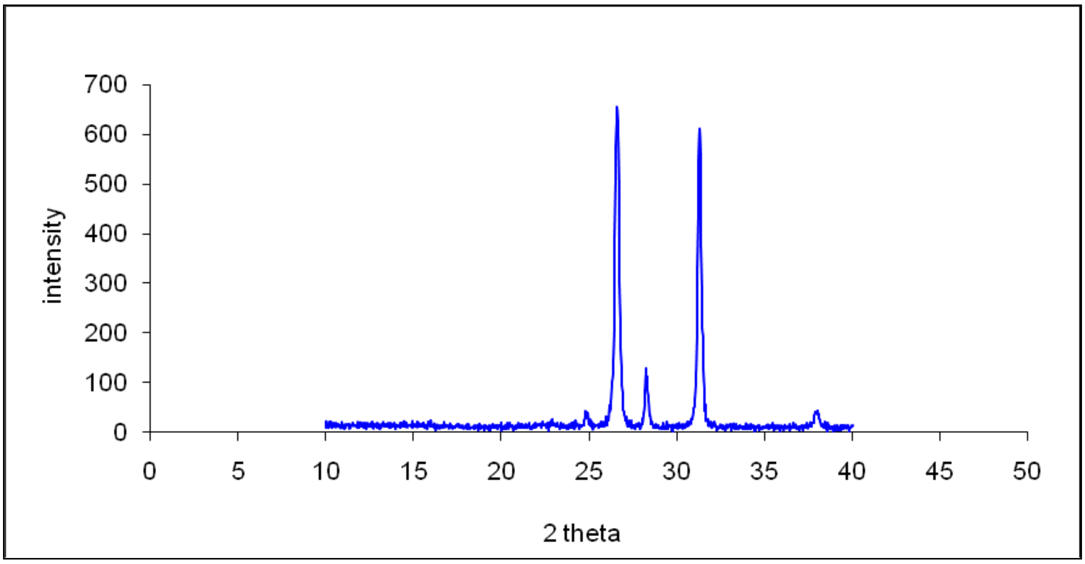


Fig.25.7. *X-ray diffractograms of painted linen with vermillion after TA.*

PDF #04-006-3903 (HgS; Cinnabar, syn)

2 Theta	d(A)	I	h	k	L
26,6181	3,34609	999	1	0	1
31,3388	2,85198	750	0	1	2
52,9702	1,72722	258	1	1	3
46,0138	1,97082	228	1	0	4
28,3235	3,14837	199	0	0	3
43,7846	2,06585	194	1	1	0
54,9168	1,67051	141	0	1	5
51,9784	1,75782	140	0	2	1
54,8264	1,67305	126	2	0	2
70,2509	1,33876	95	2	1	1
72,6625	1,30015	73	1	2	2
65,3905	1,42599	59	0	2	4
75,9318	1,2521	59	1	1	6
44,8753	2,01814	50	1	1	1
88,9305	1,09965	44	1	2	5
58,5918	1,57418	43	0	0	6
82,0458	1,17356	42	2	1	4
38,0383	2,36366	36	1	0	3
75,1956	1,26252	36	1	0	7

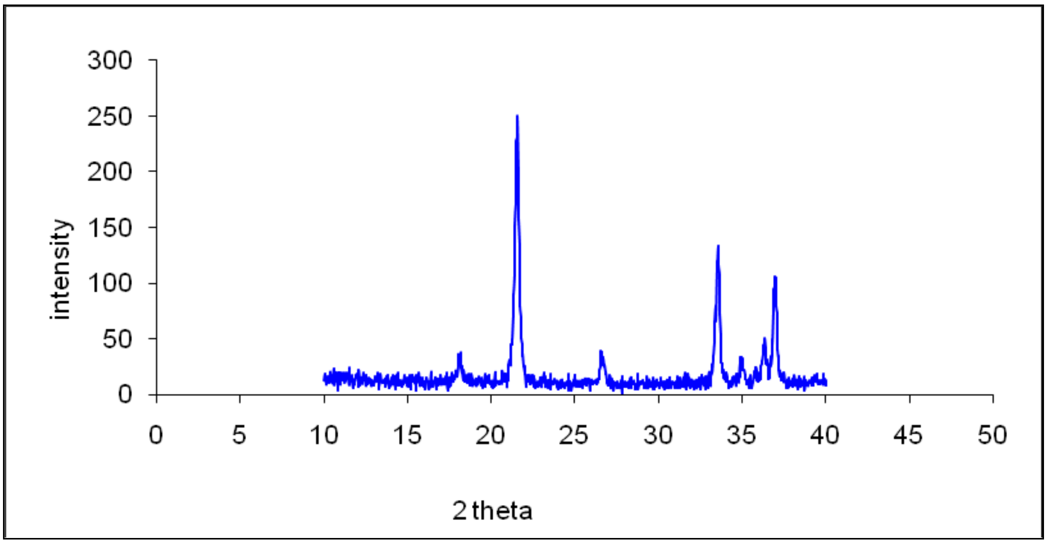


Fig.25.8. *X-ray diffractograms of painted linen with yellow ochre after TA.*

PDF #01-081-0464 (FeO(OH); Goethite, syn)

2 Theta	d (A)	I	h	k	L
21,2397	4,17968	999	1	1	0
36,6574	2,44947	618	1	1	1
33,2417	2,69294	390	1	3	0
53,2418	1,71905	282	2	2	1
34,6849	2,58412	213	0	2	1
58,9957	1,56436	173	1	5	1
41,1819	2,1902	147	1	4	0
17,7968	4,97975	144	0	2	0
36,0419	2,48988	128	0	4	0
26,3392	3,38088	102	1	2	0
39,9744	2,25353	96	1	2	1

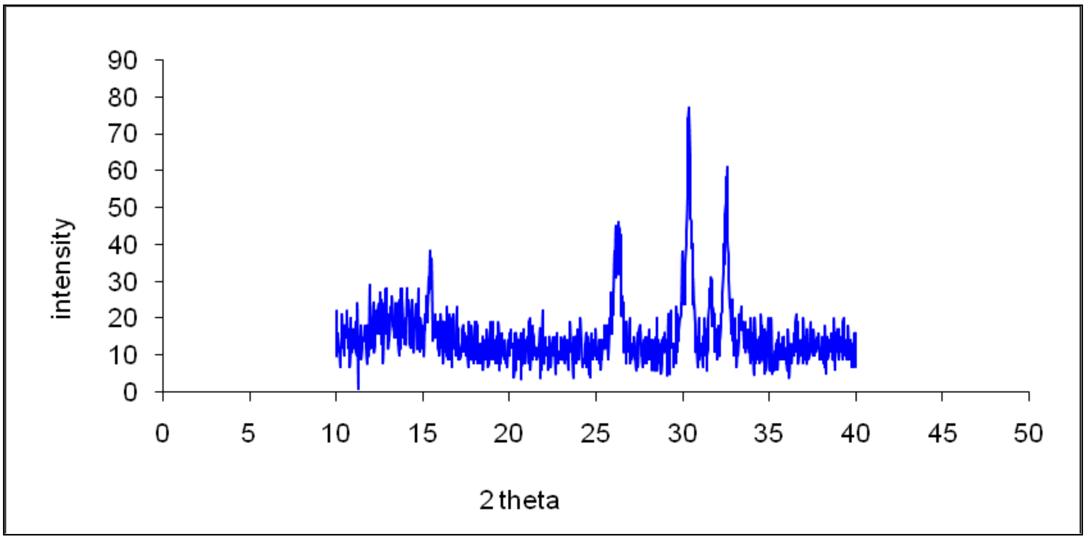


Fig.25.9. *X-ray diffractograms of painted linen with gypsum after TA.*

PDF #00-043-0606 (Ca SO_4; calcium sulfate, anhydrite, syn)

2 Theta	d (A)	I	H	k	L
14,6611	6,037	100	1	0	0
29,5742	3,018	90	2	0	0
25,5387	3,485	80	1	1	0
31,9711	2,797	50	1	0	2
49,2677	1,848	40	2	1	2
52,4539	1,743	30	2	2	0
53,9892	1,697	30	3	0	2
61,3884	1,509	30	4	0	0
84,9227	1,141	30	4	2	0
32,8642	2,723	20	2	0	1

PDF #00-006-0046 (Ca $SO_4 \cdot 2H_2O$; Gypsum

2 Theta	d (A)	I	h	k	L
11,6959	7,56	100	0	2	0
29,1691	3,059	55	-1	4	1
20,7854	4,27	50	-1	2	1
33,4197	2,679	28	0	2	2
31,1704	2,867	25	0	0	2
23,453	3,79	20	0	3	1

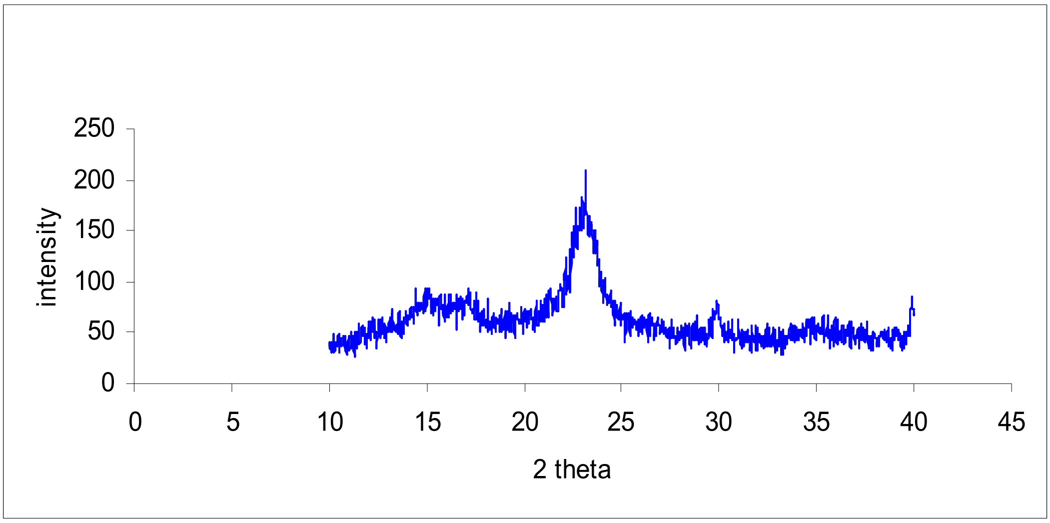


Fig.25.10. *X-ray diffractograms of painted linen with charcoal after TA.*

5.4. Tensile strength and elongation measurements

The results shown from the tables 1.4, 1.5 and the fig.26.1, 26.2., suggest that the process of thermal ageing at 140°C for 72h caused a minor degradation of the physical properties of the linen textiles. In accordance with SEM results, the percentage losses in tensile strength and elongation of unpainted linen sample after thermal ageing are (-29.52%, -8.58%) respectively. Thermal ageing causes limited chain scission of the molecular chains of cellulose polymer, resulting of rupture of the glycosidic bond between the units of the cellulose fibers as well as the oxidation of hydroxyl groups, causing decrease in DP, thereby changing its mechanical properties. In general, this thermal degradation increases with increasing the temperature degree and the duration of ageing[13,14].

The results illustrate significant improvement in tensile properties of all painted linen samples comparing with the standard unpainted and unaged linen sample except of painted fibers with Egyptian blue and hematite. The results confirmed that the colored linen fiber with malachite pigment exhibited the highest increasing in tensile strength (116.93%), followed by Yellow Ochre (72.90%), Vermillion (63.88%), Gypsum (46.45%) and Charcoal (36.18%) respectively. Nevertheless, comparing with the unpainted linen sample after ageing it is clear that the painting linen even with Egyptian blue and hematite still improves the tensile strength of the fibers (-22.02% and -28.15%) respectively.

On the other hand, the results show reduction in the elongation-to-break capabilities of the painted fibers. The colored linen fiber with malachite pigment exhibited the lowest reduction in elongation properties (-10.87%), followed by Yellow Ochre (-15.06%), Vermillion (-16.40%), Gypsum (-15.65%) and Charcoal (-19.67%) respectively. Therefore, tensile strength and elongation properties depend specifically on the type of the pigment used. In general, the main reason for the significant increasing in tensile strength and decreasing in the elongation properties of the linen fibers painted with pigments may be due to the particles of the pigments which deposited in the inter-spaces between and on the textile fibers during the painting process which eventually bring the fibers tightly together. Moreover, it is evident that the pigments are acting as a protective layer reducing heat degradation.

Table.1.4. *Results of tensile strength measurements of painted and standard unpainted linen sample.*

Samples	**Tensile strength (MPa)**	**%loss or increase in tensile strength**
standard unpainted, unaged linen	26.39	---------
unpainted linen after thermal ageing	18.60	-29.52
linen painted with Egyptian blue after thermal ageing	20.58	-22.02
linen painted with Malachite after thermal ageing	57.25	116.93
linen painted with Hematite after thermal ageing	18.96	-28.15
linen painted with Vermillion after thermal ageing	43.25	63.88
linen painted with Yellow Ochre after thermal ageing	45.63	72.90
linen painted with Charcoal after thermal ageing	35.94	36.18
linen painted with Gypsum after thermal ageing	38.65	46.45

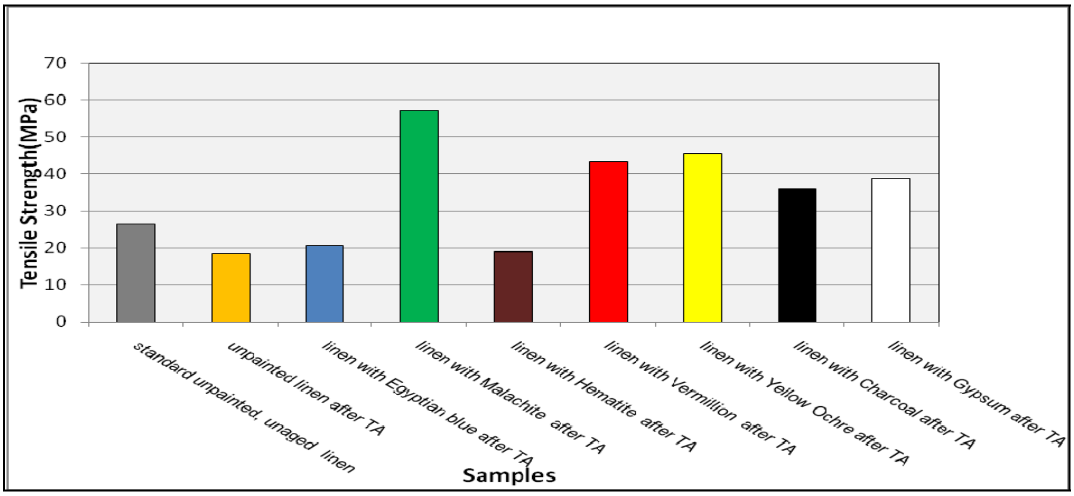


Fig.26.1. *Results of tensile strength measurement of all painted linen with pigments and the standard one.*

Table.1.5. *Results of elongation measurements of painted and standard unpainted linen samples.*

Samples	Elongation%	%loss in Elongation
standard unpainted, unaged linen	49.17	---------
unpainted linen after thermal ageing	40.59	8.58
linen painted with Egyptian blue after thermal ageing	27.44	-21.73
linen painted with Malachite after thermal ageing	38.30	-10.87
linen painted with Hematite after thermal ageing	26.04	-23.13
linen painted with Vermillion after thermal ageing	32.76	-16.40
linen painted with Yellow Ochre after thermal ageing	34.12	-15.06
linen painted with Charcoal after thermal ageing	29.49	-19.67
linen painted with Gypsum after thermal ageing	33.52	-15.65

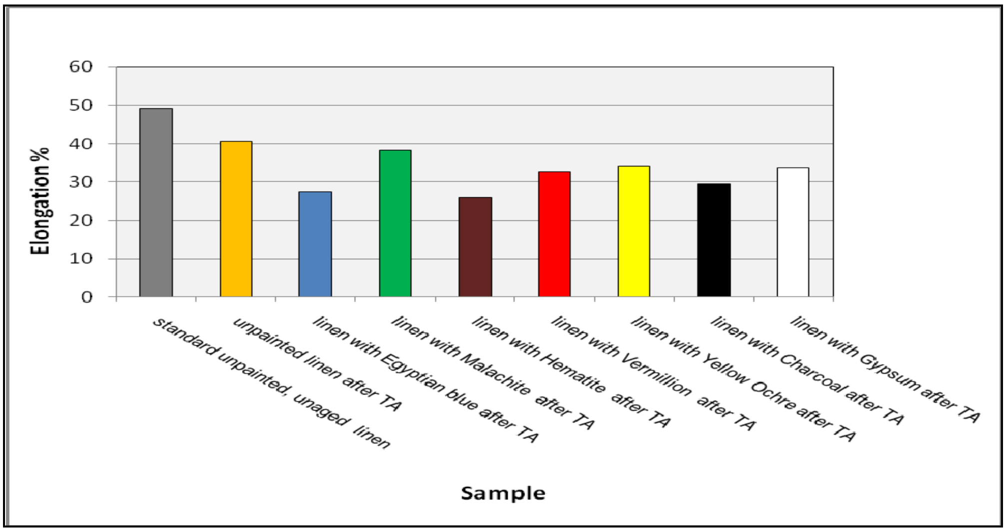


Fig.26.2. *Results of elongation measurement of all painted linen with pigments and the standard one.*

5.5. References

---

[1] L.K. Herrera, A. Justo, A. Duran, M.C.J. de Haro, M. Franquelo, J.L.P. Rodriguez, "Identification of Cellulose Fibres Belonging to Spanish Cultural Heritage using Synchrotron High Resolution X-ray Diffraction," Appl. Phys. A. Mater. Sci. Process. 99(2) 391–398 (2010).

[2] P. Garside, P. Wyeth, "Characterization of silk deterioration", in Preprints of the North American Textile Consrvation Conference, NATCC, Philadelphia, 55-60 (2002).

[3] P. Mravelaki-Kalaitzaki, N. Kallithrakas-Kontos, "Pigment and Terracotta Analyses of Hellenistic Figurines in Crete," Anal. Chim. Acta. 497(1) 209 (2003).

[4] D. Kovala-Demertzi, D. Hadjipavlou-Litina, A. Primikiri, M. Staninska, C. Kotoglou, M.A. Demertzis, "Anti-Inflammatory, Antiproliferative, and Radical-Scavenging Activities of Tolfenamic Acid and Its Metal Complexes. Che. Biodivers. 6(6) 948-960 (2009).

[5] D. Kovala-Demertzi, D. Hadjipavlou-Litina, M. Staninska, A. Primikiri, C. Kotoglou, M.A. Demertzis, "Anti-Oxidant, in Vitro, in Vivo Anti-Inflammatory Activity and Antiproliferative Activity of Mefenamic Acid and Its Metal Complexes With Manganese(II), Cobalt(II), Nickel(II), Copper(II) And Zinc(II)," J. Enzym. Inhib. Med. Chem. 24(3) 742 (2009).

[6] E. Kendix, G. Moscardi, R.Mazzeo, P. Baraldi, S. Prati, E. Joseph, S. Capelli, "Far Infrared and Raman Spectroscopy Analysis of Inorganic Pigments" J. Raman Spectrosc. 39: 1104-1112 (2008).

[7] R.J. Gettens, E. West Fitzhugh, "Pigments- A Handbook of their History and Characteristics", Oxford University Press, New York, National Gallery of Art, 2th ed., 375-390 (1993).

[8] D. Skrzypeka, B. Szymanska, D. Kovala-Demertzi, J. Wiecek, E. Talik, M.A. Demertzis, "Synthesis and Spectroscopy Studies of Iron (III) Complex with A Quinole Family Member (Pipemicid Acid)" J. Phys. Chem. Solids 67: 2550-58 (2006).

[9] M.J. Wilson, "Clay Mineralogy: Spectroscopic and Chemical Determinative Methods", 1th ed., Chapman & Hall, London, 367 (1994).

[10] L.J. Bellamy, "The Infrared Spectra of Complex Molecules," 3rd ed., Chapman & Hall, London, 315 (1975).

[11] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 5thed., John Wiley & Sons, New York, 87-90(1986).

[12] R.A. Blanchette, "Novel Bacterial Community Associated with 500-Year-Old Unpreserved Archaeological Wood from King Henry VIII's Tudor Warship the Mary Rose," Biodeterior. Biodegrad. 46:189–204 (2000).

[13] A. Timar-Balazsy, D. Eastop, "Chemical Principles of Textile Conservation", 1th ed., Oxford, Butter worth –Heinemann, London, 19-55(1998).

[14] M. Eric & M. Jones, "Conservation Science Heritage Materials," The Royal Society of Chemistry, Cambridge, UK, 67-68 (2006).

---

[15] J. Scheirs, "Compositional and Failure Analysis of Polymers: A Practical Approach", Wiley Series in Polymer Science, John Wiley & Sons, UK. 50(9) 1054 (2000).

16 R. H. Atalla & D. L. Vanderhart, "Native Cellulose: A Composite of Two Distinct Crystalline Forms," J. Science 223: 283-285 (1984).

[17] M. C. Jarvis, "Sensing the Structural Differences in Cellulose from Apple and Bacterial Cell Wall Materials by Raman and FT-IR Spectroscopy," Carbohydr. Res. 325: 150-154 (2000).

[18] K.H. Meyer, L. Misch, "Systematic Absences and the X-Ray Diagram of Cellulose," Helv. Chim. Acta 20: 232 (1937).

[19] A. Thygesen, J. Oddershede, H. Lilholt, A.B. Thomsen & K. Stahl, "On the Determination of Cellulose Content and Crystallinity in Plant Fibres", Cellulose 12(6) 563-576 (2005).

[20] S.Y. Oh, D.I. Yoo, Y. Shin, H.C. Kim, H.Y. Kim, Y.S. Chung,W.H Park, J.H. Youk, "Crystalline Structure Analysis Of Cellulose Treated With Sodium Hydroxide And Carbon Dioxide by Means Of X-Ray Diffraction and FTIR Spectroscopy," J. Carbohydr Res. 31(15) 2376-91 (2005).

[21] S.J. Eichhorn, R.J. Young, R.J. Davies, C. Riekel, "Characterization of the Microstructure and Deformation of High Modulus Cellulose Fibres," J. Polymer, 44: 5901-5908 (2003).

[22] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, "An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer," J. Tex. Res. 29: 786-794 (1959).

[23] B.D. Cullity, "Elements of X-ray Diffraction", 2nd ed., Addison Wesley, Massachusetts, 3-569 (1978).

[24] J.I. Langford, in E. Prince, J.K. Stalick (Eds.), "Accuracy in Powder Diffraction II" (NIST Spec. Publ. No. 846, NIST, Gaithersburg, MD (1992).

[25] PDF Database, International Centre for Diffraction Data, Newtown Square, Pensylvania, USA (2003).

CHAPTER 6

Results and Discussion of dyed linen samples with natural dyes

6.1. FTIR spectroscopy

Characteristic infrared bands of all samples are shown in Table1.6 and figs.27.1, 27.2, 27.3, 27.4, 27.5, 27.6 and 27.7.

The FTIR spectra of aged and normal linen have been discussed in detail previously in chapter 5. Generally in all spectra there is a significant overlapping between the bands of aged linen and the organic dyes indicating a strong binding to lignin and cellulose compounds resulting in a possible degradation[1,2,3]. There is a significant band shifting upon binding, which mainly localized in the "fingerprint region" (1500–800 cm^{-1}) where the dyes feature characteristic absorption bands, Table 1.6. Conceivably, thermal ageing also affects the shape and the location of the absorption bands but this is mostly manifested in the absorption of carboxyl and carbonyl groups in the 1730–1630 cm^{-1} regions[4]. Our results show that the intensity of the band at 1639 cm^{-1}, attributed to the carbonyl functional group, varies among different dyed samples but constantly increases due to the degradation of glycosidic linkages in the cellulose fibers[5]. The dyes seem to mainly interact with the cellulose compounds of the aged linen.

The spectrum of indigo exhibits a broad strong band at 3275 cm^{-1} attributable to strong intra-molecular bond that stabilizes the *trans* configuration of indigo, Fig.27.8a. The spectral pattern of indigo exhibits bands at 1628, 1483, 1460, 1299, 1173, 1126 cm^{-1} and 1074 cm^{-1} (Table1.6). The spectral profile of the aged linen dyed by indigo, Fig.27.1 shows differences compared to the spectrum of aged linen and indigo. The bands of indigo are overlapped by the bands of aged linen. The band at 1639 cm^{-1} of aged linen has been shifted to lower frequency at 1628 cm^{-1} (ν(C=C) and ν(CO), lignin compounds). The band at 1431 cm^{-1} has been shifted at 1483 cm^{-1} (ν(CH) cellulose compounds) and the bands at 1114 and 1061 cm^{-1} have moved to higher frequency at 1126 and 1074 cm^{-1} (C-O-C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the indigo of the aged linen binds strong to lignin and cellulose compounds resulting in possible degradation of them[1,6,7,8,9]

Alizarine (1,2-dihydroxy-anthraquinone) and purpurine (1,2,4-trihydroxy- anthraquinone) are the main constituents of madder natural dyestuff. Also, other anthraquinones such as, pseudopurpurin (1,2,4-trihydroxyanthraquinone-3-carboxylic acid), and munjistin(1,3 dihydroxyanthraquinone-2-carboxylic acid) are also present, mostly in glycoside forms, Fig. 27.8b[6,10]. The absorption band at 3422 cm^{-1} in the infrared spectrum of madder indicates the presence of hydroxyl groups, broadened due to the inter- and intra-hydrogen bonding.

The spectrum of madder exhibits bands at 1646, 1616, 1430, 1319, 1266 cm^{-1} and 1040 cm^{-1} [6]. The bands of madder are overlapped by the bands of aged linen. The bands at 1114 and 1061 cm^{-1} of aged linen have moved to lower frequency at 1108 and 1057 cm^{-1} (C-O-C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the madder binds to cellulose compounds resulting in possible inter-molecular hydrogen bonds[2,8,9,11]

Turmeric is a complex mixture system and its infrared spectrum shows substantial overlap of various compounds. Turmeric contains up to 5% essential oils and up to 5% curcumin, (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione,apolyphenol. Curcumin is the active substance of turmeric. It can exist at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution, the yellow colour of crude turmeric oil has been attributed to the presence of curcuminoids, curcumin-I (1), curcumin-II (2), and curcumin-III (3), Fig.27.8c. The spectral pattern of turmeric exhibits bands at 3405, 2926, 1676, 1634, 1514, 1430, 1282, 1158 and 1030 cm^{-1} (Table1.6). The spectral profile of the aged linen dyed by turmeric, Fig.27.3 shows differences compared to the spectrum of aged linen and turmeric. The bands of turmeric are overlapped by the bands of aged linen. The band at 3405, 2926 and 1676 cm^{-1} of turmeric has been shifted to higher frequency at 3412, 2903 and 1708 cm^{-1} to the spectrum of aged linen dyed by turmeric. The band at 1373 cm^{-1} of the aged linen has been shifted at 1371 cm^{-1} to the spectrum of aged linen dyed by turmeric (*v*(CH) cellulose compounds) and the bands at 1061 and 1032 cm^{-1} have moved to lower frequency at 1058 and 1029 cm^{-1} (C-O-C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the turmeric binds to lignin and cellulose compounds of the aged linen resulting in possible degradation of them[2, 9,12,11]

Henna's active agent is 2-hydroxy-1,4-naphthoquinone, fig.27.8d. The band at 3404 cm^{-1} is attributed to the stretching vibration of *v*(OH) group. Its position at relatively low wave numbers is attributed to the intra-molecular hydrogen bond between the (OH) group and the neighbouring oxygen atom[11]. Henna's spectral profile exhibits bands at 3404, 2925, 2855, 1734, 1648, 1637, 1437, 1383, 13211241 and 1035 cm^{-1}. The spectral profile of the aged linen dyed by henna, Fig.27.4 shows pronounced differences compared to the spectrum of aged linen and henna's. The strong broad band centered at 3406 and the band at 2900 cm^{-1} of aged linen has been shifted at the spectrum of aged linen dyed by henna at 3397 and 2922 cm^{-1}. The bands of the aged linen at 1431 and 1373 cm^{-1} (cellulose compounds) are shifted at the spectrum of aged linen dyed by henna at 1432 and 1379 cm^{-1}. The two bands of the aged linen at 1112 and 1060 cm^{-1} are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (β-glycoside linkages, cellulose compounds) are shifted at the spectrum of aged linen dyed by henna's at 1058 and 1032 cm^{-1}. From these data, it is concluded that the henna binds very strong to cellulose compounds resulting in possible degradation of them[9,13]

The main constituent of cochineal is carminic acid, an anthraquinone derivative shown in Fig. 27.8e. The spectrum of cochineal exhibits a broad strong band at 3293 cm^{-1} attributable to strong intra- and inter- molecular hydrogen bonds. The bands of cochineal at 2920 and 2850 cm^{-1} are assigned to stretching vibrations of methyl and methylene groups $\nu(CH_3)$ and $\nu(CH_2)$. The broad bands at 1653 and 1637 cm^{-1} are assigned to vibrations of ν(C=C), δ(OH) and ν(C=O) bonds (derived from carbonyl, or carboxyl groups). The spectral pattern of cochineal exhibits bands at 1559, 1542, 1457, 1377, 1244, 1078 and 1046 cm^{-1}, Table1.6. The spectral profile of the aged linen dyed by cochineal, Fig.27.5 shows differences compared to the spectrum of aged linen and cochineal. The bands at 1647 and 1638 cm^{-1} of aged linen has been shifted to higher frequency at 1654 and 1639 cm^{-1} (ν(C=C) and ν(CO), lignin compounds) of aged linen dyed by cochineal. The band at 1431 cm^{-1} has been shifted at 1436 cm^{-1} (ν(CH) cellulose compounds) and the bands at 1061 and 1032 cm^{-1} have moved to higher frequency at 1078 and 1046 cm^{-1} (C-O-C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the cochineal binds very strong to lignin and cellulose compounds resulting in possible degradation of them[2,7,9,11]

The pigment in safflower (*Carthamus Tinctorius*) is carthamin, Fig.27.8g. Safflower is a complex mixture system and its constituents are α-linolenic acid, palmitic acid, γ-linolenic acid and a-tocopherol, so its infrared spectrum shows substantial overlap of various compounds[14]. The spectrum of safflower exhibits a broad strong band at 3398 cm^{-1} attributable to stretching ν(OH) vibrations. Some of the most significant bands of safflower are the following: the bands at 2921 and 2852 cm^{-1} due to the asymmetric and symmetric stretching vibration of the aliphatic ($CH_{2)}$ functional group; the band at 1735 cm^{-1} due to the ester carbonyl functional group of the triglycerides; the band near 1647 cm^{-1} associated with the stretching vibration of the v(C=C) double bonds of cis-olefins, the band near 1457 cm^{-1} due to the bending vibrations of the ($CH_{2)}$ and ($CH_{3)}$ aliphatic groups; the band at 1420 cm^{-1} tentatively assigned to rocking vibrations of (CH) bonds of cis-disubstituted olefins; the band near 1377 cm^{-1} due to bending vibrations of ($CH_{2)}$ groups; bands near 1244 is associated with the stretching vibration of the (C-O) ester groups and with the bending vibration of the ($CH_{2)}$ group[15]. The spectral profile of the aged linen dyed by safflower, Fig.27.6 shows differences compared to the spectrum of aged linen and safflower's. The strong broad band centered at 3406 and the band at 2900 cm^{-1} of aged linen has been shifted at the spectrum of aged linen dyed by henna at 3415 and 2915 cm^{-1}. The bands of the aged linen at 1431 and 1373 cm^{-1} (cellulose compounds) are shifted at the spectrum of aged linen dyed by safflower at 1432 and 1371 cm^{-1}. The two bands of the aged linen at 1112 and 1060 cm^{-1} are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (β-glycoside linkages, cellulose compounds) are shifted at the spectrum of aged linen dyed by safflower at 1088 and 1062 cm^{-1}. From these data, it is concluded that the safflower binds to cellulose compounds resulting in possible degradation of them[2,9,11].

The chemical composition of saffron has been thoroughly studied and numerous volatile and non-volatile constituents have been identified. Characteristic constituents of saffron are crocin and congeners, which are a family of water soluble glycosides of crocetin contributing to the red colour of saffron, numerous monoterpenoids such as safranal, responsible for the aroma of saffron, and picrocrocin, which is a precursor of safranal. Saffron is a complex mixture system, so its infrared spectrum shows substantial overlap of various compounds. The broad peak centered at about 3400 cm^{-1} is due to hydroxyl (–OH) groups. The spectral region 3000–2830 cm^{-1} presents two peaks at 2929 and 2851 cm^{-1} which correspond to ν(C–H) stretching vibrations. The spectral region 1800–1500 cm^{-1} is the characteristic groups region. The carbonyl (–C=O) group (esters, ketones, aldehydes), the non-removed water and the aromatic ring absorb in this region. The region 1500–800 cm^{-1} is the "fingerprint region". The peaks in this region are associated with the skeletal vibrations of the components and have been attributed to $–CH_2–$, $CH_3–$, –OH, C–C, C–O, C–O–C groups. Particularly, the 1200–800 cm^{-1} spectral region has been correlated with the presence of sugars and polysaccharides. The spectral profile of the aged linen dyed by saffron, Fig.27.7 shows differences compared to the spectrum of aged linen and saffron. The bands of saffron are overlapped by the bands of aged linen dyed by saffron. The bands at 3396, 2925 and 2854 and 1651 cm^{-1} of saffron have been shifted at 3411, 2916 and 1639 cm^{-1} to the spectrum of aged linen dyed by saffron. The bands at 1431 and 1373 cm^{-1} of the aged linen have been shifted at 1430 and 1372 cm^{-1} to the spectrum of aged linen dyed by saffron (ν(CH) cellulose compounds) and the bands at 1061 and 1032cm^{-1} have moved to lower frequency at 1060 and 1030 cm^{-1} (C-O-C, glycosidic linkage, cellulose compounds). From these data, it is concluded that the saffron binds slightly to lignin and cellulose compounds[2, 9,11,16,17]

From all these data it is concluded that spectral profile of the aged linen colored with these natural dyestuffs shows the spectral pattern of dyes superimposed a lot of bands of the aged linen. Furthermore, the dyes seem to interact mainly to cellulose compounds of the aged linen.

Table.1.6. *Characteristic infrared band of standard and dyed samples in cm*$^{-1}$

Sample	**Wave numbers (cm^{-1})**
Standard unaged linen	3370 *vsbr*, 2900 *s*, 1639 *vs*, 1431 *vs*, 1373 *vs*, 1112 *vs*, 1062 *vs*, 668 *ms*, 615 *vs*, 560 *m*
Aged linen	3406 *vsbr*, 2900 *s*, 1639 *vs*, 1431 *vs*, 1373 *vs*, 1112 *vs*, 1060 *vs*, 668 *ss*, 615, 560*m*
Indigo	3265*vs*, 2926*w*, 1627*vs*, 1613*sh*, 1483*s*, 1460*s*, 1396*s*, 1317*s*, 1299*ms*, 1196*sh*, 1173*s*, 1073*vs*,1010*sh*, 878*mw*, 751*s*, 698*s*, 637*mw*, 562*s*, 508*m*, 467*m*, 422*m*,
Aged linen dyed by indigo	3275*vs*, 2901*ms*, 1628*vs*, 1586*sh*, 1483*ms*, 1461*vs*, 1429*ms*, 1395*ms*, 1318*ms*, 1172*s*, 1126*vs*, 1074*vvs*, 1033*w*, 752*m*, 699*ms*, 614*ms*, 562*s*, 470*w*, 434*w*
Madder	3422*vs*, 2927*s*, 1646*vs*, 1616*vs*, 1541*w*, 1509 *w*, 1430*vs*, 1319*s*, 1040*vs*, 920*vw*, 874*w*, 781*m*, 664*m*, 521*s*, 470*s*, 397*w*
Aged linen dyed by madder	3387*vs*, 2914*s*, 1640v*s*, 1431*vs*, 1372*vs*, 1320*vs*, 1236*w*, 1152*w*, 1108*sh*, 1057*vvs*, 1034*sh*, 780*w*, 668*s*, 613*vs*, 521*s*, 434*w*
Turmeric	3405*vsbr*, 2926*ms*, 2156*mbr*, 1676*sh*, 1634*vsbr*, 1514*ms*, 1457*m*, 1430 *m*, 1380*mw*, 1320*mw*, 1282*mw*, 1158*m*, 1077*sh*, 1030*vs*, 858*w*, 764*mw*, 706*mw*, 606*sh*, 574*s*, 522*s*, 473*w*, 421*w*, 399*w*
Aged linen dyed by turmeric	3412*vsbr*, 2903*ms*, 2140*wbr*, 1708*w*, 1651*sh*, 1638*vs*, 1512*w*, 1431*vs*, 1371*vs*, 1320*ms*, 1282*w*, 1234*w*, 1157*m*, 1112*vs*, 1058*vs*, 1029*vs*, 669*s*, 612*s*, 560*ms*, 521*mw*, 433*w*
Henna	3397*vs(br)*, 2925*m*, 2855*w*, 1734*w*, 1648*vs*, 1637*vsbr*, 1543*vw*, 1437*mwbr*, 1383*m*, 1321*m*, 1241*m*, 1069*sh*,1035*vs*, 778*m*, 669*m*, 521*s*, 469*s*, 398*vw*
Aged linen dyed by henna	3404*vsbr*, 2922*m*, 2855*sh*, 1736*sh*, 1638*vs*, 1546*vw*, 1432*s*, 1379*s*, 1321*s*, 1236*m*, 1058*vs*, 1032*vs*, 779*w*, 670*m*, 615*m* 558*m*, 520*ms*, 470*w*, 435*sh*
Cochineal	3293*vsbr*, 2920*vs*, 2852*s*, 1653*vs*, 1637*vsbr*, 1559*s*, 1542*s*, 1457*m*, 1417*mw*, 1377*m*, 1244*ms*, 1078*s*, 1046*s*, 887*w*, 837*w*, 777*w*, 719*w*, 645*m*, 598*m*, 528*mw*, 458*w*, 421*w*, 396*w*
Aged linen dyed by cochineal	3353*vsbr*, 2920*s*, 2852*w*, 1654*vs*, 1639*vs*, 1562*mw*, 1547*mw*, 1436*s*, 1373*s*, 1319*mw*, 1283*w*, 1234*mw*, 1206*mw*, 1153*w*, 1112*ms*, 1078*vs*, 1057*vs*, 896*w*, 669*ms*, 602*s*, 560*ms*, 457*w*, 435*w*

Safflower	3398*vsbr*, 2921*ms*, 2852*mw*, 1735*mw*, 1717*w*, 1649*vsbrvs*, 1637*vs*, 1559*w*, 1543*w*, 1518*w*, 1457*m*, 1420*m*, 1377*w*, 1244*ms*, 106*vsbr*, 833*mw*, 775*mw*, 663*sh*, 612*s*, 522*ms*, 421*w*, 397*w*
Aged linen dyed by safflower	3468*vsbr*, 3415*vsbr*, 2915*s*, 2902*sh*, 1711*w*, 1639*vs*, 1548*vw*, 1432*vs*, 1371*vs*, 1337*w*, 1319*w*, 1234*mw*, 1205*mw*, 1151*mw*, 1088*vs*, 1062*vs*, 1027*s*, 815*vw*, 669*s*, 617*vs*, 559*m*, 518*m*, 433*w*
Saffron	3396*vsbr*, 2925*m*, 2854*w*, 1734*w*, 1651*vsbr*, 1544*w*, 1456*w*, 1417*vs*, 1319*vw*, 1246*m*, 1143*sh*, 1103*w*, 1073*vs*, 1053*vs*, 774*mw*, 662*s*, 619*s*, 535*ms*, 422*w*.
Aged linen dyed by saffron	3411*vsbr*, 2916*m*, 2855*sh*, 1705*w*, 1639*vs*, 1546*vw*, 1430*s*, 1372*vs*, 1319*w*, 1335*w*, 1154*w*, 1112*vs*, 1060*vs*, 1030*s*, 700*sh*, 669*s*, 616*s*, 560*m*, 520*vw*, 437*w*

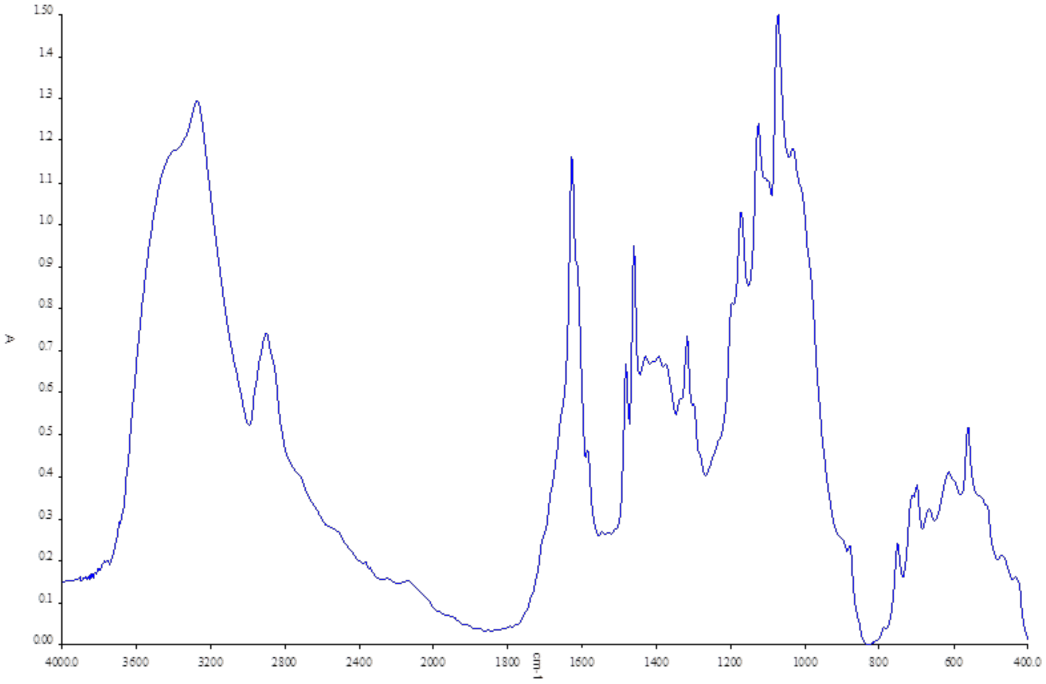


Fig.27.1. *FTIR spectra of dyed linen sample with indigo after thermal ageing.*

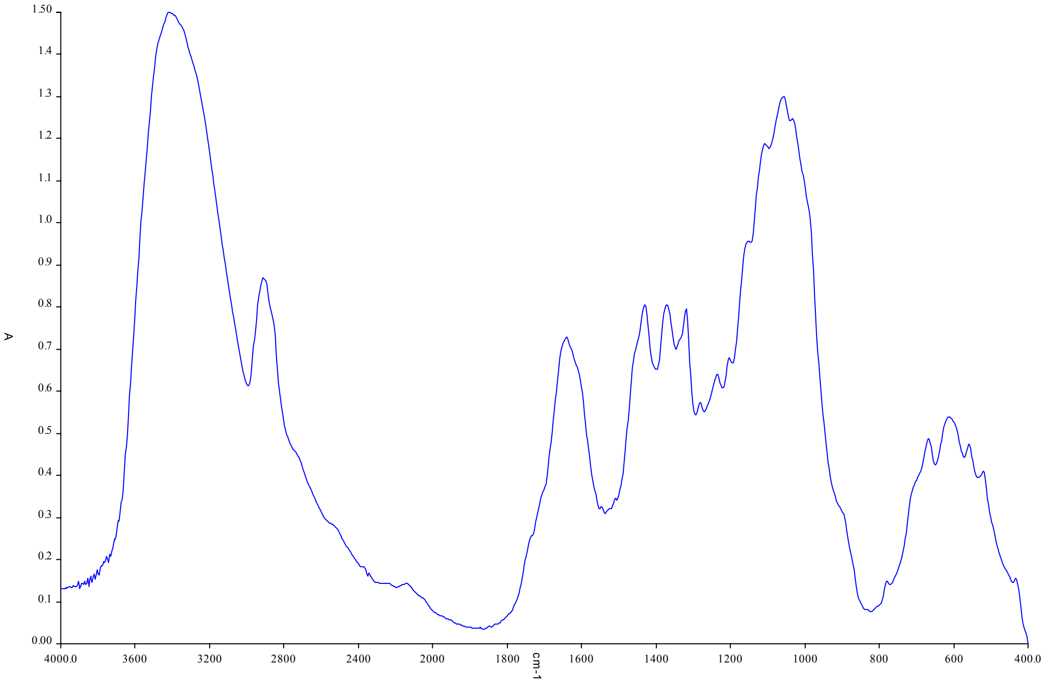


Fig.27.2. *FTIR spectra of dyed linen sample with madder after thermal ageing.*

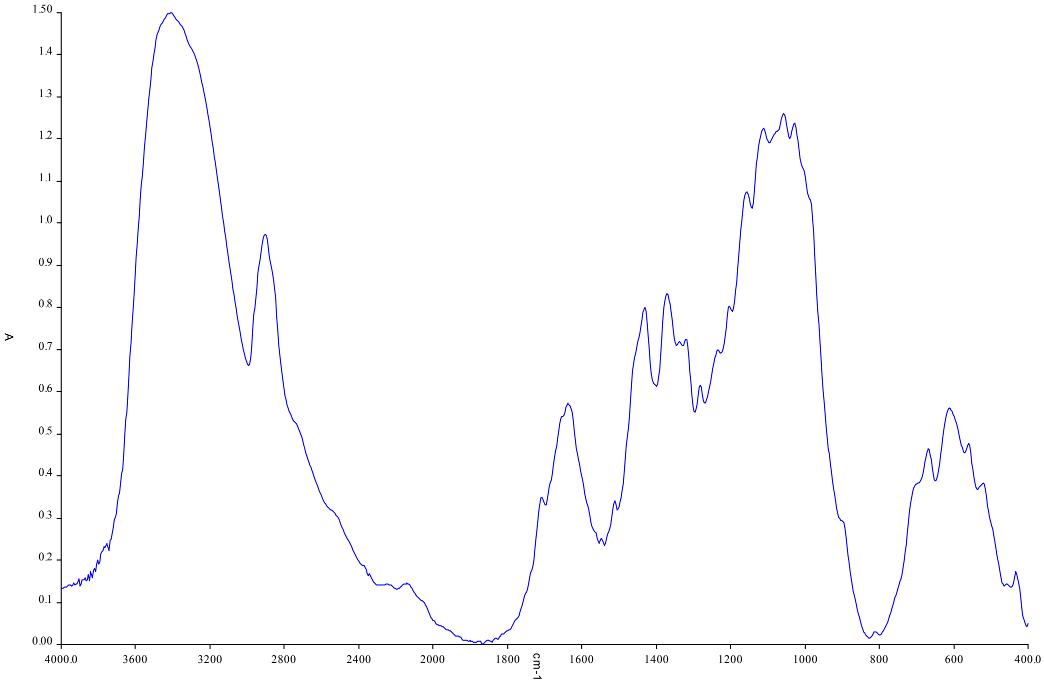


Fig.27.3. *FTIR spectra of dyed linen sample with Turmeric after thermal ageing.*

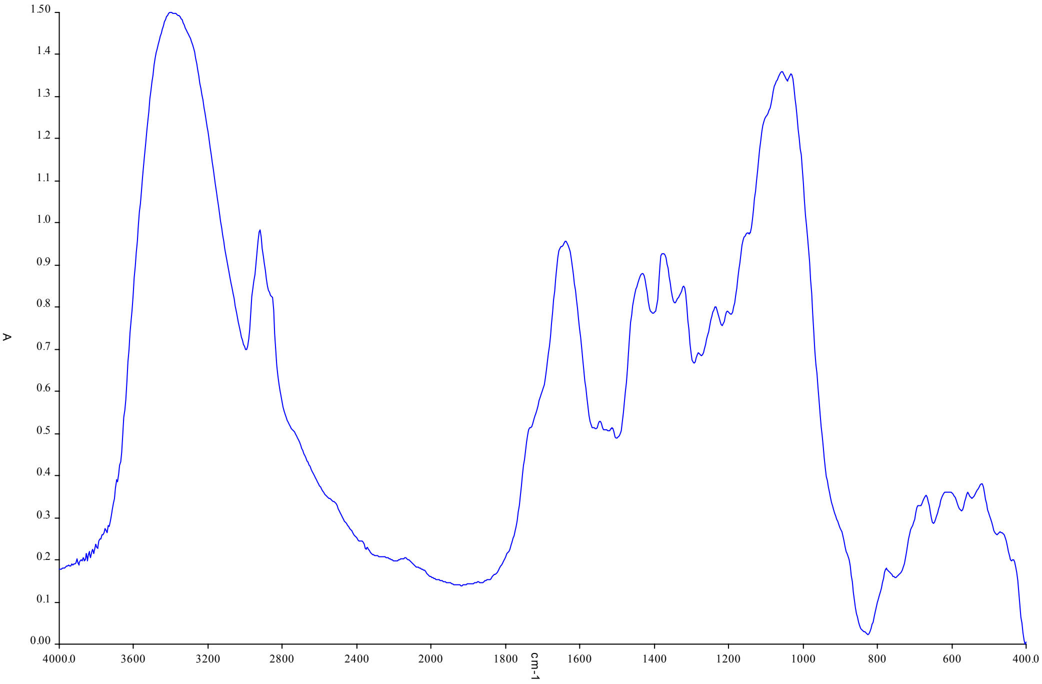


Fig.27.4. *FTIR spectra of dyed linen with Henna after thermal ageing.*

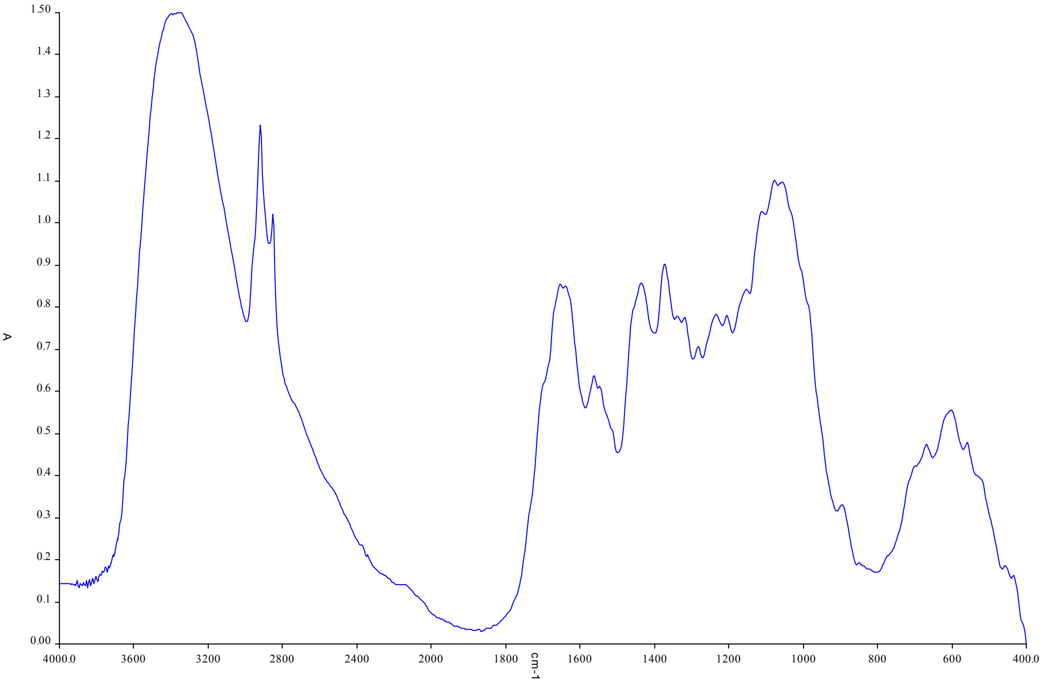


Fig.27.5. *FTIR spectra of dyed Linen sample with Cochineal after thermal ageing.*

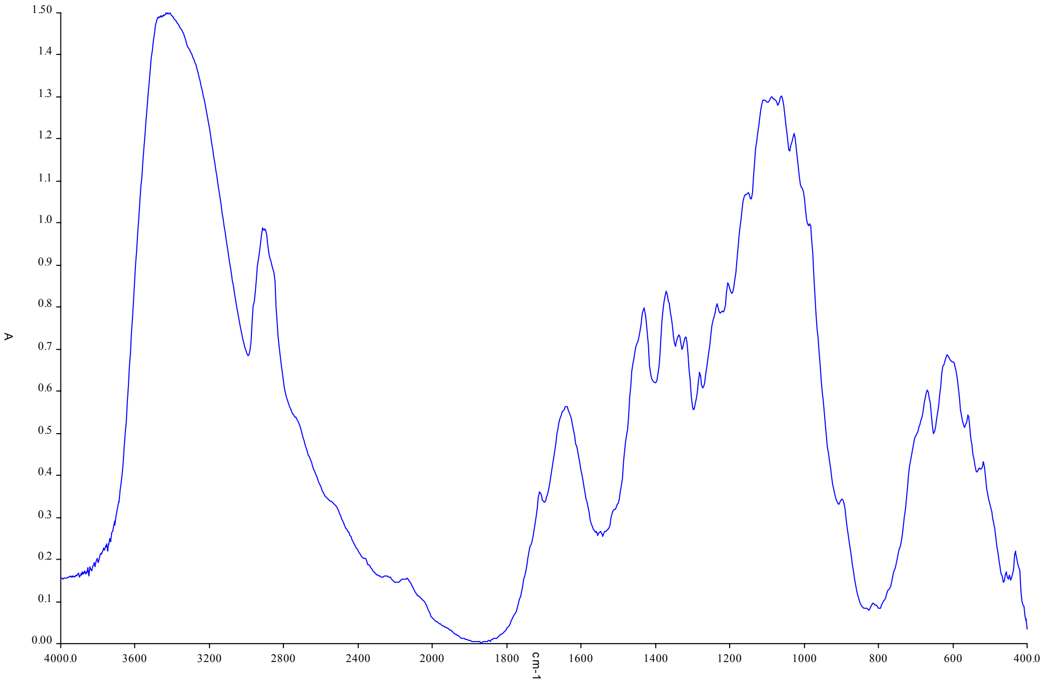


Fig.27.6. *FTIR spectra of dyed Linen sample with Safflower after thermal ageing.*

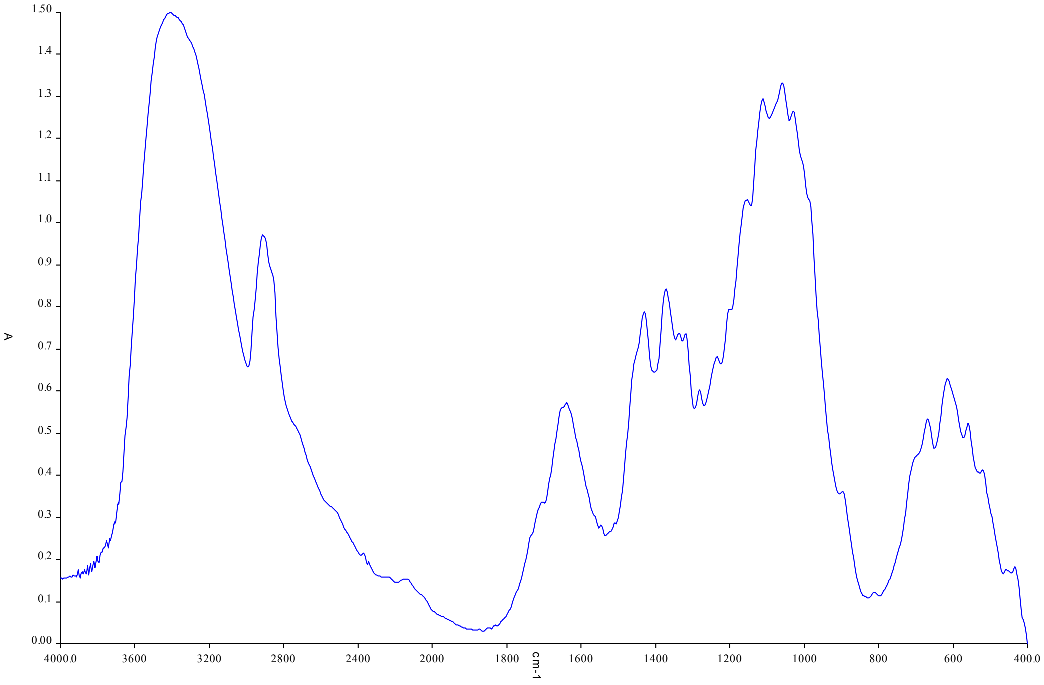
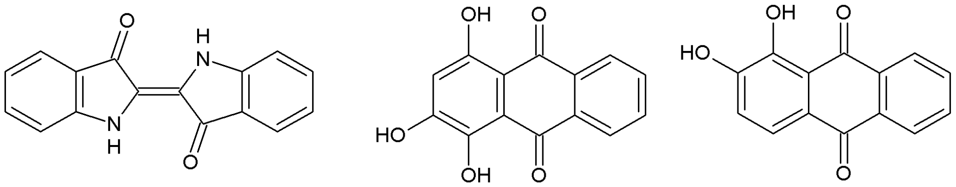
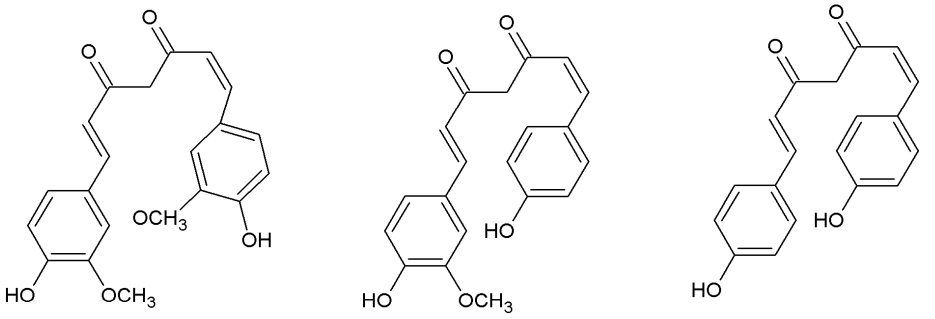


Fig.27.7. *FTIR spectra of dyed Linen sample with Saffron after thermal ageing.*

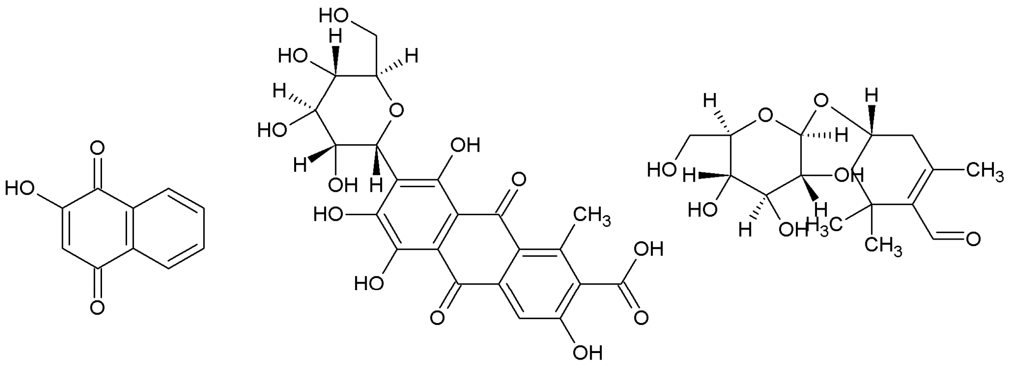


(a) Indigo (b) Purpurin Alizarin

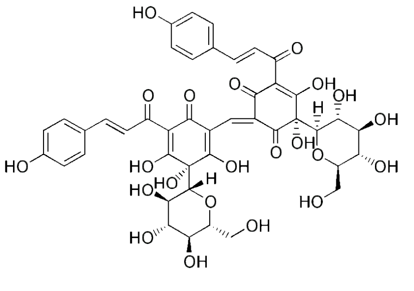


Curcumin Demethoxycurcumin Bisdemethoxycurcumin

(c)



(d) Lawsone (e) Carminic acid (f) Picrocrocin



(g) Carthamin

Fig.27.8. *Schematic representation of the tested organic natural dyestuffs.*

6.2. Scanning electron microscope (SEM-EDS)

SEM photos of the standard undyed and unaged linen sample Fig.24.1(a,b) show the typical morphology of the linen fiber. The nodes structure is clearly observed in the fibers and the weave pattern of the linen textile sample is plain weave 1:1. Thermal ageing at 140°C for 72 h, does not significantly alter the fibers morphology nor of the weave structure, Fig.24.1(c,d,e). Nevertheless, some fibers are damaged sustaining a brush–like fracture. This damage probably stems from the rupture of the glycosidic bond between the units of the cellulose fibers. A second reason could also be the oxidation of hydroxyl groups which may be initially formed during thermal oxidation. The outcome is scission of the molecular chains of the cellulose polymer. Yet, this ageing does not modify appreciably the morphology of the linen fibers[18].

On the other hand, SEM analysis of all natural dyes applied in dyed thermally aged linen do not cause noticeable changes in the morphology and weave structure of the dyed linen fibers. The surface morphology, which is characteristic of the linen fibers, is very clear and only a few fibers are broken with transverse cracking and longitudinal splitting characterized by small scratches on the fibers surfaces. This degradation profile, exhibiting severely damaged fibres with broken ends, is more obvious in the TA linen dyed with henna and this confirms the significant changes found with FTIR. In general, the results confirm that most natural dyes play a protective role and reduce the deterioration of surface morphology of linen fibers after thermal ageing. Cochineal, turmeric and madder dyes exhibit the greatest protection on the morphology of linen fibers, while henna dye showed the greatest deterioration compared with the standard undyed linen fibers before thermal ageing. The conditions of dyeing process may also have a differential effect on the morphological properties of the dyed linen.

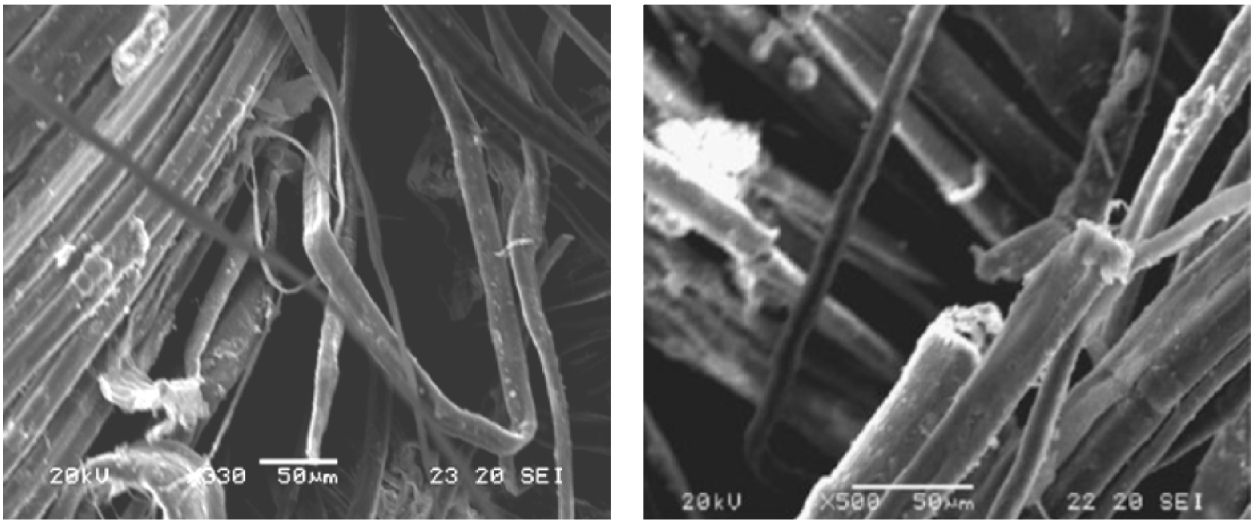


Fig.28.1. *SEM microphotographs of dyed linen sample with indigo dye after TA.*

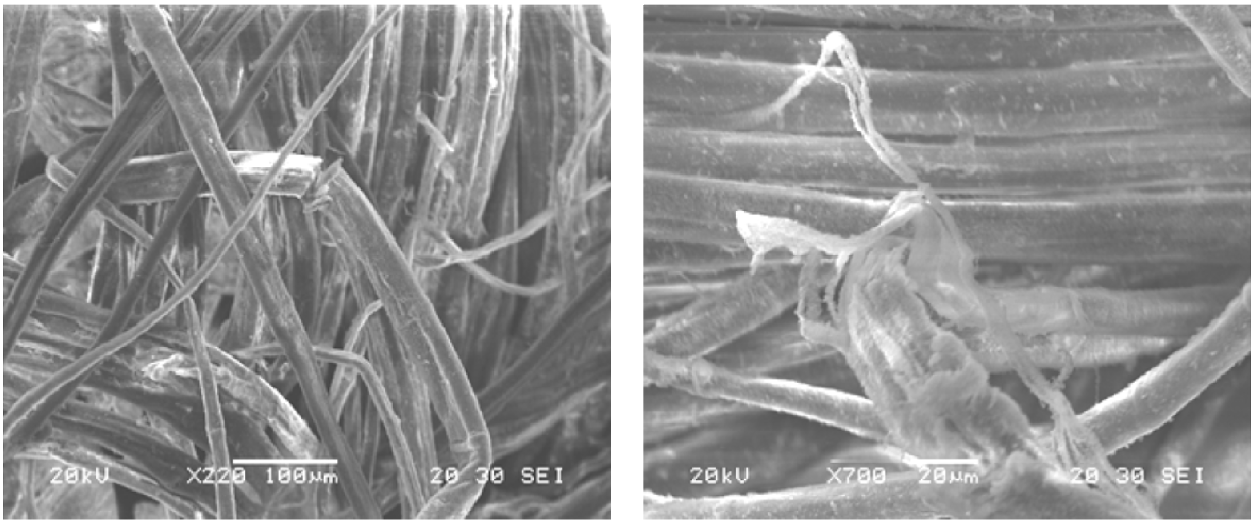


Fig.28.2. *SEM microphotographs of dyed linen sample with madder dye after TA.*

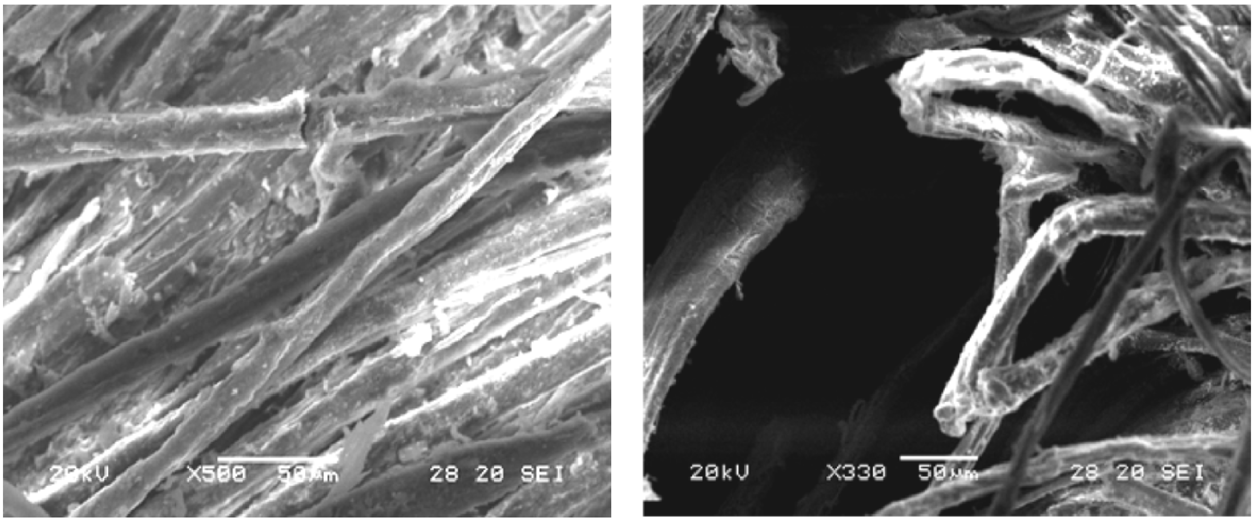


Fig.28.3. *SEM microphotographs of dyed linen sample with turmeric dye after TA.*

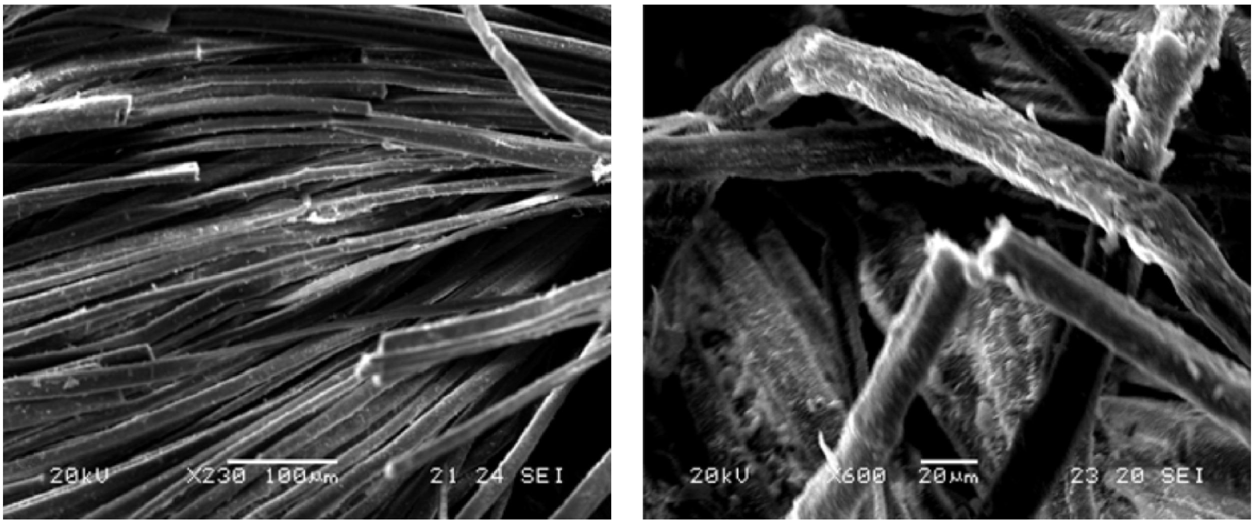


Fig.28.4. *SEM microphotographs of dyed linen sample with henna dye after TA.*

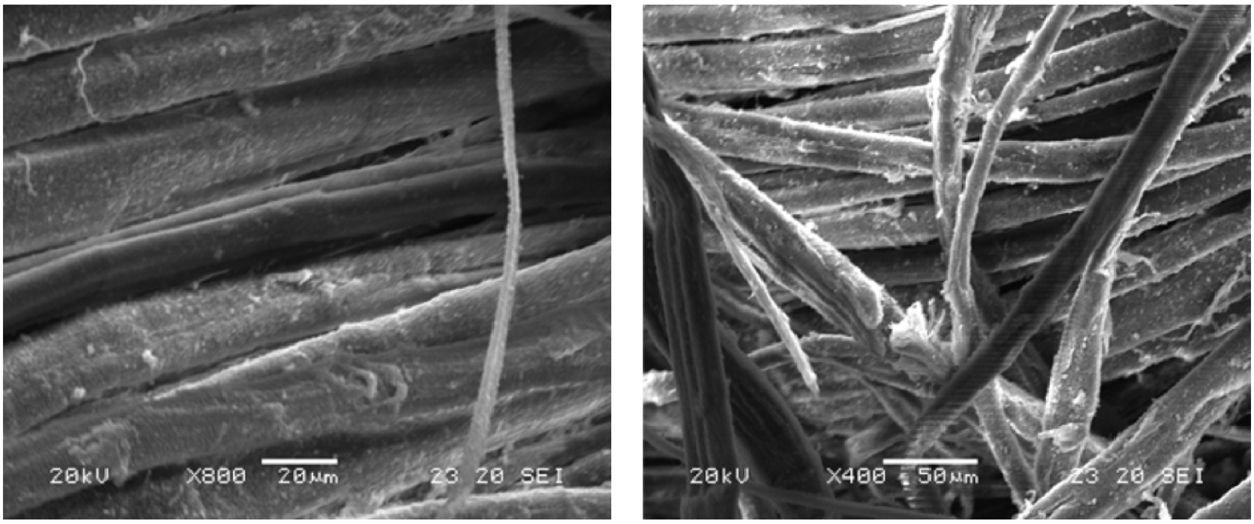


Fig.28.5. *SEM microphotographs of dyed linen sample with cochineal dye after TA.*

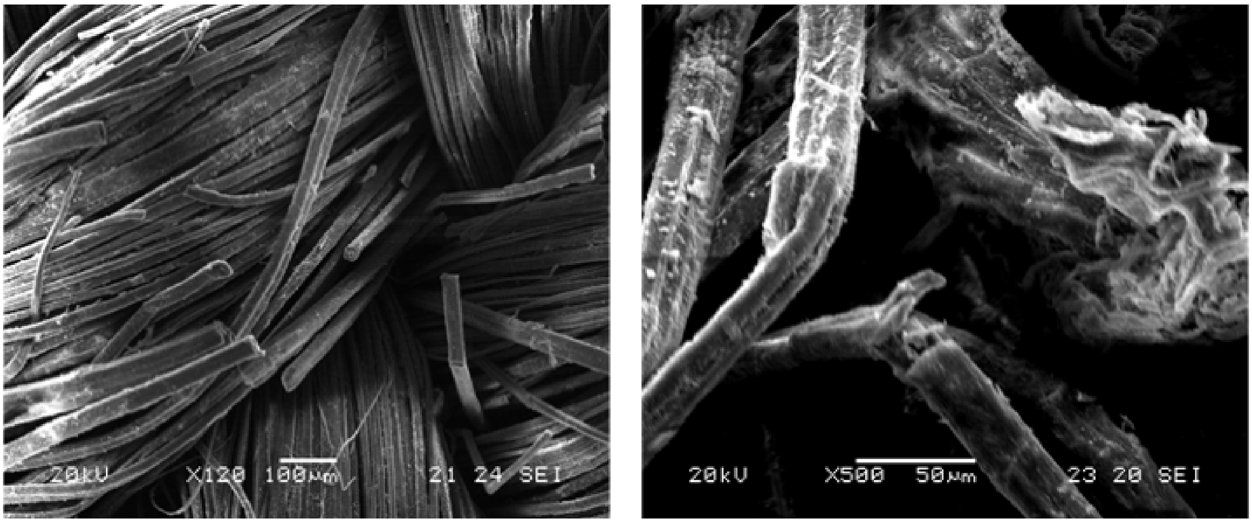


Fig.28.6. *SEM microphotographs of dyed linen sample with safflower dye after TA.*

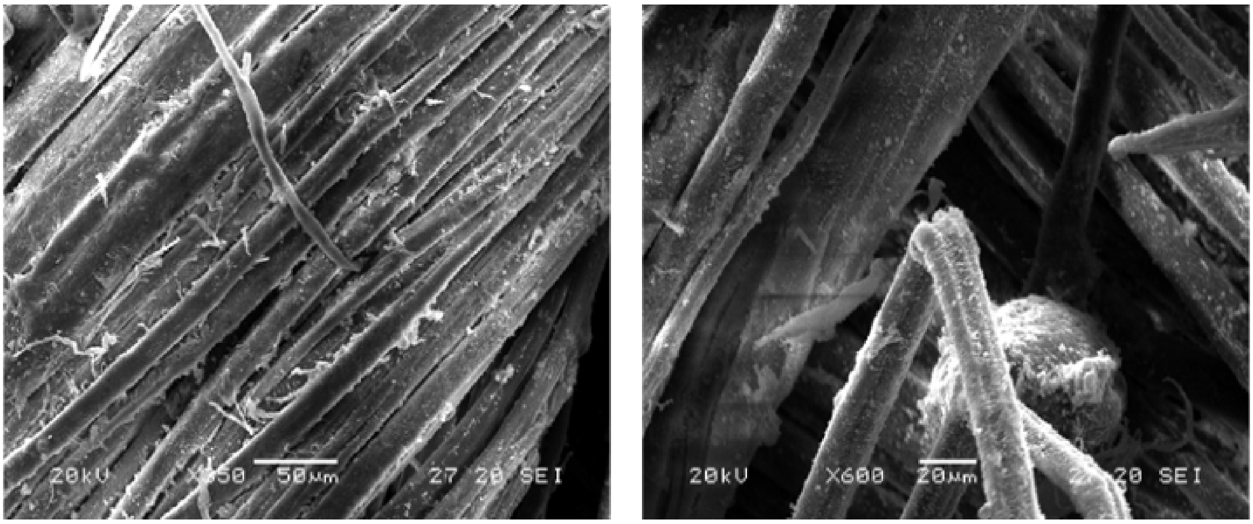


Fig.28.7. *SEM microphotographs of dyed linen sample with saffron dye after TA.*

6.3. X-ray diffraction

Figs.29.1, 29.2, 29.3, 29.4, 29.5, 29.6 and 29.7 depict the diffractograms of dyed linen samples after TA. The peak at 2θ= 29.9° evident in all dyed samples, is attributed to ($KAl_3(SO_4)_2(OH)_6$) which is probably a by-product formed during the mordanting procedure.

The sample dyed with all natural dyes have the same diffraction pattern, with decreased cellulose peaks intensity, with standard linen due to the amorphous nature of natural dyes and the absence of their peaks in the selected 2θ region. The intensity of the cellulose peak of standard linen samples was higher than dyed and undyed ones after thermal ageing. The diffraction patterns of aged and normal linen have been discussed in detail previously in chapter 5.

From the diffraction patterns of dyed samples it is concluded that natural dyestuffs interact with cellulose without affecting its crystal structure. All CI values are slightly lower than the CI values of the standard linen sample, indicating an increase in the amorphous areas upon dyeing. The CI values were as follows: cochineal, henna, indigo and turmeric (91%). The highest CI values were observed for saffron, safflower and madder (93%). The breadth of the (002) reflection which is marker of the crystallite size of cellulose is calculated to approximately 4.8±0.2 nm in accordance with previous results[2].

Studies have shown that dyes are usually absorbed into the non-crystalline regions without affecting the crystallinity of the samples[19]. The minor decrease in the CI of the dyed samples can be attributed to the possible formation of *van der Walls* bonds at the areas with high crystallinity on the surfaces of the fibers dyes while interacting with the mordant which presence is evident in the x-ray diffractograms. Also, this may be due to the damage of hydrogen-bond system in the network structure of linen fiber during dyeing process. This leads to the increase of the amorphous or disordered region in the linen fiber.

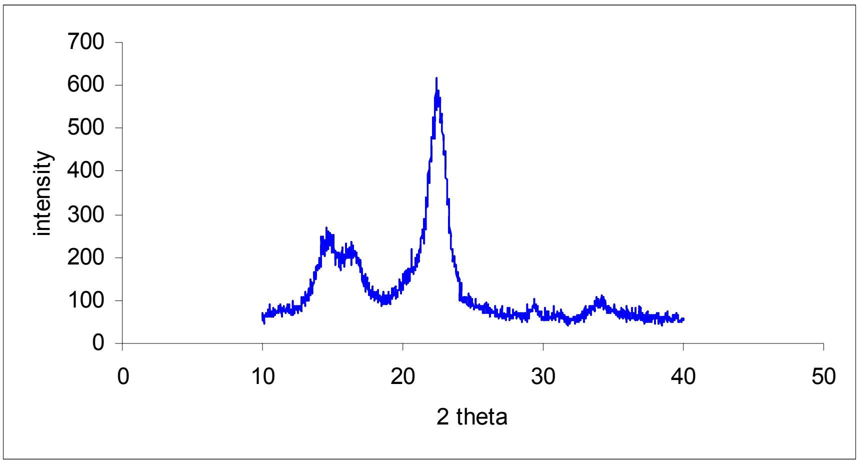


Fig.29.1. *X-ray diffractograms of dyed linen with indigo after thermal ageing.*

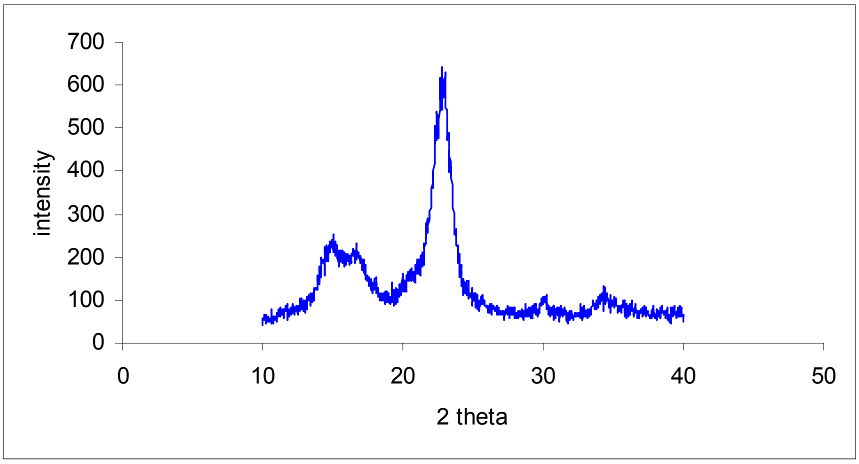


Fig.29.2. *X-ray diffractograms of dyed linen with madder after thermal ageing.*

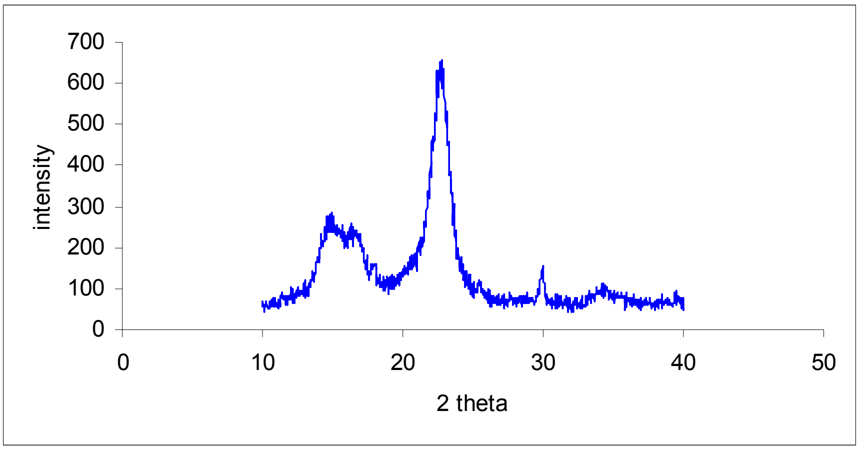


Fig.29.3. *X-ray diffractograms of dyed linen with turmeric after thermal ageing.*

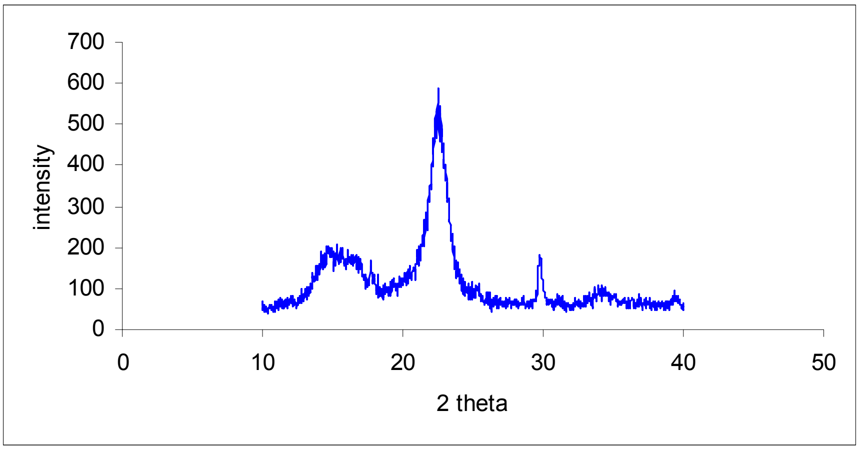


Fig.29.4. *X-ray diffractograms of dyed linen with henna after thermal ageing.*

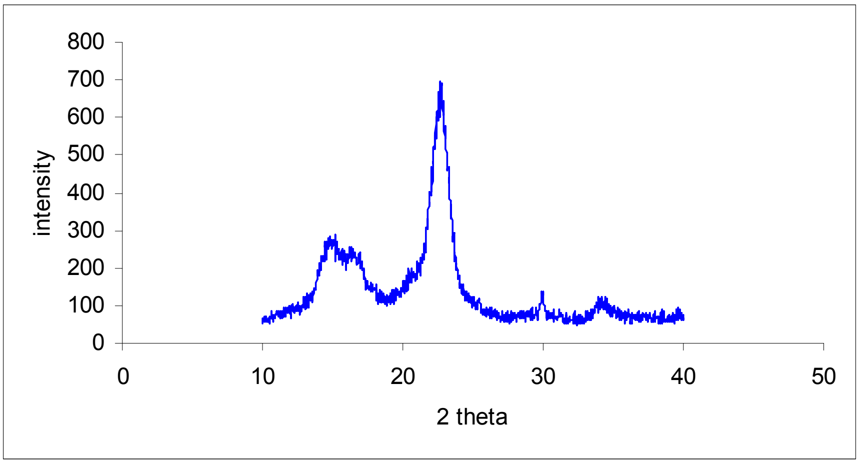


Fig.29.5. *X-ray diffractograms of dyed linen with cochineal after thermal ageing.*

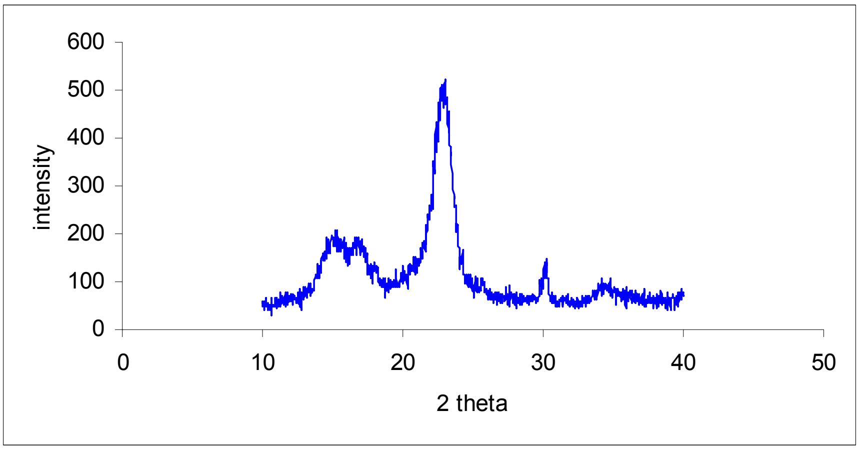


Fig.29.6. *X-ray diffractograms of dyed linen with safflower after thermal ageing.*

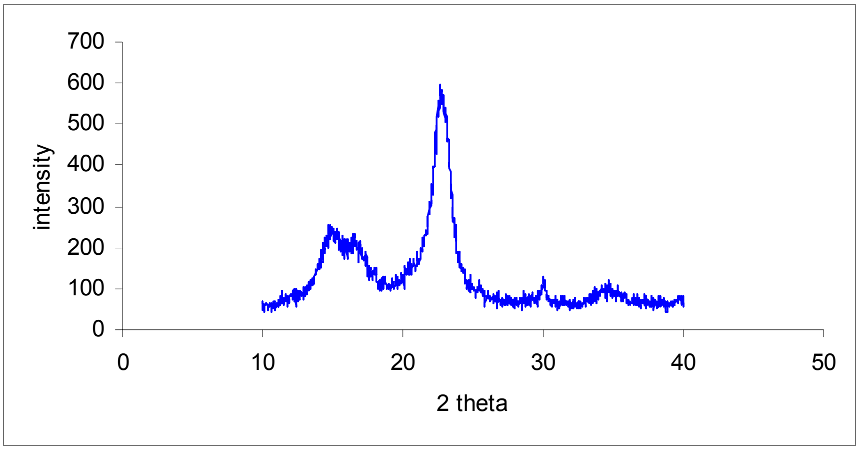


Fig.29.7. *X-ray diffractograms of dyed linen with saffron after thermal ageing.*

6.4. Tensile strength and elongation measurements

The results from the tables1.7, 1.8 and the figs.30.1, 30.2, show that a minor degradation of the physical properties of the linen textiles is evident after thermal ageing at 140°C for 72 h, In accordance with SEM results. Thermal ageing causes limited chain scission of the cellulose polymer, thereby changing its mechanical properties. In general, this thermal degradation increases with increasing temperature and the duration of ageing.

The results illustrate slightly reduction in tensile strength and elongation properties of all dyed linen samples after TA, comparing with the standard undyed and unaged linen sample. The different percentage of decreasing in tensile strength and elongation depends specifically on the type of the dye used. The conditions used during the dyeing process may also have a differential effect on the physical properties of the linen fibres.

On the other hand by comparing all dyed linen samples after TA, with undyed and aged one, it is clear that all natural dyes enhanced tensile strength properties. The results confirmed that the dyed linen fiber with cochineal exhibited the greatest percentage increase in tensile strength and in elongation properties compared with the standard undyed linen after thermal ageing (-2.96, -5.00%) respectively. The same trend regarding tensile strength is followed by dyed linen fiber with turmeric (-7.46), henna (-9.92), Madder (-17.43), Indigo (-23.26), Saffron (-25.88) and Safflower (-27.66) respectively. Linen dyed with henna however exhibits a loss in its elongation ability by 13 % compared with the standard undyed linen after thermal ageing. This result can be possibly attributed to the increased amount of henna compared to the other dyes used in the dyeing process. Furthermore, it seems that the weak inter-molecular forces between the dye and the fiber are dependent on the molecular dye size[20] and lawsone is rather small compared to the other dye molecules used in this study

It becomes clear that the dyes enhanced tensile strength properties and therefore the fibers durability throughout time. Dyes probably act as a protective agents reducing heat degradation. This may be due to the bonds formed between the fibers and the dyes and also to the formation of complex compounds with mordant metal ions[18,21]

Table.1.7. *Results of tensile strength measurements of dyed and standard undyed linen.*

Samples	Tensile strength (MPa)	%loss in tensile strength
standard undyed, unaged linen	26.39	---------
Standard undyed linen after thermal ageing	18.60	-29.52
linen dyed with Indigo after thermal ageing	20.25	-23.26
linen dyed with Madder after thermal ageing	21.79	-17.43
linen dyed with Turmeric after thermal ageing	24.42	-7.46
linen dyed with Henna after thermal ageing	23.77	-9.92
linen dyed with Cochineal after thermal ageing	25.61	-2.96
linen dyed with Safflower after thermal ageing	19.09	-27.66
linen dyed with Saffron after thermal ageing	19.56	-25.88

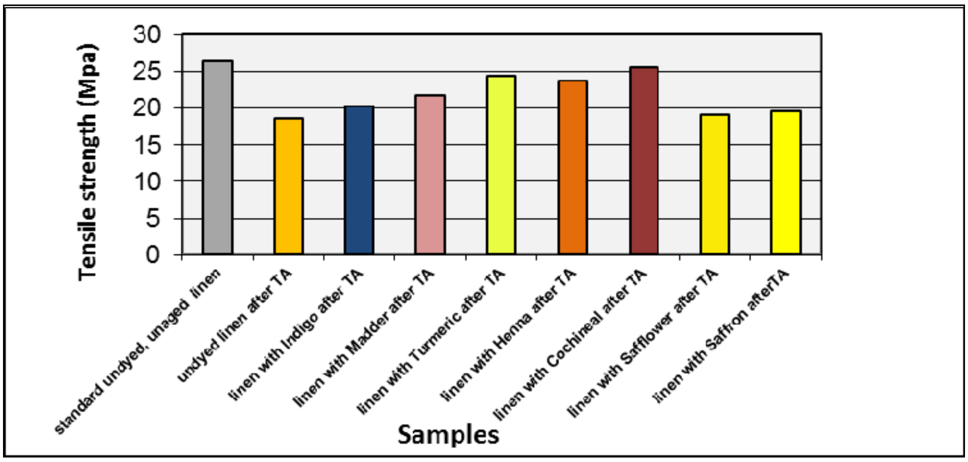


Fig.30.1. *Results of tensile strength measurement of all dyed linen with natural dyes and the standard one.*

Table.1.8. *Results of elongation measurements of dyed and standard undyed linen samples*

Samples	Elongation%	%loss in Elongation
standard undyed, unaged linen	49.17	----------
Standard undyed linen after thermal ageing	40.59	-8.58
linen dyed with Indigo after thermal ageing	38.64	-10.53
linen dyed with Madder after thermal ageing	39.77	-9.39
linen dyed with Turmeric after thermal ageing	43.58	-5.59
linen dyed with Henna after thermal ageing	35.44	-13.73
linen dyed with Cochineal after thermal ageing	44.17	-5.0
linen dyed with Safflower after thermal ageing	36.96	-12.22
linen dyed with Saffron after thermal ageing	37.97	-11.19

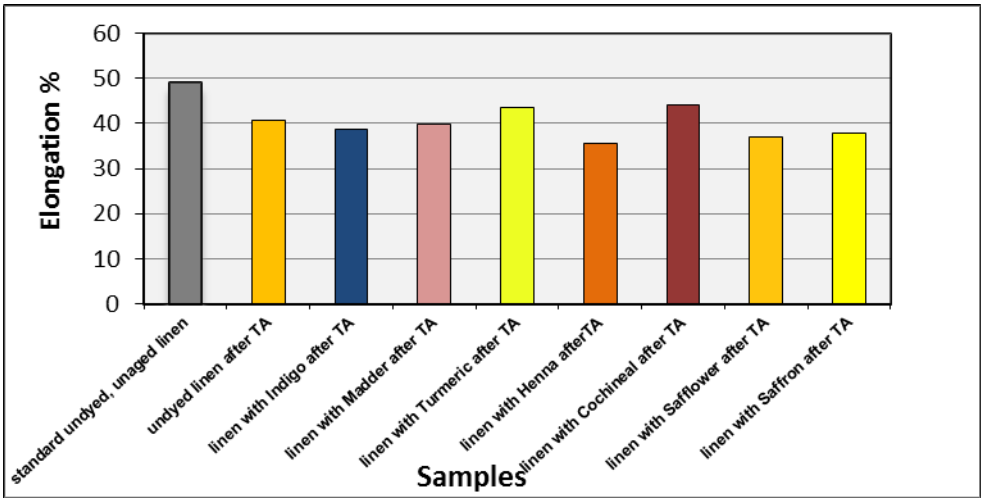


Fig.30.2. *Results of elongation measurement of all dyed linen with natural dyes and the standard one.*

6.5. References

---

[1] M. Sequinfrey, "The chemistry of plant and animal dyes," J. Chem. Educ. 58(4) 301 (1981).

[2] H. El-Gaoudy, N. Kourkoumelis, E. Varella, D. Kovala-Demertzi, Appl. "The effect of thermal ageing and color pigments on the Egyptian linen properties evaluated by physicochemical methods," Phys.A, Mater.105 (2) 497 (2011).

[3] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 5thed. John Wiley & Sons, New York, 87-90 (1986).

[4] F. Ferrero, F. Testore, G. Malucelli, C. Tonin, "Thermal Degradation of Linen Textiles: The Effects of Ageing and Cleaning," J. Text. Inst. 89(1) 562-569 (1998).

[5] O.M. Abdel-Kareem,"The Long-Term Effect of Selected Conservation Materials Used in the Treatment of Museum Artifacts on Some Properties of Textiles," J. Polymer Degradation and Stability (87) 121-130 (2005).

[6] K. M. Frei, I. Vanden Berghe, R. Frei, U. Mannering and H. Lyngstrom, "Textiles and Provenance," J. Archaeol Sci. 37 (9) 2136-2145 (2010).

[7] E. Tatsch and B. Schrader, "Near-Infrared Fourier Transform Raman Spectroscopy of Indigoids," J. Raman Spectrosc 26(6) 467-473 (1995).

[8] C. Clementi, W. Nowik, A. Romani, F. Cibin and G. Favaro, "A spectrometric and Chromatographic Approach to the Study of Ageing of Madder (Rubia tinctorum L.) Dyestuff on Wool," J. Anal Chim Acta, 596 (1) 46-54 (2007).

[9] M. Koperska, T. Lojewski and J. Lojewska, "Vibrational Spectroscopy to Study Degradation of Natural Dyes. Assessment of Oxygen-Free Cassette for Safe Exposition of Artefacts," Analytical and Bioanalytical Chemistry 399(9) 3271-3283 (2011).

[10] I. Degano, E. Ribechini, F. Modugno and M. P. Colombini, "Analytical Methods for the Characterization of Organic Dyes in Artworks and in Historical Textiles," Appl Spectrosc Rev. 44(5) 363-410 (2009).

[11] L. K. Herrera, A. Justo, A. Duran, M. C. J. de Haro, M. Franquelo and J. L. P. Rodriguez," Identification of Cellulose Fibres Belonging to Spanish Cultural Heritage Using Synchrotron High Resolution X-ray Diffraction," J. Appl Phys A: Mater 99(2) 391-398 (2010).

[12] H. Chowdhury, S. Walia and V. S. Saxena, "Isolation, Characterization and Insect Growth Inhibitory Activity of Major Turmeric Constituents and Their Derivatives Against Schistocerca Gregaria (Forsk) and Dysdercus Koenigii (Walk)," Pest Manag Sci. 56(12)1086-1092 (2000).

[13] H. Rostkowska, M. J. Nowak, L. Lapinski and L. Adamowicz, "Molecular Structure and Infrared Spectra of 2-hydroxy-1,4- naphthaquinone, Experimental Matrix Isolation and Theoretical Hartree-Fock and Post Hartree-Fock Study," Spectrochim Acta A. 54(8)1091-1103 (1998).

[14] M. Hiramatsu, T. Takahashi, M. Komatsu, T. Kido and Y. Kasahara, "Antidiabetic Effect of Hydroalcoholic Extract of Carthamus *tinctorius L.* in Alloxan-Induced Diabetic Rats," Neurochem Res. 34(4) 795-805 (2009).

[15] M. D. Guillen and N. Cabo, "Some of the Most Significant Changes in the Fourier Transform Infrared Spectra of Edible Oils Under Oxidative Conditions," J. Sci Food Agr. 80 (14) 2028-2036 (2000).

---

[16] A. Yilmaz, N. T. Nyberg, P. Molgaard, J. Asili and J. W. Jaroszewski, "NMR Metabolic Fingerprinting of Saffron Extracts," Metabolomics 6 (4) 511-517 (2010).

[17] E. Anastasaki, C. Kanakis, C. Pappas, L. Maggi, C. P. del Campo, M. Carmona, G. L. Alonso and M. G. Polissiou, "Differentiation of Saffron from Four Countries by Mid-Infrared Spectroscopy and Multivariate Analysis," Eur Food Res Technol. 230 (4) 571-577 (2010).

[18] A. Timar-Balazy, D. Eastop, "Chemical Principles of Textile conservation," 1thed., Butterworth-Heinemann, London 19-55 (1998).

[19] M.K. Inglesby, S.H. Zeronian,"The Accessibility of Cellulose as Determined by Dye Adsorption," Cellulose 3: 165-181 (1996).

[20] G. Buschle-Diller, M.K. Traore, "Effect of Enzymatic Treatment on Dyeing and Finishing of Cellulosic Fibers: A Study of the Basic Mechanisms and Optimization of the Process," J. Tex. Res. 68: 185-192 (1998).

[21] M. Eric, M. Jones, "Conservation Science Heritage Materials", Royal Society of Chemistry, Cambridge, UK. 67-70 (2006).

Chapter 7

Archaeological Samples

7.1. Introduction

The main aim of this chapter is analyzing and identifying some of archaeological textile fibers and their colors from different places and periods of ancient Egypt and also three inorganic pigments of a color palette from a tomb at al-Mina, in order to disclose the nature of the dyes, pigments, mordants and binding media employed in their production. The aim of evaluating the historic textiles was to identify the fibers, to establish their state of conservation, or their degree of damage. The evaluation of archaeological textiles states should also provide information about the causes of deterioration, whether due to environmental factors or effects from other conditions.

In conservation science, the amount of material that can be investigated is usually limited because of a lack of material and the high value of the objects. Thus, sampling objects is often a highly difficult task. When analyzing historical textile objects the samples which jut out of the object are usually chosen for analysis to cause no or minimal disintegration of the object. In such circumstances, methods that use only a small amount of sample material or that are non-destructive are needed[1]. Furthermore, methods for dye detection that avoid extraction and use smaller sample sizes represent a significant step forward in any study of dyes on archaeological artifacts[2]

In the present chapter some non-destructive and destructive analytical techniques have been employed for this purpose such as scanning electron microscopy (SEM) equipped with an EDS microanalysis detector, X-ray powder diffraction (XRD), X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR).

The results, obtained using different physical–chemical and analytical methodologies and evaluating their relationship, gave useful information for the knowledge of the employed materials, coloring technique and their state of degradation as the result of natural ageing.

7.2. Experimental

7.2.1. Materials and methods

7.2.1.1. Ancient samples

The ancient samples selected for this work were collected from different Egyptian artworks and periods. Table1.9. shows the details of the ancient samples.

Table.1.9. *Description of the studied ancient samples*

Code No.	Sample type	Provenance	location	Period
T -56	uncolored linen fragment of mummy's warping		Egyptian museum	Late period (ca. 712 - 332 B.C.)
Z -57	colored linen fragment with black color of mummy's shroud		Egyptian museum	Greek -Roman period (*ca.* 332 B.C. - 395 A.D.)
S -58	dyed linen fiber with dark red dye		Coptic museum.	Coptic period (284 - 641A.D.)
R5 -59	undyed linen fragment of tunic	Italian mission's excavations	bani ebada at Al-Minya-Egypt	Greek -Roman period (*ca.* 332 B.C. - 395 A.D.)
R-60-2	dyed linen fiber with blue dye of tunic	Italian mission's excavations	bani ebada at Al- Minya -Egypt	Greek -Roman period (*ca.* 332 B.C. - 395 A.D.)
51	Red pigment of a color palette	A tomb at Al- Minya	Egyptian museum	New kingdom (1550-1070 B.C.)
52	Green pigment of a color palette	A tomb at Al- Minya	Egyptian museum	New kingdom (ca. 1550-1070 B.C.)
53	Yellow pigment of a color palette	A tomb at Al- Minya	Egyptian museum	New kingdom (ca. 1550-1070 B.C.)

7.2.1.2. New Fibres

Reference samples were prepared with unbleached, scoured plain linen yarns supplied by Egylan Co., at the Second Industrial Zone, Alexandria, Egypt. The count of warp and weft threads /1 cm are 20 and 18 respectively. Fabric was further purified in the laboratory by scouring by boiling in water for 1 hour[3] and then boiled in a solution containing 2.0 g/L of sodium carbonate at a temperature of 60°C for 1- 1½ hour in order to remove natural wax and other impurities. Samples were thoroughly washed with tap water and dried at ambient conditions[4](N. S-17).

7.2.1.3. Chemicals

1- Commercial, natural indigo and cochineal dyes, kindly provided by Department of Chemistry, Aristotle University of Thessaloniki. The details of the dyes have been discussed in chapter 2.

2- Commercial carbon black (charcoal) (C), (N.10350), from Kremer (pertinent information included in parentheses has been provided by “Kremer pigmente”

3- Arabic Gum was used as a binding media of the black pigments, supplied by Elatar shop, Egypt.

7.2.2. Preparation of references samples

1- The reference linen sample was painted directly by utilizing the brush on the linen sample without a ground layer because this technique is the most common used in painting textiles in ancient Egypt[5]. The procedure followed involved dissolving 15.0 g of Arabic gum in 300 mL of hot water, stirred it thoroughly and left overnight until it was completely dissolved. The cake of pigment was made by mixing finely 5.0 g of carbon black pigment with 10 mL of Arabic gum solution and let them to dry. It was used in the same manner as modern watercolor painting, namely, by dipping the brush in water and rubbing it on the pigment and then paints the sample[6,7]. The sample was left to dry completly in ambient temperatures (N. G-1).

2- The reference linen samples were dyed with indigo as “vat dye” (N. I-1) and cochineal dye “as a mordant dye with alum” (N .M-1). The dyeing process was performed by using recipes based on historical information and practice according to Helmut Schweppe (1986)[8].

Mordanting procedure

Alum (potassium aluminum sulphate $(KAl(SO_4)_2 12H_2O)$ was the most important mordant for dyeing with natural dyes in ancient times and was also used in this study. The linen samples were treated with the mordant solution. The alum (2.4 g) was first well dissolved in a small quantity of water and then added to 300 mL of hot soft water (40°C). 6.0 g of linen fibers were entered into the mordant solution, and then slowly heated to 90°C, turned the linen occasionally to ensure that it takes up the mordant evenly. Left the mordant solution for 1 h at this temperature, and let the linen fibers cool in this solution at room temperature (RT). The linen sample was removed, squeezed and air dried, until it was dyed.

Dye bath and dyeing process

1.8 g of cochineal was wrapped loosely in a cotton cloth and the bundle was soaked in 180 ml of deionized water for 12 hours at RT. The temperature of the dyebath was increased very slowly to 70- 80°C and the solution of the dyebath was boiled for 10-15 min. After cooling, the bundle with the dyestuff was removed from the bath and pressed as much dye as possible out of the bundle. Then the dyebath was diluted with water to 180 mL. 6.0 g of alum-mordanted linen was then rinsed with water and was immersed in a dyebath at 40°C, heated slowly to boiling point for 1 h. After cooling the dyebath, the linen was rinsed with deionised water and dried in the dark.

For the indigo a different process was followed. 3.0 g of indigo powder was stirred with 15 mL of warm deionized water in a glass beaker until a paste is formed. 6.0 g of sodium carbonate (Na_2CO_3) in 24 mL of distilled water was added to the indigo paste and the mixture was stirred. 6.0 g of sodium dithionite ($Na_2S_2O_4$) was added to the mixture and 200 mL of deionized water was added. The mixture was heated to 55°C resulted in a yellowish solution. After 20 min the color turned to yellow-green. 6.0 g of the scoured, unmordanted linen was wetted in warm water and then was immersed in the dye bath of indigo at 55°C for some minutes, so that no oxygen can enter into the vat "dyebath". Then the linen fibre was taken out of the vat and squeezed the liquor out thoroughly. When the linen fibers came out of the vat, they had a green-yellow colour, which turned to blue in 20 min, when the material was exposed to the air. Finally, it was dried completely and rinsed thoroughly with deionised water[8].

7.3. Analytical Technique

All studied ancient samples were taken from damaged areas of archaeological textiles. Some non-destructive and destructive analytical techniques have been employed for analyzing and identifying the ancient samples such as Scanning Electron Microscopy (SEM) equipped with an EDS microanalysis detector, X-Ray Powder Diffraction (XRD), X-Ray Fluorescence (XRF) and Fourier Transform Infrared Spectroscopy (FTIR).The operating systems have been discussed in details in chapter 4.

 uncolored linen fragment of mummy's warping (T-56)	 colored linen fragment with black color of mummy's shroud (Z-57)	 dyed linen fiber with dark red dye- Coptic period (S-58)
 undyed linen fragment of tunic- Greek -Roman period (R5-59)	 dyed linen fiber with blue dye of tunic- Greek -Roman period (R-60-2)	

Fig.31.1. *Studied ancient textile samples.*

7.4. Results and disscussion

7.4.1.1. FTIR spectroscopy of Ancient textile samples

Characteristic infrared bands of all ancient samples and the standard linen fabric are shown in Table1.10 and Figs.32.1, 32.2, 32.3 ,32.4, 32.5, 32.6, 32.7, 32.8 and 32.9.

1- Fig.32.1. Shows the IR spectra obtained from the standard uncolored new linen fiber (S-17) Fig.32.2. Show the IR spectra obtained from unknown, uncolored fiber of mummy's warping, late period (T-56) And Fig.32.3. Show the IR spectra obtained from unknown, uncolored fiber of a tunic from The Italian mission's excavations of bani ebada at Al-Minya (R5-59).

The bands at 3370 cm^{-1}of (S-17), 3350 cm^{-1} of (T-56) and at 3416 cm^{-1} of (R5-59) indicate the presence of hydroxyl groups and are assigned to the stretching *v*(OH) vibrations. These bands are indicative of inter and intramolecular hydrogen bonds. Flax cellulose exhibits strong inter and intramolecular bonding interactions between adjacent cellulose chains, involving the hydroxyl groups. The bands at 2900 cm^{-1}of (S-17), at 2901 cm^{-1} of (T-56) and at 2899 cm^{-1} of (R5-59) are assigned to stretching vibrations of methyl and ethyl groups *v*(CH3*)* and *v*(CH2*)* (cellulose compounds). The bands at 1639 cm^{-1}of (S-17), 1640 cm^{-1} of (T-56) and at 1644 cm^{-1} of (R5 -59) are assigned to vibrations of *v*(C=C) (lignin compounds), *δ*(OH), and *v*(CO) bonds (derived from carbonyl, or aldehyde, or carboxyl groups). The bands at 1431, 1373 cm^{-1}of (S-17), 1432, 1373 cm^{-1} of (T-56) and at 1430, 1372 cm^{-1} of (R5-59) are assigned to bending vibrations of methyl and ethyl groups *v*(CH3*)* and *v*(CH2*)* (cellulose compounds). The bands at 1112, 1062 cm^{-1}of (S-17), 1113, 1058 cm^{-1} of (T-56) and at 1114, 1058 cm^{-1} of (R5-59) are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (*β*-glycoside linkages, cellulose compounds[9,10]. The bands at 668, 615 cm^{-1}of (S-17), 668, 614 cm^{-1} of (T-56) and at 667, 613 cm^{-1} of (R5-59) are attributed to Aromatic CH bending[11]. So the results illustrate that the fibers of a mummy's warping, (T-56) and of a tunic from The Italian mission's excavations(R5-59) are linen fibers.

2- Fig.32.4. Shows the IR spectra obtained from the standard colored linen fiber with carbon black"charcoal" (G-1) by using Arabic gum as a binder. And Fig.32.5. shows the IR spectra obtained from unknown fiber of a mummy's shroud colored with black pigment , Greek -Roman period (Z -57).

The bands at 3424 cm^{-1} of(G-1) and at 3346 cm^{-1} of (Z-57) respectively, indicate the presence of hydroxyl groups and are assigned to the stretching ν(OH) vibrations. The bands at 2901 cm^{-1} of (G-1) and at 2900 cm^{-1}of (Z-57) are assigned to stretching vibrations of methyl and ethyl groups $\nu(CH_3)$ and $\nu(CH_2)$ (cellulose compounds), also assigned to stretching ν(CH) of gum arabic. The bands at 1638 cm^{-1} of (G-1) and at 1646 cm^{-1} of (Z-57) are assigned to vibrations of ν(C=C) (lignin compounds), δ(OH), and ν(CO) bonds (derived from carbonyl, or aldehyde, or carboxyl groups)[1,2]. The bands at 1432 cm^{-1} of (G-1) and at 1430 cm^{-1} of (Z-57) are attributed to bending ν(CH) ,assigned to Arabic gum. The bands at 1372 cm^{-1} of (G-1) and at 1373 cm^{-1} of (Z-57) are assigned to bending vibrations of methyl and ethyl groups $\nu(CH_3)$ and $\nu(CH_2)$ (cellulose compounds), also attributed to(C-H bending) which assigned to Arabic gum[12]. The bands at 1283, 1230 cm^{-1} of (G-1) and at 1282, 1235 cm^{-1} of (Z-57) are assigned to carbon[13]. The bands at 1115, 1059 cm^{-1} of (G -1) and at 1113, 1059 cm^{-1} are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (β-glycoside linkages, cellulose compounds, also assigned to (C-O stretching) Arabic gum. The bands at 667, 611, 668, 611cm-^{1} respectively are attributed to Aromatic CH bending[14]. So the results illustrate that the unknown fiber of a mummy's shroud colored with black pigment (Z-57) is linen fiber colored with carbon black "charcoal" and its binding media is Arabic gum.

3- Fig.32.6. Shows the IR spectra obtained from the standard dyed linen fiber with cochineal dye (M-1) and Fig.32.7. shows the IR spectra obtained from unknown dyed fiber with dark red dye of tunic, Coptic period (S -58).

The bands at 3353 cm^{-1} of (M-1) and at 3410 cm^{-1} of (S-58) indicate the presence of hydroxyl groups and are assigned to the stretching ν(OH) vibrations. The bands at 2920 cm^{-1} of (M-1) and at 2917cm^{-1} of (S-58) are assigned to stretching vibrations of methyl and ethyl groups $\nu(CH_3)$ and $\nu(CH_2)$ (cellulose compounds). The bands at 1654 cm^{-1} of (M-1) and at 1650, 1709 cm^{-1} of (S-58) are assigned to vibrations of ν(C=C) (lignin compounds), δ(OH), and ν(CO) bonds (derived from carbonyl, or aldehyde, or carboxyl groups) [1,2], also assigned to carminic acid "the main commponent of cochineal dye". The bands at 1562 cm^{-1} of (M-1) and at 1543 cm^{-1} of (S-58) are assigned to carminic acid[15]. The bands at 1436, 1373 cm^{-1}of (M-1) and at 1432, 1370 cm^{-1} of (S-58) are attributed to C-O-H bending, also assigned to bending vibrations of methyl and ethyl groups $\nu(CH_3)$ and $\nu(CH_2)$ (cellulose compounds). The bands at 1112, 1113 cm^{-1} respectively are attributed to C-O-C symmetric stretching. The bands at 1057, 1058 cm^{-1} respectively are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (*β*-glycoside linkages, cellulose compounds). and the bands at 669, 602, 667, 614 cm^{-1} are attributed to Aromatic CH bending out of plane, also the bands at 602, and 614 cm^{-1} respectively are assigned to sulphate ion of alum mordant[16]. So the results illustrate that the unknown dyed fiber with dark red dye of tunic, Coptic period (S -58) is dyed linen fiber with cochineal dye.

4- Fig.32.8. Shows the IR spectra obtained from the standard dyed linen fiber with indigo (I-1) and Fig.32.9. shows the IR spectra obtained from unknown dyed fiber with blue dye of a tunic from The Italian mission's excavations of bani ebada at AL- Minya (R60-2). The bands at 3275, 3421 cm^{-1} respectively, indicate the presence of hydroxyl groups and are assigned to the stretching *v*(OH) vibrations, also assigned to stretching (N-H) of indigo compound [16] . The bands at 2901, 2932 cm^{-1} are assigned to stretching vibrations of methyl and ethyl groups *v*(CH3*)* and *v*(CH2*)* (cellulose compounds) . The bands at 1628, 1653cm^{-1} are assigned to vibrations of *v*(C=C) (lignin compounds), *δ*(OH), and *v*(CO) bonds (derived from carbonyl, or aldehyde, or carboxyl groups) [1-2]. The bands at 1483, 1461, 1429, 1395, 1448, 1386 cm^{-1} are attributed to bending (N-H) of indigo compound. The bands at 1318, 1317 cm^{-1} are attributed to stretching (C-N) aromatic amine (indigo compound). The bands at 1172, 1126, 1169, 1125 cm^{-1} are attributed to out of plane (C-H) bending of alkene[17], also assigned to (*β*-glycoside linkages, cellulose compounds). the bands at 1074,1033, 1073, 1042 cm^{-1} are assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration (*β*-glycoside linkages, cellulose compounds). the bands at 699, 562, 698, 699, 614, 600 cm^{-1} are attributed to Aromatic (CH) bending out of plane. So the results illustrate that the unknown dyed fiber with blue dye of a tunic from The Italian mission's excavations of bani ebada at AL- Minya may be dyed linen fiber with indigo dye.

Also the results indicate shifting to higher or lower frequneces and increasing of the intensity absorption bands of carbonyl function group of all ancient fibers comparing with the standard new linen fiber. the highest increasing of the intensity absorption band of carbonyl function group in the dyed linen fibers with blue dye of tunic from The Italian mission's excavations of bani ebada at Al- Minya (R60-2) Followed by the linen fiber of a mummy's shroud colored with carbon black, Greek -Roman period (Z-57), the fiber dyed with dark red dye of tunic, Coptic period (S-58), uncolored fiber of a tunic from The Italian mission's excavations of bani ebada at Al- Minya (R5-59) and finally uncolored fiber of a mummy's warpping, late period (T-56) respectively. This carbonyl functional group could be derived from either aldehyde group at 1600 cm^{-1} or carboxyl group at 1720 cm^{-1} resulting of the oxidation of the hydroxyl group, reflecting the degradation of glycosidic linkages in the cellulose fibers[18,19,20]. Moreover, the high degree of degradation reduced the intensity of IR absorption bands which present in the spectrums of the ancient fibres due to natural ageing.

Table.1.10. *Characteristic infrared band of the standard and ancient textile samples in cm^{-1}*

Sample	Wave numbers (cm^{-1})
standard uncolored new linen	3370, 2900, 1639, 1431, 1373, 1112, 1062, 668, 615, 560
uncolored linen fragment of mummy's wrapping	3350, 2899, 1640, 1432, 1373, 1162,1113, 1058, 668, 615, 560
undyed linen fragment of tunic from The Italian mission's excavations	3416, 2901,1644, 1430, 1372, 1162, 1114, 1058, 1031, 667, 613, 559
standard linen painted by black charcoal	3424, 2901, 1638, 1432, 1372, 1283, 1230, 1156, 1115, 1059, 667, 611
colored linen fragment with black color of mummy's shroud	3346, 2900, 1646, 1430, 1373,1321, 1282, 1235,1159, 1113, 1059, 668, 611, 560
standard dyed linen fiber with cochniel dye	3353, 2920, 2852, 1654, 1639, 1562, 1547, 1436, 1373, 1319, 1283, 1234, 1206, 1153, 1112, 1078, 1057, 896, 669, 602, 560, 457, 435
dyed fiber with dark red dye of a tunic, Coptic period	3410, 2917, 1709, 1650, 1543, 1432, 1370, 1163, 1113, 1058, 667, 614, 516.
standard dyed linen fiber with indigo dye	3275, 2901, 1628, 1586, 1483, 1461, 1429, 1395, 1318, 1172, 1126, 1074, 1033, 752, 699, 614, 562, 470, 434
dyed fiber with blue dye of a tunic from The Italian mission's excavations	3421, 2932, 2960, 1653, 1543, 1448, 1386, 1317, 1226, 1169, 1125, 1073, 1042, 600, 562

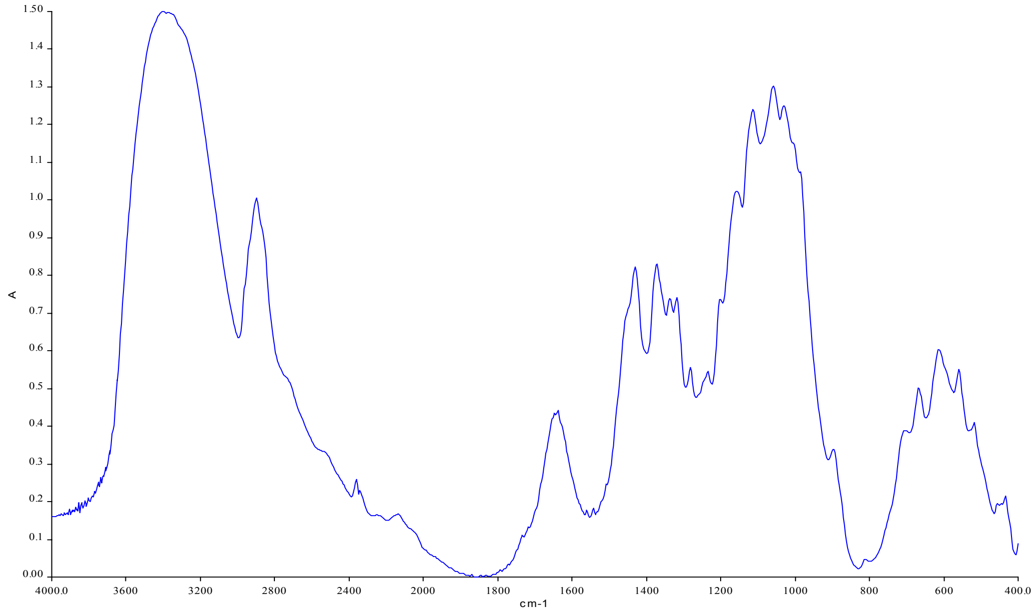


Fig.32.1. *FTIR spectra of standard uncolored new linen fiber.*

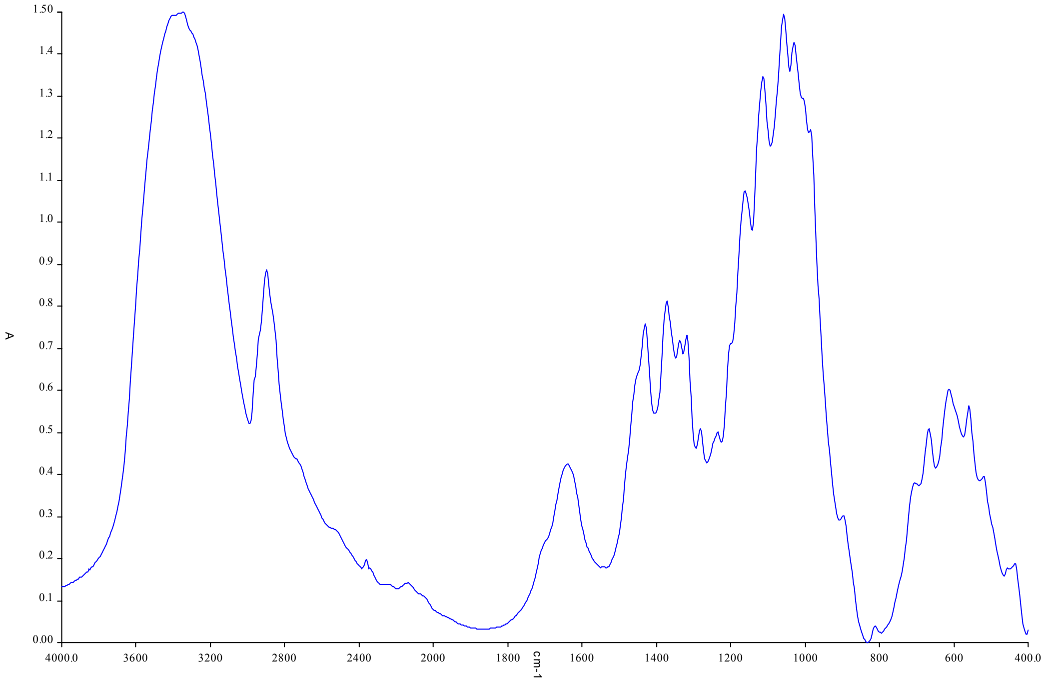


Fig.32.2. *IR spectra of uncolored fiber of mummy's warping, late period- Egyptian museum .*

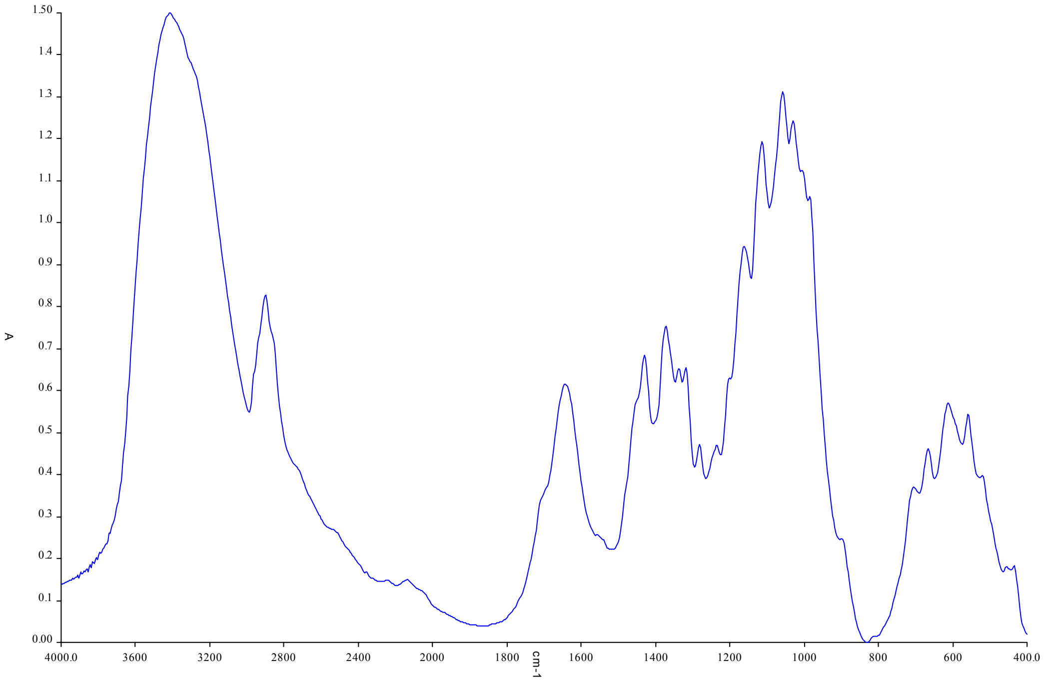


Fig.32.3. *IR spectra of uncolored fiber of a tunic from The Italian mission's excavations of bani ebada at Al- Minya.*

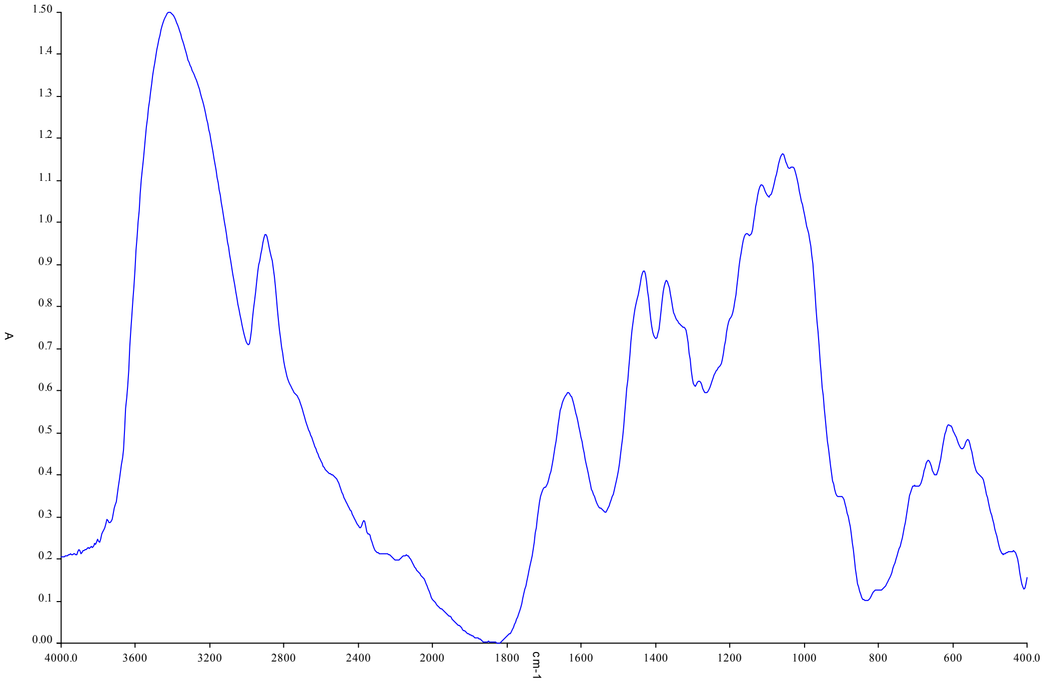


Fig.32.4. *IR spectra of standard painted linen fiber with carbon black "charcoal"*

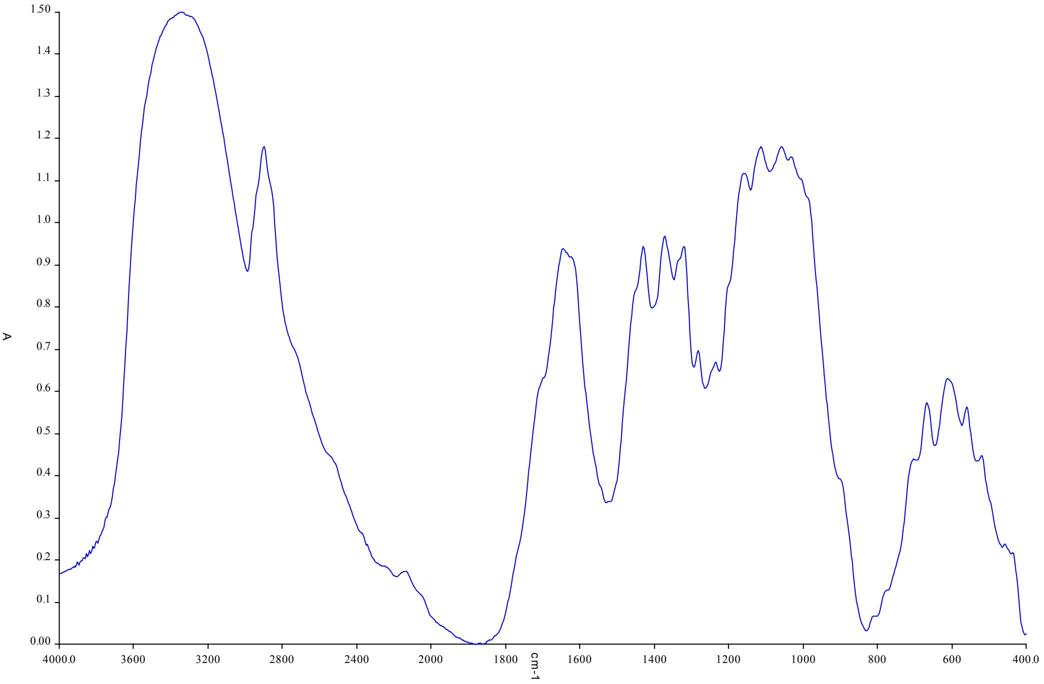


Fig.32.5. *IR spectra of ancient colored fiber with black pigment of a mummy's shroud, Greek –Roman.*

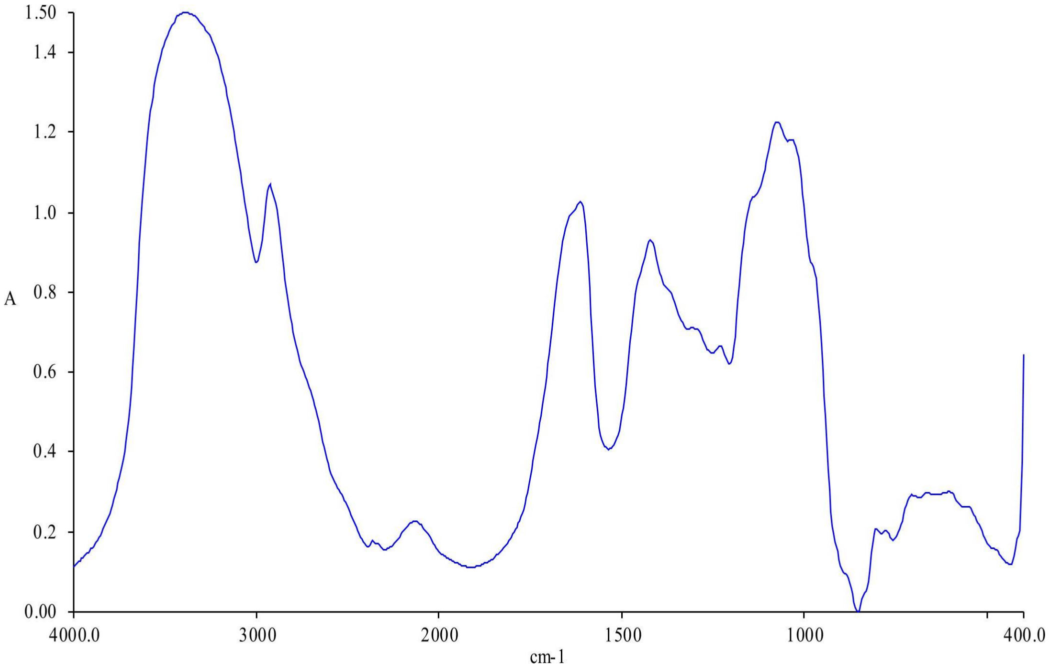


Fig.32.5.A. *IR spectra of Arabic gum.*

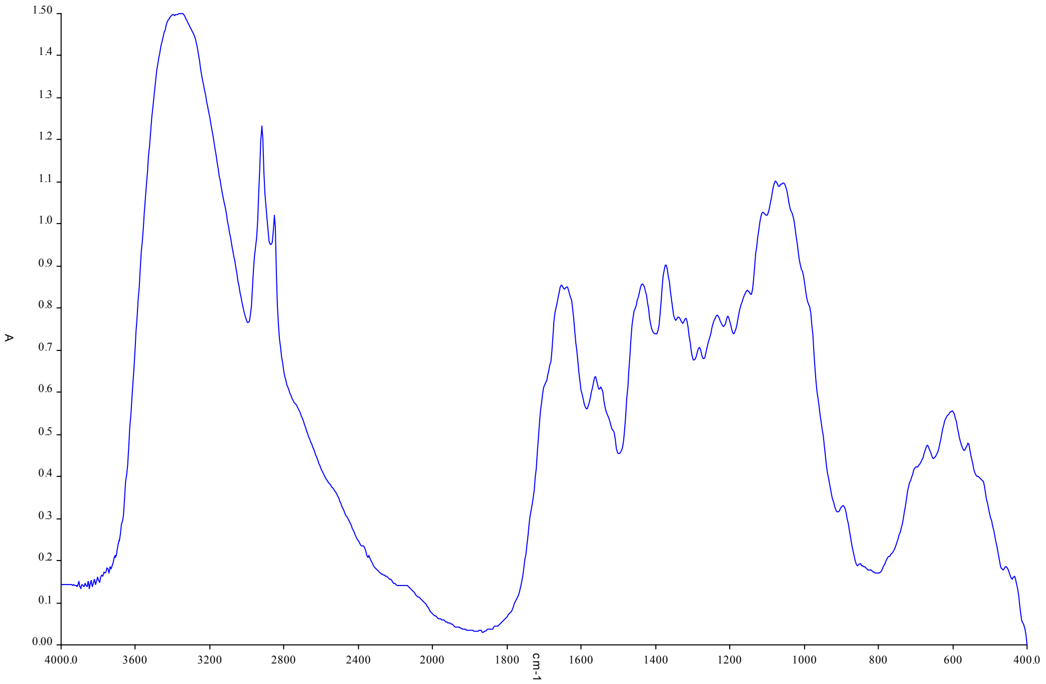


Fig.32.6. *IR spectra of standard dyed linen fiber with cochniel dye.*

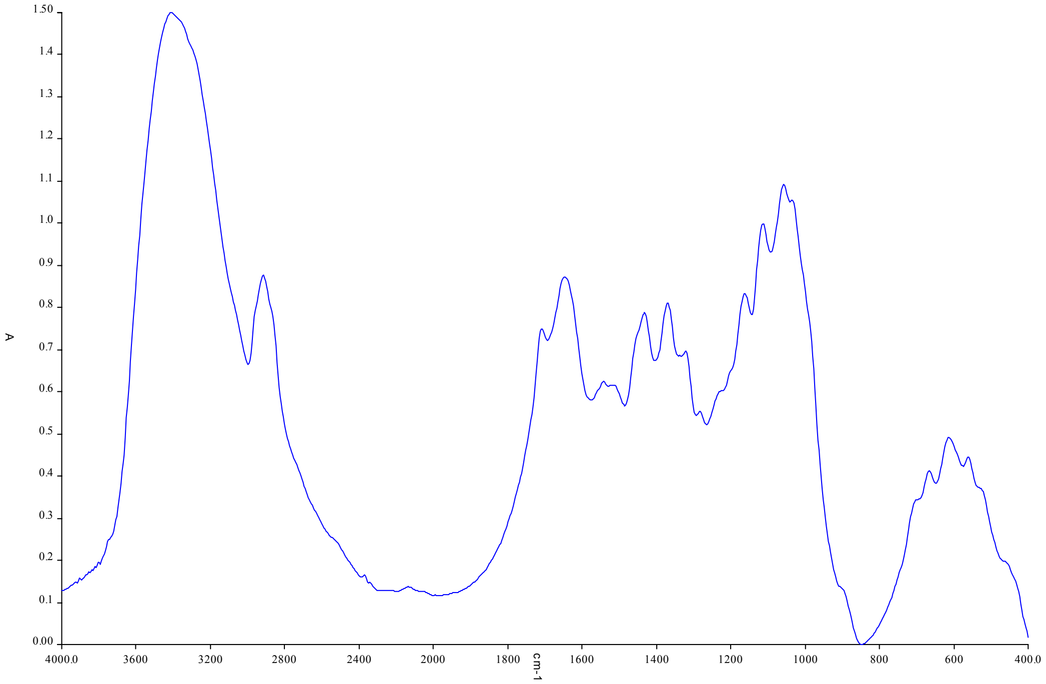


Fig.32.7. *IR spectra of ancient dyed fiber with dark red dye of a tunic-Coptic period.*

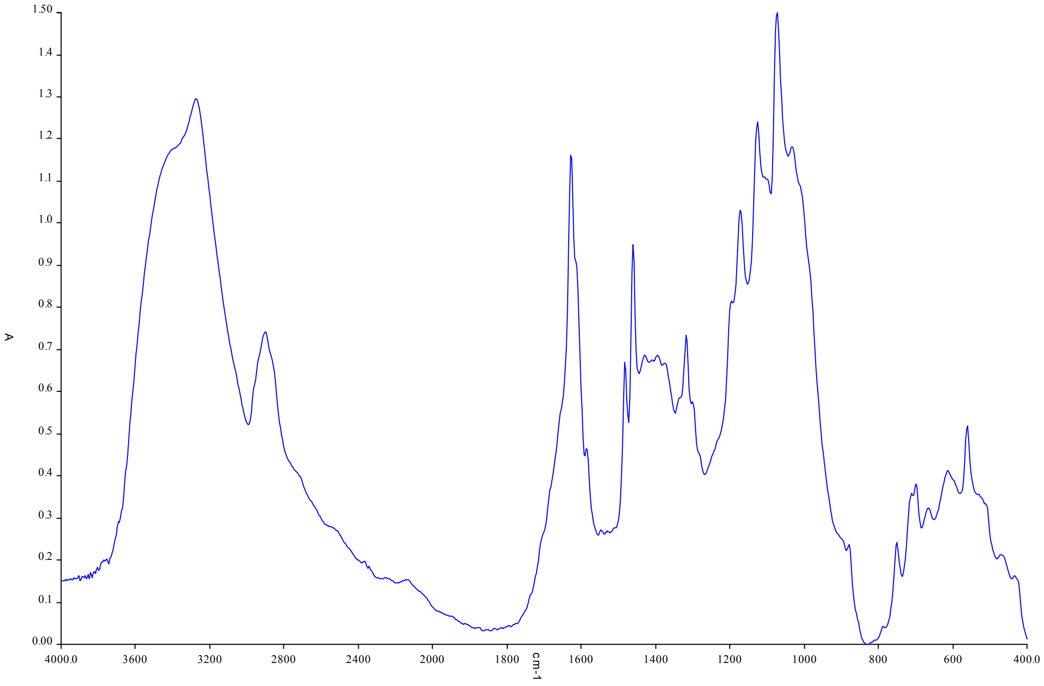


Fig.32.8. *IR spectra of the standard dyed linen fiber with indigo dye .*

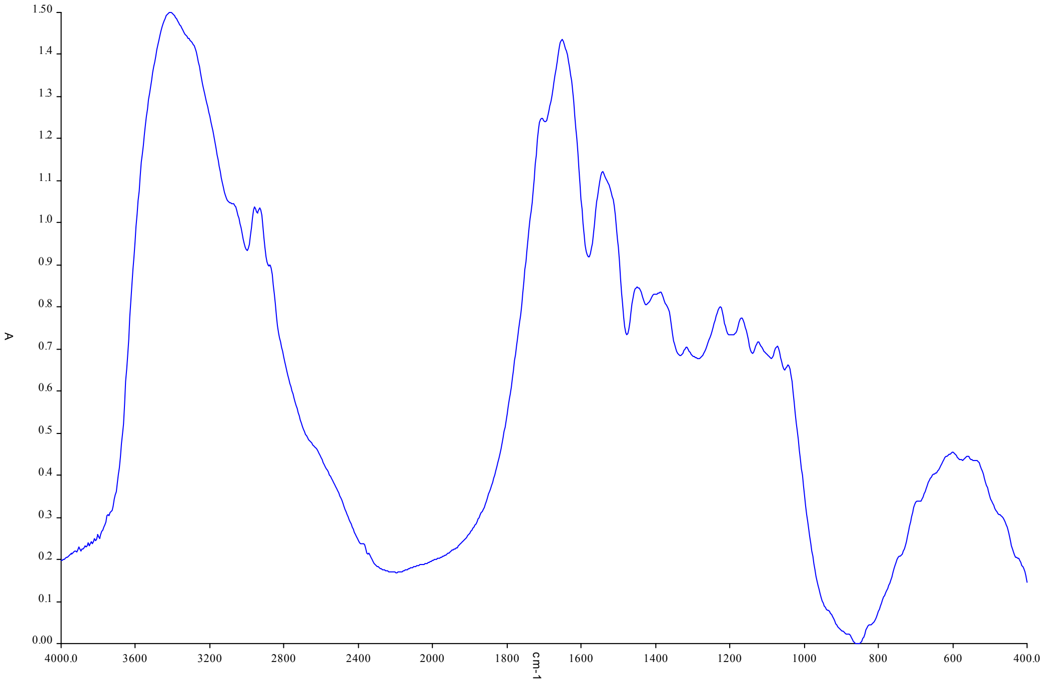


Fig.32.9. *IR spectra of ancient dyed fiber with blue dye of a tunic from The Italian mission's excavations of bani ebada at AL- Minya .*

7.4.1.2.1. FTIR spectroscopy of Ancient inorganic pigments

1- It is clear from the Fig.33.1 that the most intense band at 3398 cm^{-1} is attributed to stretching vibration of (O-H), bands at 571, 476 cm^{-1} are attributed to hematite “iron oxide” [21,22,]. The bands at 1636 cm^{-1} “bending vibration (O-H)”, 1428 cm^{-1} “bending (C-H)” and at 1384, 1090 cm^{-1} stretching (C-O)” are assigned to Arabic gum[23]. The band at 1024 cm^{-1} is assigned to Si-O-Si clay minerals “kaolinite” ($Al_2Si_2O_5(OH)_4$) as a contamination[24,25] .So the results illustrate that the red pigment from a tomb at Al- Minya, New kingdom is hematite and the binder is Arabic gum.

2- The results of Fig.33.2. Illustrate that the most intense band at 3441 cm^{-1}, stretching vibration of (O-H). The band at 1624 cm^{-1} is assigned to bending vibration (O-H) of Arabic gum[23]. The bands at 1417, 874 cm^{-1} are attributed to ($CaCO_3$). The bands at 903, 791, 620 cm^{-1} are attributed to Cu, the band at 1092 cm^{-1} is attributed to silicate ion[22,26]. The band at 475 cm^{-1} is attributed to goethite.[27,28] So the above result illustrate that the light green pigment is a mixture of Egyptian blue, goethite and calcite and the binder is Arabic gum.

3- The results of Fig.33.3. Illustrate that the most intense band at 3350 cm^{-1} is attributed to stretching vibration of (O-H). The band at 1636 cm^{-1} is assigned to bending vibration (O-H), of Arabic gum[23]. The bands at 1098, 1010, 628 cm^{-1} are attributed to sulphate ion (SO_4). The bands at 518, 428, 429 cm^{-1} are attributed to (FeO_6) [29]. Consequently, the above results illustrate that the yellow pigment may be jarosite ($KFe_3(SO_4)_2(OH)_6$) or Natrojarosite (other form of Jarosite composed of $NaFe_3(SO_4)_2 (OH)_6$).

Natrojarosite is an excellent mineral pigment in mural paintings, and ceramic products. Natrojarosite was used as yellow pigment in Dunhuang Mogao Caves of China, the nation key cultural relic which is world famous by the fine mural. Recently, it has been detected on the surface of Mars. However, natural natrojarosite is very rare. It is usually associated with Carbonaceous beds[29].

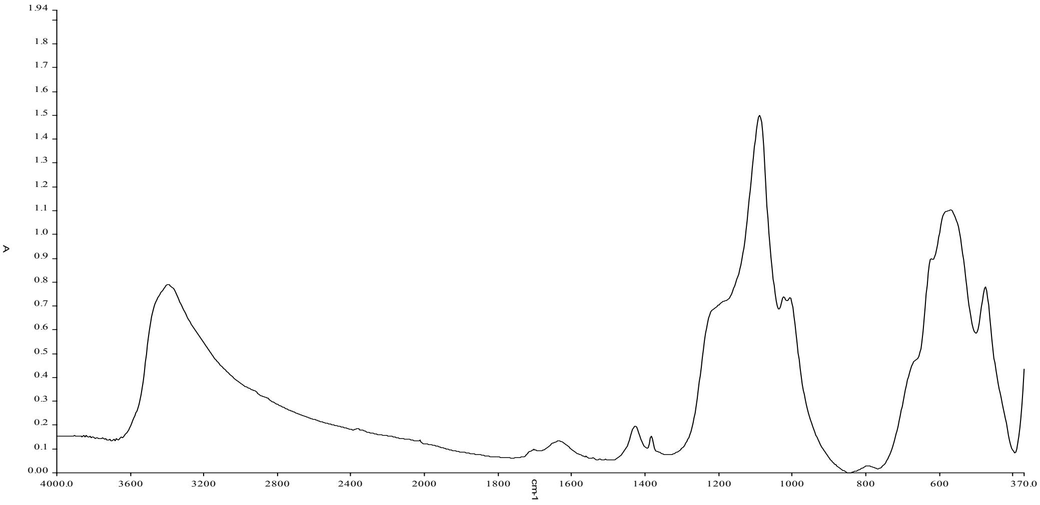


Fig.33.1. *IR spectra of red pigment of a tomb at Al- Minya, New kingdom.*

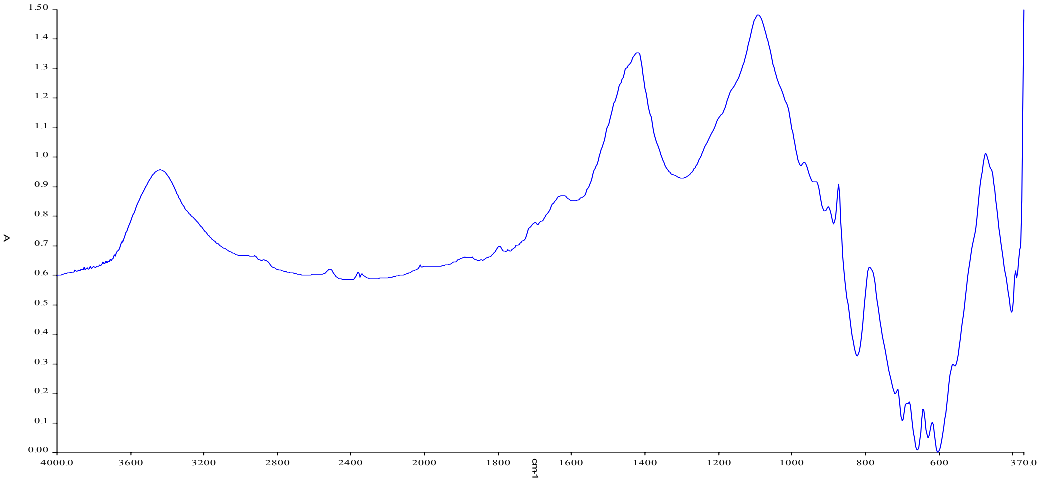


Fig.33.2. *IR spectra of green pigment from a tomb at Al-Minya, New kingdom.*

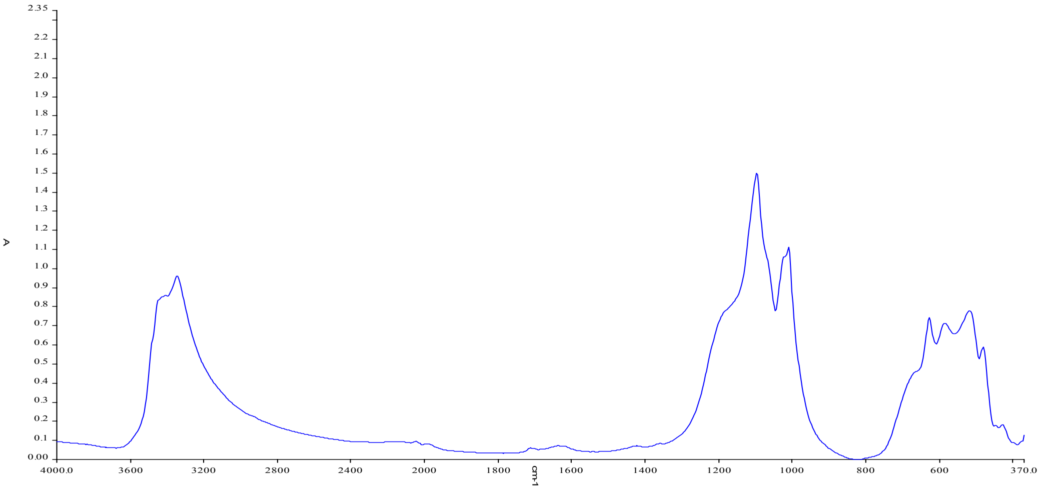


Fig.33.3. *IR spectra of yellow pigment of a tomb at Al- Minya, New kingdom.*

7.4.2.1. X- Ray Diffraction (XRD) of Ancient textiles

The data of X-ray diffraction spectra for each ancient samples and standard new linen sample are presented in Figs.34.1, 34.2, 34.3, 34.4, 34.5 and 34.6. It is clear from the results that the x-ray diffractograms of standard new linen samples and the ancient linen samples from different period of ancient Egypt" except the sample of undyed linen tunic from The Italian mission's excavations of bani ebada at Al- Minya (R5-59)" are very similar and differ only in the intensity counts but not in the shape. Also it can be shown that the x-ray diffractogram exhibits three principal planes of reflection (101), (10$\bar{1}$), (002) with peaks at 2θ= 14.9°, 16.6° and 22.8° respectively, which correspond to cellulose I of linen fibre[30], this indicate that the ancient fibres are made of linen fibres.

The characteristic (101) and (10$\bar{1}$) peaks found in linen are severely overlapped forming a broader doublet region. Reduced crystallite size as well as other impurities can contribute to this effect[1]. The lower intensity of these peaks is attributed to the relative orientation of the crystals within the fibers[31]. On the other hand, the (002) reflection is the most intense peak and corresponding to the crystallographic planes of the charged glycosidic moieties[32].

The degree of crystallinity (or the crystallinity index, CI) of standard and ancient samples was evaluated according to the Segal method by using the empirical equation[33].

The results have shown significant decreasing in the crystalline properties of all ancient linen fibre comparing with standard new linen, indicating an increase in the amorphous areas upon natural ageing. The crystallinity index was found to be approximately 94% for the standard new linen, followed by sample of the mummy's shroud colored with carbon black from Greek-Roman period 84%, sample of uncolored linen of mummy's warping, late period 83%, sample of dyed linen fiber with blue dye of tunic from The Italian mission's excavations 77% and sample of dyed linen fibre with dark red dye, Coptic period 73%.

The assessment of the crystallite size of cellulose has been done using the Scherrer equation[34] . The results illustrate greatly decreased the crystallite size of the longitudinal dimension and change the orientation of the linen microfibril crystals[35], decreasing the total crystallinity of the ancient linen fibers. The crystallite size perpendicular to (002) of sample (Z-57) 128.36A^{o} approximately followed by sample (R60-2) 125.72A^{o} sample (T-56) is 124.45A^{o}, and sample (S-58) 114.31A^{o}.

The results have indicated also that the sample of undyed linen tunic from The Italian mission's excavations of bani ebada at Al- Minya is amorphous (R5-59), where as the peak at $2\theta = 22.8°$ which assigned to the cellulose I of the linen is disappeared, this is indicate that this sample is most deteriorated, and sample of the mummy's shroud colored with carbon black from Greek -Roman period (Z-57) is more crystalline than the other ancient samples.

Generally, the reduction of crystalline properties of ancient textile samples implies the formation of amorphous material.

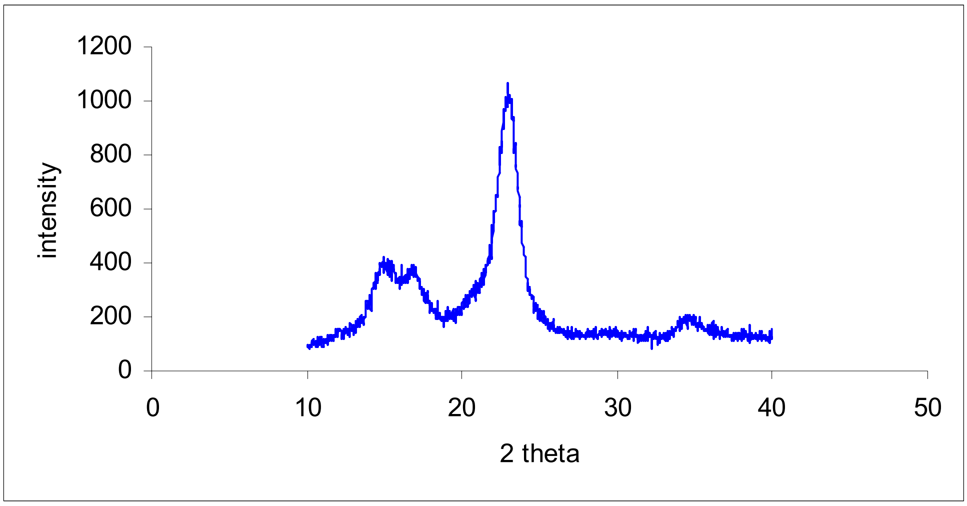


Fig.34.1. *X-ray diffractograms of standard linen sample.*

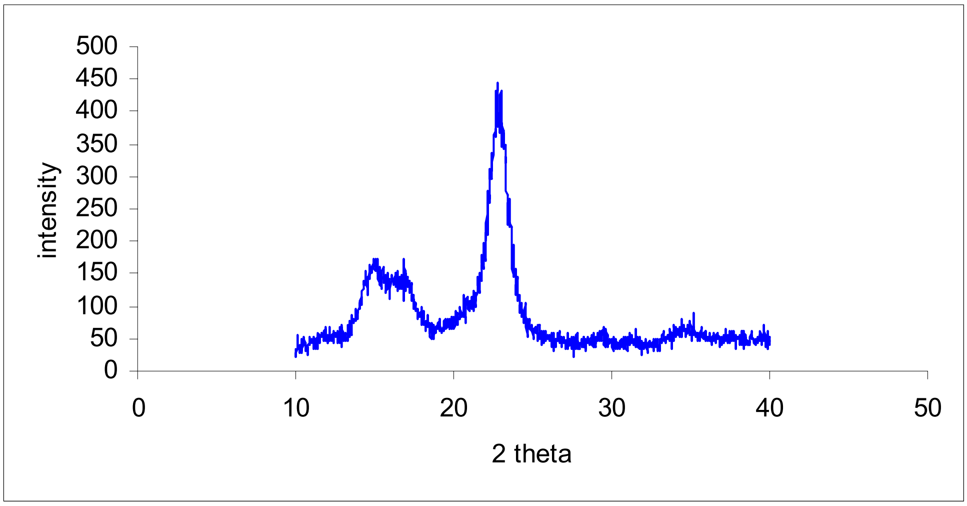


Fig.34.2. *X-ray diffractograms of uncolored linen sample of the mummy's warping, late period, Egyptian museum.*

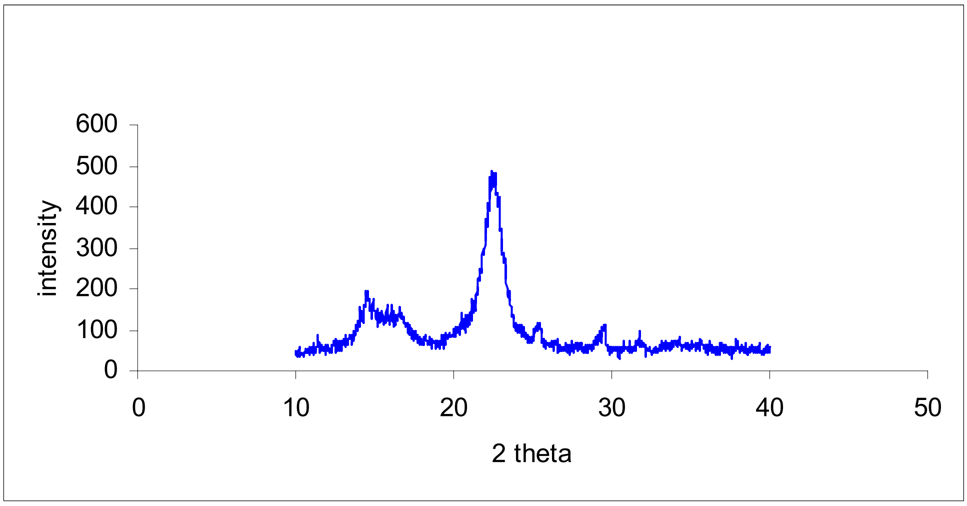


Fig.34.3. *X-ray diffractograms of colored linen sample with carbon black of the mummy's shroud, Greek-Roman period, Egyptian museum.*

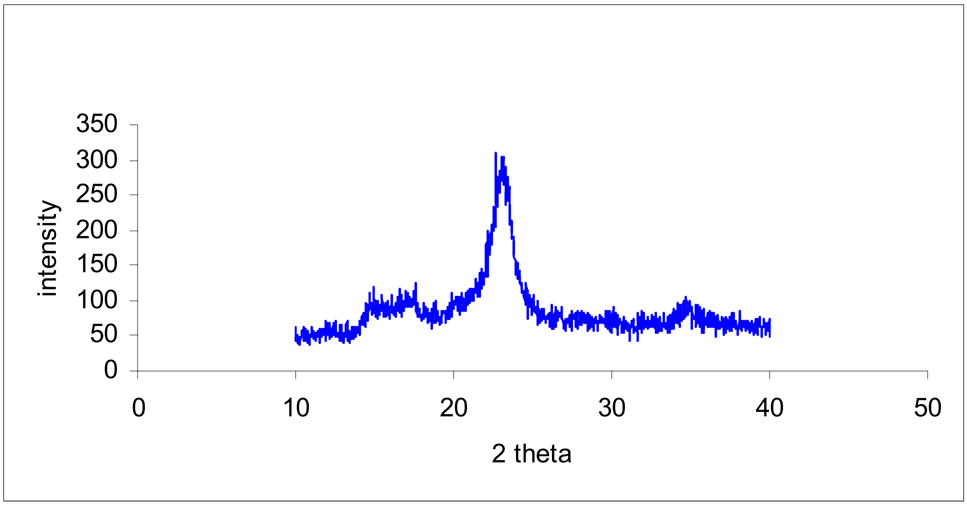


Fig.34.4. *X-ray diffractograms of dyed linen sample with dark red dye, Coptic period, Coptic museum.*

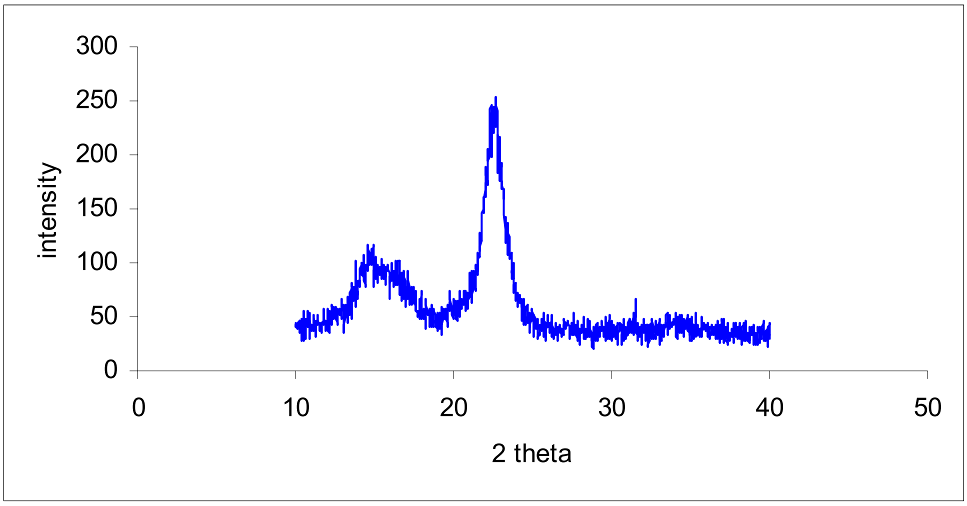


Fig.34.5. *X-ray diffractograms of dyed linen sample with blue dye of the Greek- Roman tunic from The Italian mission's excavations of bani ebada at Al- Minya.*

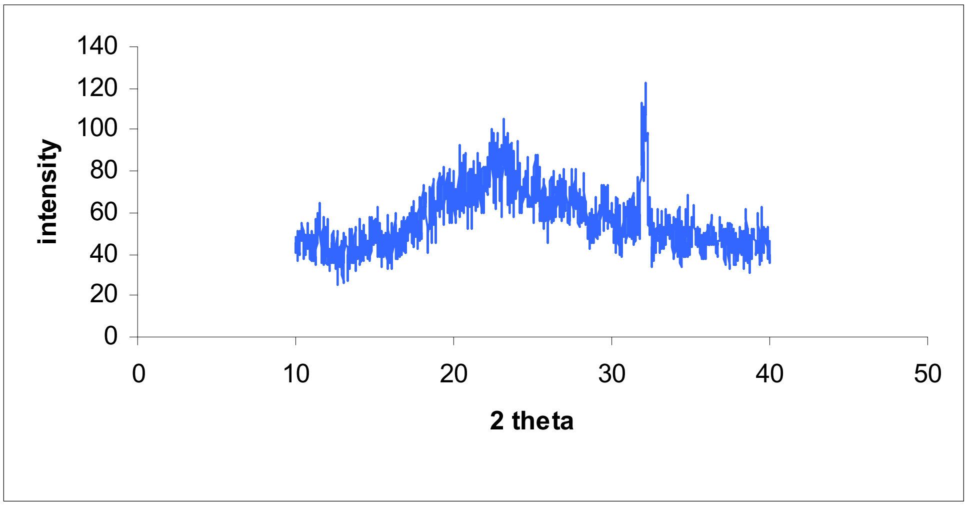


Fig.34.6. *X-ray diffractograms of undyed linen sample of the Greek-Roman tunic from The Italian mission's excavations of bani ebada at Al- Minya.*

7.4.2.2. X- Ray Diffraction (XRD) results of Ancient pigments

Powder XRD patterns were recorded of each of the pigment samples in figs.34.7, 34.8 and 34.9. On the basis of the highest intensities and color references of International Centre for Diffraction Data (PDF database)[36], the three pigments were established. The Three pigments were identified by the presence of two or more characteristic elements and the findings summarized as follows:

Sample No. 51: very intense peaks at $2\theta = 33.15^o$, 35.63^o, 54.06^o and intense peaks at 33.08^o, 49.46^o, 62.43^o, 64.005^o are assigned to hematite.

Sample No. 52: very intense peak of Egyptian blue at $2\theta = 27.10^o$, 26.53^o, 29.78^o, 23.51^o, intense peak of goethite (yellow ochre) at $2\ \theta = 21.23^o$, 34.68, 36.65, $^o39.97$ and calcite at $2\theta = 29.40^o$, 22.86^o, 39.41^o, 59.97^o.

Sample No. 53: very intense peak at $2\theta = 32.291^o$, 29.32^o, 28.79^o, 17.63^o, 40.58^o, and intense peak at $2\theta = 49.31^o$, 63.24^o are attributed to Natrojarosite ($NaFe_3\ (SO_4)_2\ (OH)_6$.

Consequently, the above results illustrate that the sample No.51 is hematite, No.53 is Natrojarosite, and the light green sample No.52 is mixture of Egyptian blue, goethite and calcite to form light green pigment. This result is in agreement with the results of FTIR and XRF.

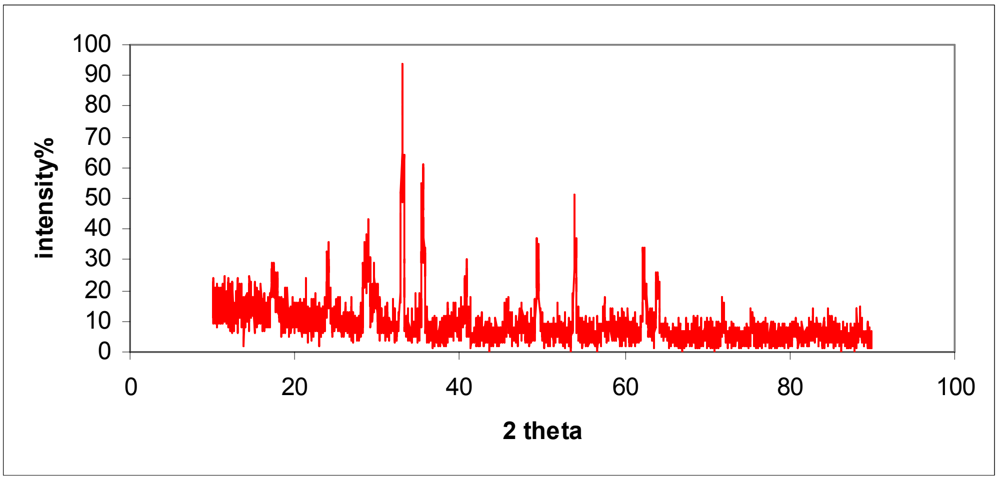


Fig.34.7. X*-ray diffraction pattern of unknown red pigment of a tomb at Al- Minya, New kingdom.*

PDF #01-087-1166, hematite					
2 theta	d (A)	I	h	K	L
33,1582	2,69953	999	1	0	4
35,6309	2,51765	712	1	1	0
54,0688	1,69469	411	1	1	6
49,4622	1,84119	341	0	2	4
24,1486	3,68238	312	0	1	2
62,4358	1,48618	264	2	1	4
64,0005	1,45357	257	3	0	0
40,8615	2,20663	192	1	1	3
71,9475	1,31131	88	1	0	10
57,5972	1,59898	86	0	1	8
84,9335	1,14088	65	1	3	4
93,6998	1,05581	61	2	1	10
88,5569	1,10332	59	2	2	6
122,443	0,878825	56	1	4	6
75,4551	1,25882	55	2	2	0

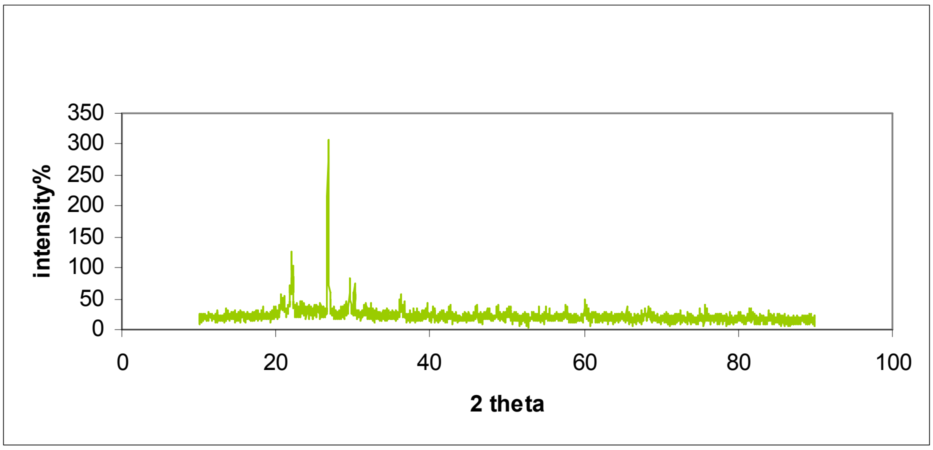


Fig.34.8. *X-ray diffraction pattern of unknown green pigment of a tomb at Al- Minya, New kingdom.*

PDF #04-007-8625 ($CaCuSi_4O_{10}$; Egyptian blue, syn)

2 Theta	d (A)	I	h	k	L
27,106	3,28695	999	2	0	2
29,7849	2,99714	961	2	1	2
26,5325	3,35669	802	1	0	4
23,515	3,78	677	0	0	4
27,9363	3,19112	445	2	1	1
29,2596	3,04973	395	1	1	4
34,729	2,58094	283	2	2	0
11,6959	7,56	267	0	0	2
39,7717	2,26455	253	1	1	6
49,9309	1,825	246	4	0	0
34,1187	2,6257	226	2	0	4
51,1367	1,78476	186	3	2	4
53,8106	1,70221	170	3	1	6
49,7947	1,82967	149	1	0	8
24,3661	3,65	134	2	0	0
38,8468	2,31631	129	3	0	2
57,7324	1,59556	120	4	2	2
56,3141	1,63233	106	4	2	0
51,9568	1,7585	100	4	1	1
66,9295	1,39689	95	2	0	10
68,0181	1,37716	91	5	1	3
57,4258	1,60335	90	4	1	4
46,0309	1,97013	85	3	1	4
17,164	5,16188	84	1	1	0
45,1443	2,00674	84	3	2	1
67,7706	1,38159	84	3	2	8
37,7333	2,38206	83	1	0	6
38,9842	2,30846	76	3	1	0
70,5208	1,3343	71	5	2	2

49,6426	1,83492	68	3	1	5
39,4545	2,28202	64	3	1	1
45,4288	1,99483	61	2	1	6
65,0055	1,43351	53	5	0	2
16,8693	5,25139	51	1	0	2

PDF #04-007-8659, calcite

2 Theta	d (A)	I	h	k	L
29,4003	3,03546	999	1	0	4
48,5056	1,87524	196	1	1	6
39,4112	2,28443	190	1	1	3
47,5034	1,91244	180	0	1	8
43,1619	2,0942	140	2	0	2
35,9728	2,4945	134	1	1	0
23,0554	3,85445	105	0	1	2
57,4035	1,60391	86	1	2	2
47,1167	1,92723	61	0	2	4
64,6663	1,4402	60	3	0	0
60,6722	1,52509	49	2	1	4

PDF #01-081-0464 (FeO(OH); goethite, syn)

2 Theta	d (A)	I	h	k	L
21,2397	4,17968	999	1	1	0
36,6574	2,44947	618	1	1	1
33,2417	2,69294	390	1	3	0
53,2418	1,71905	282	2	2	1
34,6849	2,58412	213	0	2	1
58,9957	1,56436	173	1	5	1
41,1819	2,1902	147	1	4	0
17,7968	4,97975	144	0	2	0
36,0419	2,48988	128	0	4	0
26,3392	3,38088	102	1	2	0
39,9744	2,25353	96	1	2	1

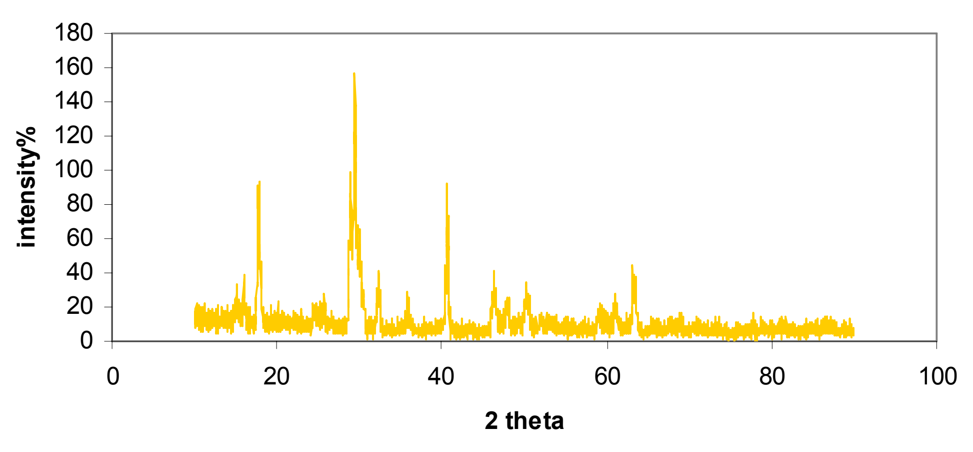


Fig.34.9. *X-ray diffraction pattern of unknown yellow pigment of a tomb at AlMinya, New kingdom.*

PDF #00-036-0425, natrojarosite ($NaFe_3(SO_4)_2(OH)_6$)

2 Theta	d (A)	I	h	k	L
14.9958	5.903000	21	1	0	1
15.9730	5.544000	73	0	0	3
17.6352	5.025000	72	0	1	2
24.4750	3.634000	11	1	1	0
25.6510	3.470000	53	1	0	4
28.7938	3.098000	79	0	2	1
29.3258	3.043000	88	1	1	3
30.2406	2.953000	42	2	0	2
30.3987	2.938000	33	0	1	5
32.2912	2.770000	100	0	0	6
35.7137	2.512000	47	0	2	4
38.1499	2.357000	9	1	2	-1
39.3293	2.289000	32m	1	2	2
39.3293	2.289000	m	2	0	5
40.5855	2.221000	91	1	0	7
46.1754	1.964300	44	3	0	3
46.8776	1.936500	13	2	1	-5
47.8739	1.898500	40	0	2	7
49.3189	1.846200	47	0	0	9
50.0951	1.819400	40	2	2	0
52.9180	1.728800	32	2	2	-3
55.7869	1.646500	29	1	1	-9
57.0890	1.612000	32	3	1	-4
58.8663	1.567500	34m	4	0	1
58.8663	1.567500	m	2	1	-8
59.6655	1.548400	31m	0	4	2
59.6655	1.548400	m	3	1	5
60.9323	1.519200	35	2	2	-6
63.2454	1.469100	54	0	2	10

7.4.3. X-ray Florescence result of ancient pigments

XRF is carried out to identify the Elemental compositions of the unknown ancient pigments. The results are given in Table1.11. The XRF spectra are shown in Fig.35.1.

Table1.11. *Elemental concentrations (in% w/w) determined through XRF analysis in ancient pigment samples.*

Code No.	Fe	Cu	Ca	Sr	Br
51	63.6 ± 5.8	-	-	-	-
52	0.25 ± 0.08	13.1± 2.9	5.4 ± 0.7	<0.05	0.21 ± 0.07
53	41.6 ± 4.2	-	-	<0.05	<0.05

1- It is clear from the XRF results shown from table1.11 and Fig.35.1, that the major compound of ancient red and yellow pigments (N.51 and 53 respectively) is Fe, this result confirms that the red pigment is hematite and the yellow one is Natrojarosite.

2- The XRF result of green pigment (N.52) show that the major compound is Cu, and the minor are Ca and Fe. This result confirms that the green pigment is mixture of Egyptian blue, yellow ochre and calcite to form light green pigment.

The XRF result is in agreement with the FTIR and XRD results.

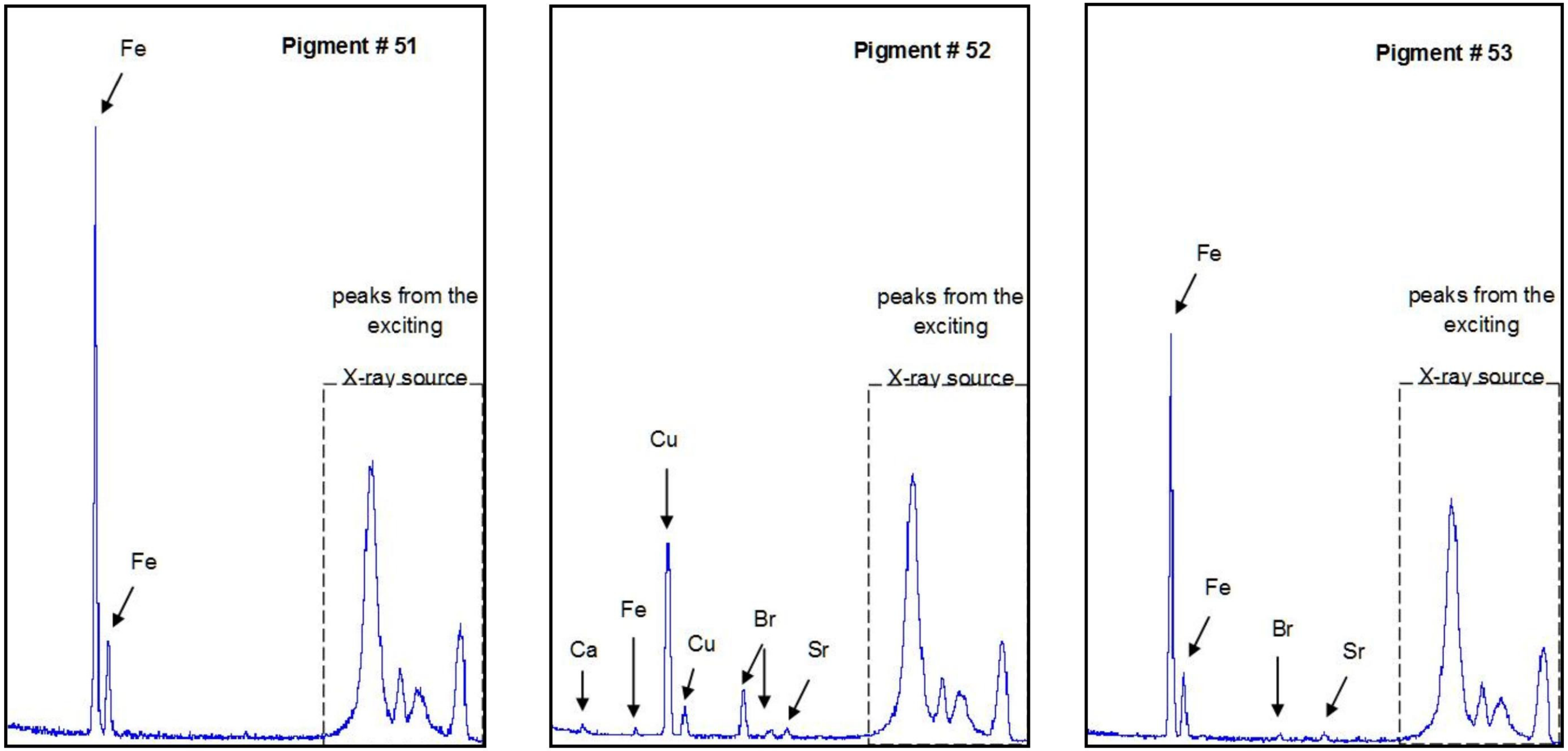


Fig.35.1. *XRF spectra of the ancient pigment samples.*

7.4.4.Results of Scanning Electron Microscope (SEM) of Ancient textile samples

S.E.M photos of examined samples are illustrated in Figs.36.1, 36.2, 36.3, 36.4 and 36.5. These photos provided clear views of the morphology of the fibres of all textile samples. SEM analysis showed that the warp and weft fibres of all textile samples have smooth surfaces, cylindrical shape, and slightly exhibit nodular thickening across their length, all of which are characteristics of cellulosic bast fibres (linen).

SEM analysis of the fibres showed that the scales of all ancient samples were degraded. The fibres break down into their structural units, macro fibrils or fibrils. This occurs after extensive flexing and is caused by heavy strain (stress) of the fibre presumably during wear or the secondary use of the textile in the ancient times, during the time they were deposited in the burial and after they were excavated. Linen fibers appear severely damaged as breaking, tearing and the other fiber with broken ends and many transverse cracks and longitudinal splits, consistent with loss of scale structure. This degradation is occurred as a result of rupture of the glycosidic bond between the units of the cellulose fibers as well as the oxidation of hydroxyl groups. This rupture cause scission on the molecular chains of the cellulose polymer[16,18]. Moreover, the results of SEM photographs exhibit that there are various contamination, where as many soil particles were often found everywhere along the fiber surfaces, this evidence indicates that the fabric appear very dirty. All these degradation views probably indicate that the fibers had deteriorated over the long period of ageing. The process of ageing due to oxidation, hydrolysis and light can lead to the formation of brittle fibres.

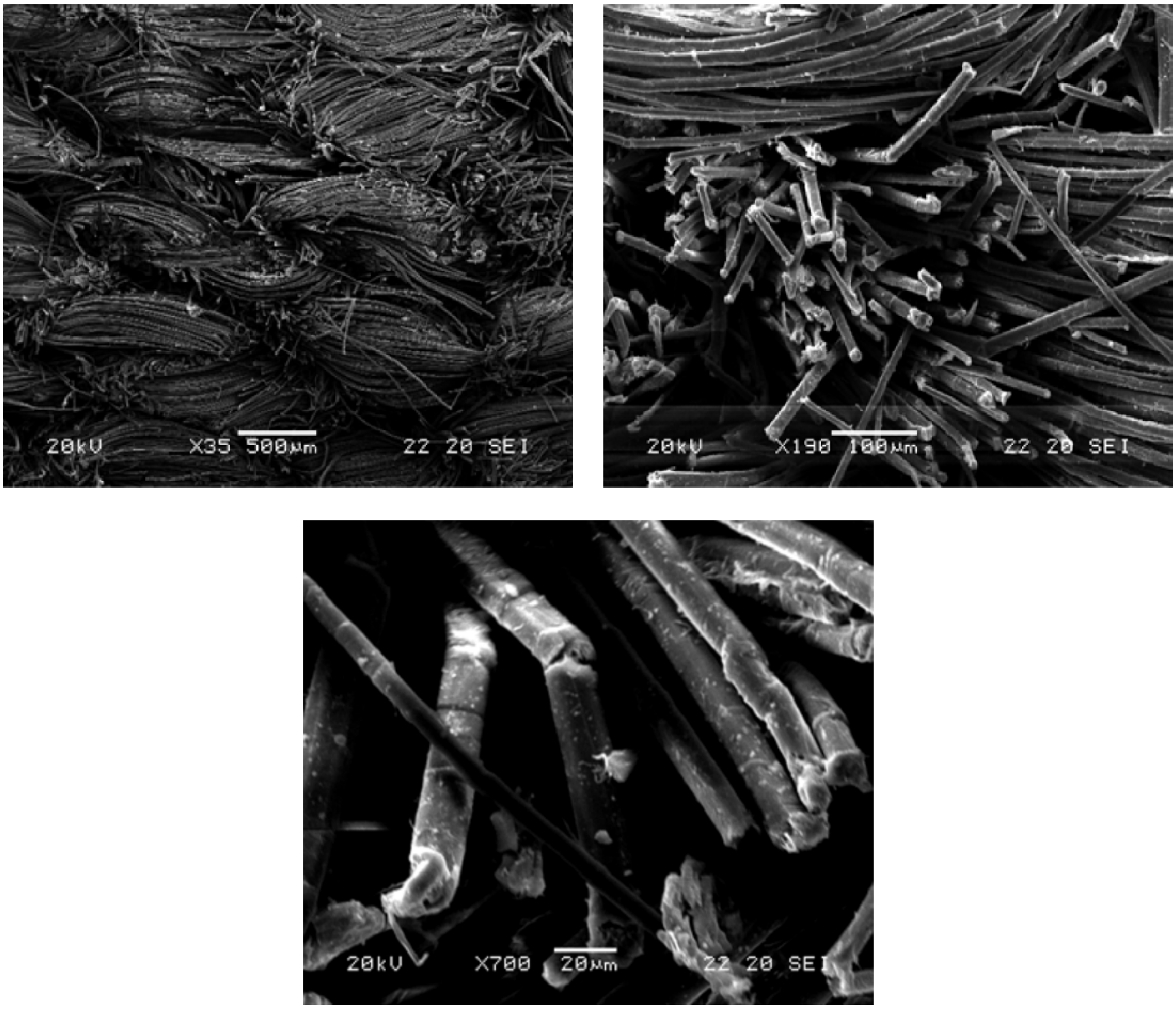


Fig.36.1. *SEM microphotographs of uncolored linen fragment of mummy's warping, Egyptian museum, late period.*

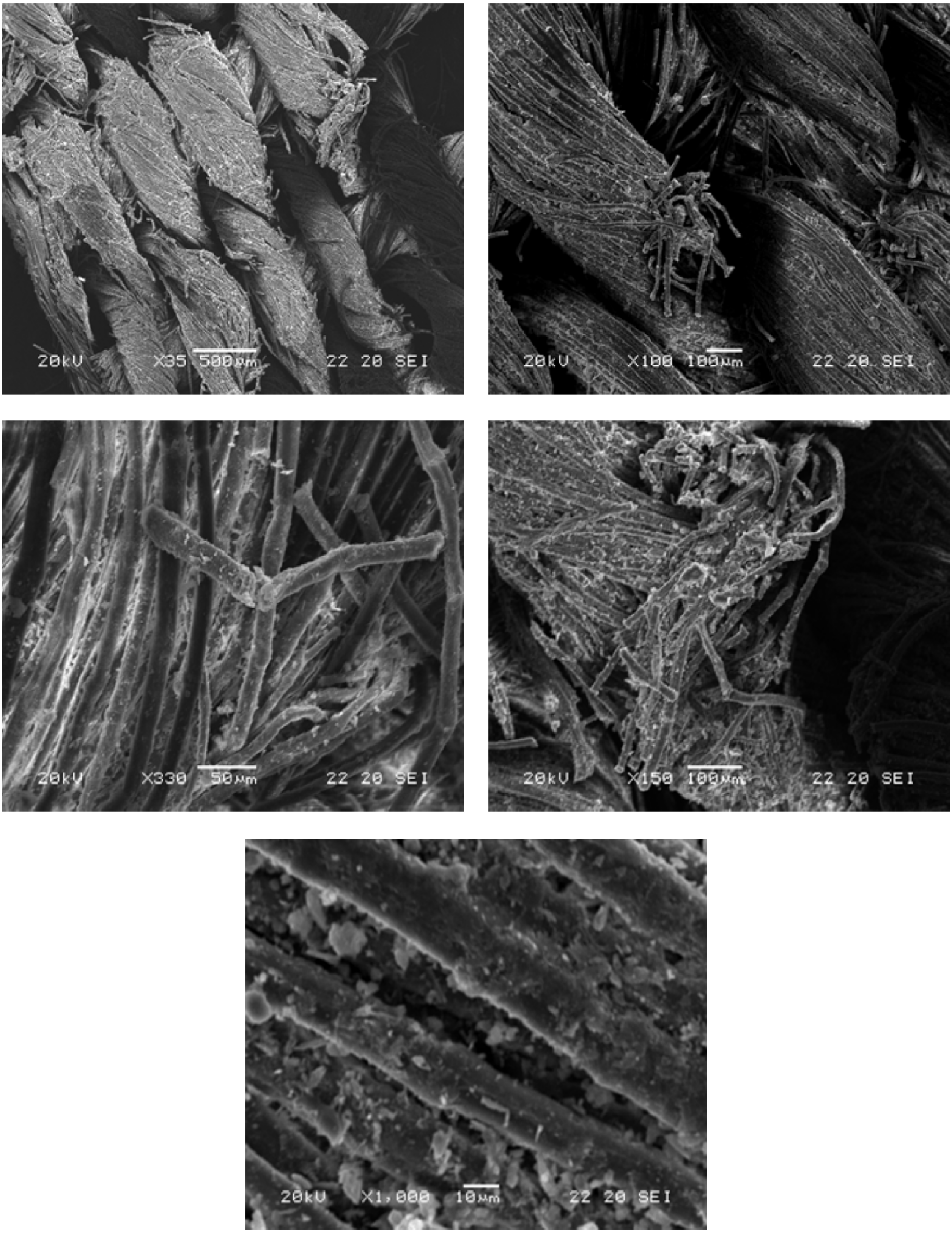


Fig.36.2. *SEM microphotographs of colored linen fragment with black color of mummy's shroud, Egyptian museum, Greek -Roman period.*

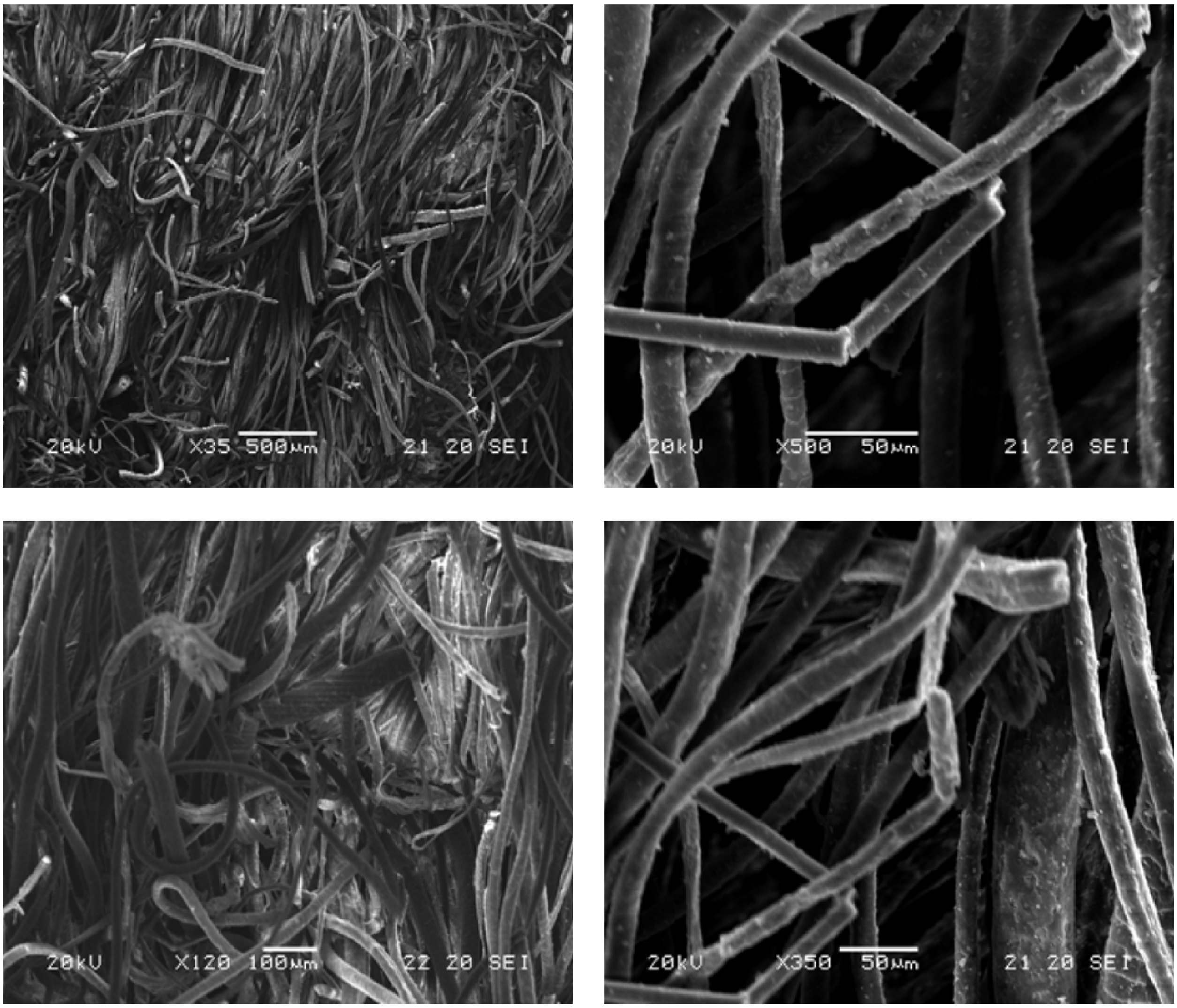


Fig.36.3. *SEM microphotographs of dyed linen fragment, Coptic museum, Coptic period.*

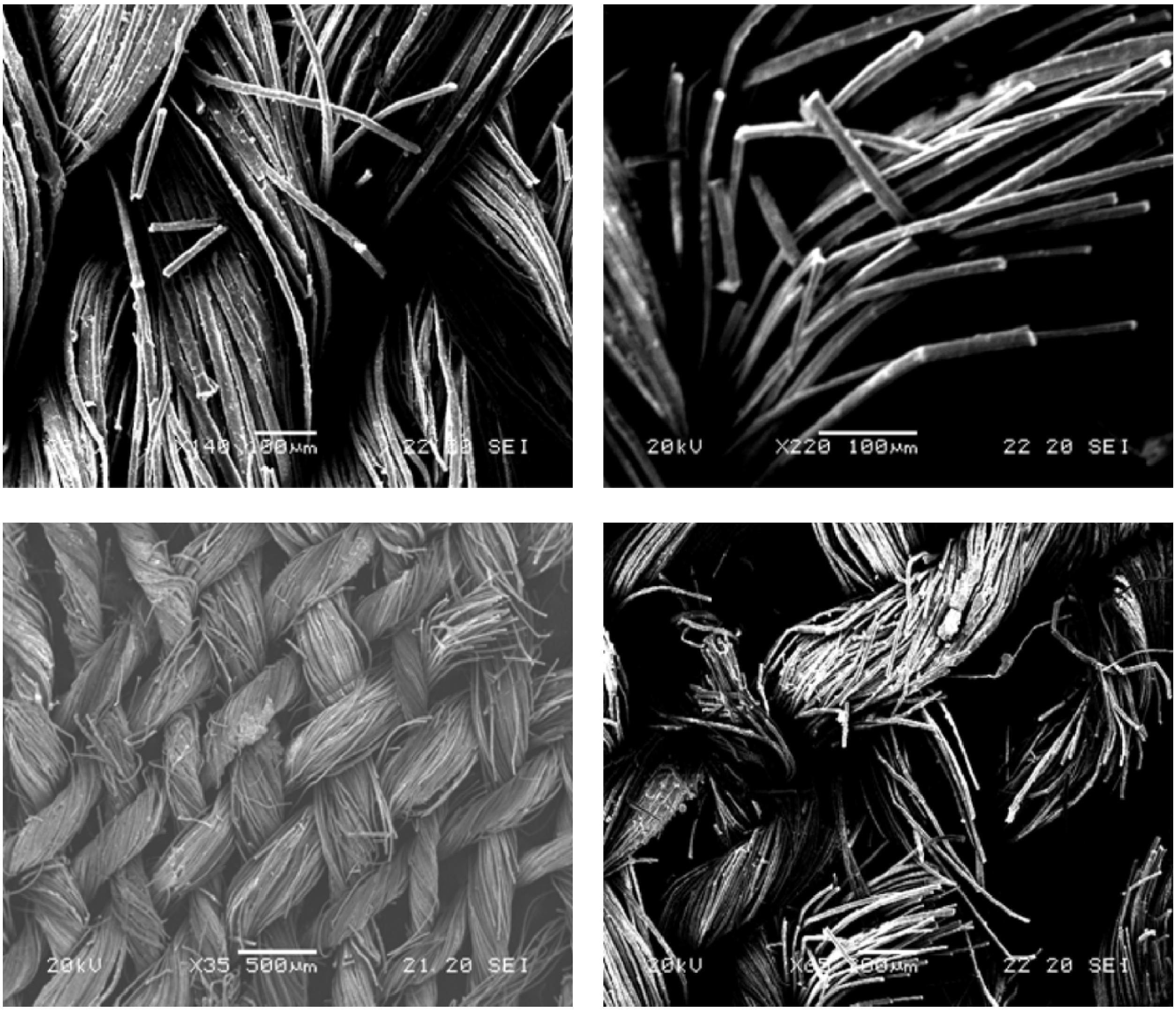


Fig.36.4. *SEM microphotographs of undyed linen fragment of tunic- Italian mission's excavations, bani ebada at Al- Minya, Greek -Roman period.*

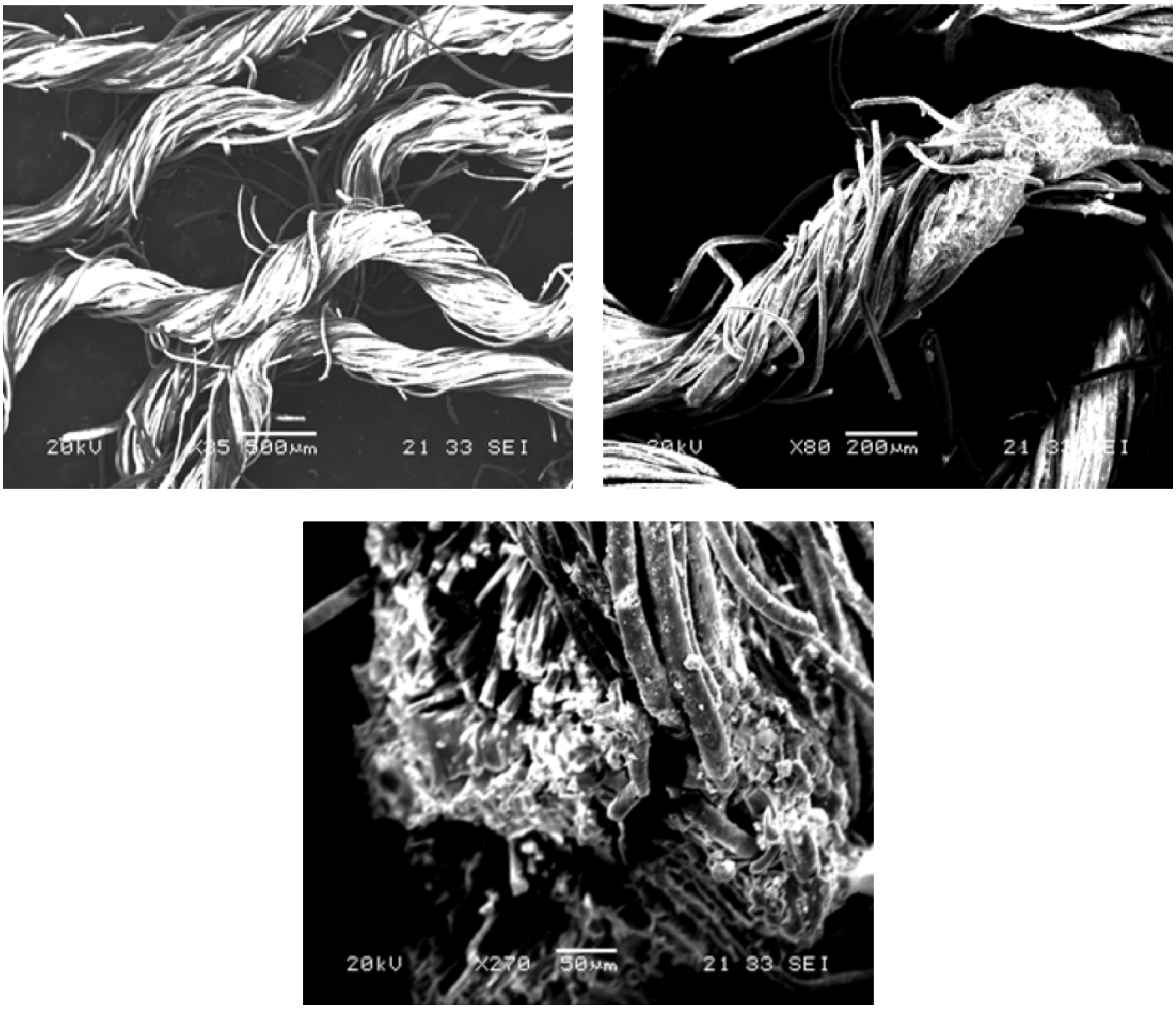


Fig. 36.5. *SEM microphotographs of dyed linen fiber with blue dye of tunic, Italian mission's excavations, bani ebada at Al- Minya, Greek, Roman period.*

7.5. References

---

[1] K. Kavkler, A. Demsar, "Examination of Cellulose Textile Fibres in Historical Objects by Micro-Raman Spectroscopy", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 96 (4) 574-582 (2011).

[2] S. Acquaviva, E.D. Anna, M.L. De Giorgi, A. Della Patria, P. Baraldi, " Physical and Chemical Investigations on Natural Dyes," Applied Physics 100: 823–828 (2010).

[3] H. Wickens, "Natural Dyes for Spinners and Weavers", 1th ed., B.T.Batsford Limited.London, 27-75(1983).

[4] M.N. Micheal, F.M.Tera and E. M.Othman, "Degradation Measurements of Linen Fabrics" J. Polymer-Plastics Technology and Engineering 43: 1377-1386 (2005).

[5] M. Taro, A. To, "Genuine of False Investigation of Metal-Prined Textiles Dated To the 11-15th Centuries", 10th Triennial Meeting Washington, D.C, ICOM Committee for Conservation, Allen Press, 325-380 (1993).

[6] A. Neuburger, "The Technical Arts and Sciences of The Ancients", 2thed., translated by Henryl Brose, Barnes & Noble Co.LTD, London, 420-433 (1969).

[7] A. Lucas, "Ancient Egyptian Materials and Industries", 4th ed., London, 57-60 (1962).

[8] H. Schweppe, "Practical Hints on Dyeing with Natural Dyes", 1th ed., Smithsonian Institution, Washington Dc. USA, 1-61(1986).

[9] L.K. Herrera, A. Justo, A. Duran, M.C. Jimenez de Haro, M.L. Franquelo, J.L. Perez Rodríguez, "Identification of Cellulose Fibres Belonging To Spanish Cultural Heritage Using Synchrotron High Resolution X-Ray Diffraction," Journal of Applied Physics, 99(2) 391-398 (2010).

[10] P. Garside, P. Wyeth, " Characterization of Silk Deterioration", in Preprints of the North American Textile Conservation Conference, NATCC, Philadelphia, 55-60 (2002).

[11] T. Espejo, A. Duran, A. Lopez-Montes, R. Blanc, " Microscopic and Spectroscopic Techniques For The Study of Paper Supports and Textile Used in The Binding of Hispano-Arabic Manuscripts from Al-Andalus: A Transition Model in the 15th century", Journal of Cultural Heritage (11) 50-58 (2010).

[12] V. Ganitis, E. Pavlidou, F. Zorba, K.M. Paraskevopoulos, D. Bikiaris, "A Post-Byzantine Icon of St Nicholas Painted on A Leather Support. Microanalysis and Characterization of Technique," Journal of Cultural Heritage (5) 349–360 (2004).

[13] L.J. Bellamy, "The Infrared Spectra of Complex Molecules", Chapman & Hall, London, 1(3) 433-440(1975).

[14] D. Ajò, U. Casellato, E. Fiorin, P.A.Vigato, C. F. Frescoes, " A Study of Painting Materials and Technique By SEM-EDS Microscopy, X-Ray Diffraction, Micro FT-IR and Photoluminescence Spectroscopy", Journal of Cultural Heritage 5(2) 333-348 (2004).

[15] P.L. Lang, C. D. Keefer, J.C. Juenemann, K.V. Tran, S.M. Peters, N. M. Huth, A. G. Joyaux , "The Infrared Microspectroscopic and Energy Dispersive X-Ray Analysis of Paints Removed From A Painted, Medieval Sculpture of Saint Wolfgang", Microchemical Journal (74) 33–46 (2003).

[16] J. Coates, "Interpretation of Infrared Spectra, A Practical Approach", in Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd, Chichester, R.A. Meyers (Ed.) 10815–10837 (2000).

---

[17] R. Silverstein, F. Webster, “Spectroscopic Identification of Organic Compounds”, 6th ed., John Wiley & Sons, New York, 73-142 (2006).

[18] A. Timar-Balazy, D. Eastop, “Chemical Principles of Textile conservation,” 1th ed., Butterworth-Heinemann, London, 19-55 (1998).

[19] O.M.. Abdel-Kareem, “The Long-Term Effect of Selected Conservation Materials Used in The Treatment of Museum Artifacts on Some Properties of Textiles,” Polymer Degradation and Stability (87) 121-130 (2005).

[20] M. Eric, M. Jones, “ Conservation Science Heritage Materials,”1th ed.,The Royal Society of Chemistry, Cambridge UK, 67-70 (2006).

[21] J.L. Mortimore , L.J.R. Marshall , M.J. Almond,, P. Hollins , W. Matthews, “Analysis of Red and Yellow Ochre Samples From Clearwell Caves And Çatalhöyük by Vibrational Spectroscopy and Other Techniques”, Spectrochimica Acta Part A (60) 1179–1188 (2004).

[22] S. Carlos Eduardo, L.P. Silva, H.G.M. Edwards, L.F.C. Oliveira, “Diffuse Reflection FTIR Spectral Database of Dyes and Pigments” Anal Bioanal Chem (386) 2183–2191(2006).

[23] M.R. Derrick, D. Stulik, J.M. Landry, “Infrared Spectroscopy in Conservation Science,” 1th ed., J. Paul Getty Trust, USA, 130-166 (1999).

[24] M.P. Colombini, A. Carmignani, F. Modugnoa, F. Frezzato, A. Olchini, H. Brecoulaki, V. Vassilopoulou, P. Karkanas, “ Integrated Analytical Techniques For The Study of Ancient Greek Polychromy,”, Talanta (63) 839–848 (2004).

[25] M.T. DomCnech Carbe, V. Perk Martinez, J.V. Gimeno Adelantado, F. Bosch Reig, M.C.M. Moreno “Fourier Transform Infrared Spectroscopy and The Analytical Study of Sculptures And Wall Decoration”, Journal of Molecular Structure (56) 559-563 (1997).

[26] H. brecoulaki, E. Fiorin, P.A. Vigato, “ The Funerary Klinai of Tomb Amphipolis and a sarcophagus from ancient Tragilos, eastern Macedonia: Aphysico-Chemical Investigation on The Painting Materials”, Journal of Cultural Heritage (7) 301-311(2006).

[27] O. Katsibiri , R.F. Howe, “Characterization of the Transparent Surface Coatings on Post-Byzantine Icons Using Microscopic, Mass Spectrometric and Spectroscopic Techniques,” J.Microchemical (94)14-23(2010).

[28] M. Zottia, A. Ferronib, P. Calvini, “Microfungal biodeterioration of historic paper: Preliminary FTIR and microbiological analyses”, International Biodeterioration & Biodegradation (62)186-194 (2008).

[29] Y. Wang, L. Hongyu i, D. Li, “Biosynthesis of Natrojarosite by Immobilized Iron-Oxidizing Bacteria,” International Journal of Mineral Processing (120) 35–38 (2013).

[30] A. Thygesen, J. Oddershede, H. Lilholt, A.B. Thomsen and K. Stahl, “On the Determination of Cellulose Content and Crystallinity in Plant Fibres”, Cellulose 12 (6) 563-576 (2005).

[31] S.Y. Oh, D.I. Yoo, Y. Shin, H.C. Kim, H.Y. Kim, Y.S. Chung,W.H Park, J.H. Youk, Carbohydr, “Crystalline Structure Analysis Of Cellulose Treated With Sodium Hydroxide and Carbon Dioxide by Means of X-Ray Diffraction and FTIR Spectroscopy,” J. Carbohydr Res.31,340(15) 2376-91 (2005).

[32] S.J. Eichhorn, R.J. Young, R.J. Davies, C. Riekel, “Characterisation of the Microstructure and Deformation of High Modulus Cellulose Fibres,” Polymer 44, 5901-5908 (2003).

---

[33] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, “An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer,” J. Tex. Res. 29: 786-794 (1959)

[34] B.D. Cullity, “Elements of X-ray Diffraction”, 2nd ed., Addison Wesley, Massachusetts, 3: 569 (1978).

[35] S. Geaa, C.T. Reynoldsc, N. Roohpura, B.W.N Soykeabkaewa, E. Bilottia, T. Peijsa, “ Investigation Into the Structural ,Morphological, Mechanical and Thermal Behavior of Bacterial Cellulose After A Two-Steps Purification Process”, Bioresource Technolog (83)253-260 (2011).

[36] PDF Database, International Centre for Diffraction Data, Newtown Square, Pensylvania, USA (2003).

Conclusions

- This study aims to give an insight in understanding the molecular changes occurring when pigments and organic dyes are incorporated into linen fibers and how these are translated to the macroscopic properties of linen.
- Accelerated ageing techniques are useful for obtaining laboratory samples which are as close as possible to the ancient samples to study them, because of the impossibility of application the studies on real archaeological specimens.
- Although the mechanism of cellulose degradation is still a matter of controversy among researchers, we found that no significant degradation is produced with accelerated thermal ageing as this was described previously.
- Pigments used in ancient years, apart from cosmetic reasons they probably did play a role as protective coatings which positively affect strength and apparently reduce deterioration in the long run. Nevertheless, it appears that beautifying reasons were more important than fabric durability, in the short run, since the treatment fibers exhibit reduced elongation to-break in comparison to nontreated textile fibers in all cases.
- FTIR measurements confirmed that spectral profile of the aged linen colored with the studied pigments shows the spectral pattern of pigments superimposed a lot of bands of the aged linen. Furthermore, the pigments seem to interact to cellulose and lignin compounds of the aged linen
- XRD diffraction diagrams of painted linen samples after thermal ageing are dominated by the presence of the natural pigments as these are found in the ICDD-PDF database. All pigments but charcoal, exhibit well defined peaks that completely mask the weak diffraction signals of cellulose I.
- Natural organic dyes, utilized in ancient years, were primarily used for the decoration of textiles but also as protective agents which positively affect their strength and act as a barrier preventing them from thermal degradation.
- Most dyes have no appreciable effect on the rate of degradation of cellulose, while they may also exhibit a protective effect due to their ability to inhibit the oxidative and photochemical reactions.
- Chemical changes in polymer chains in textile fibers, observed in the micro scale, influence their physical properties, like mechanical strength, in the macro scale. In our case, the vast majority of dyes protected the linen fibers improving their mechanical properties without significantly affecting their morphological characteristics.

- The tensile strength was increased in all dyed samples comparing with undyed linen after TA, while the elongation ability was either increased or decreased depending on the dye used. The highest values were observed for samples treated with cochineal regarding both factors in accordance with the low CI value measured with XRD. Thus, the increased disorder of the amorphous phase permits greater flexibility of the polymer, although fibers with low CI are more easily degraded due to the high proportion of amorphous regions.
- Henna has been shown to significantly reduce the elongation ability more than any other dye, probably due to the small molecular dye size which permits limited intermolecular interaction with the cellulose. The sample treated with henna also featured low CI while SEM measurements revealed a more disrupted surface morphology than the other dyed samples.
- FTIR measurements confirmed the strong binding of the organic dyes to lignin and cellulose.
- FTIR results of ancient textile samples have illustrated that all ancient fibres are made of linen fibres. The black pigment of a mummy's shroud- late period is black charcoal and the binding media is Arabic Gum. The dark red dye of tunic, Coptic period is cochineal dye. The blue dye of a tunic from The Italian mission's excavations of bani ebada at AL-Minya may be indigo dye. Also the results indicate shifting to higher or lower frequneces and increasing of the intensity absorption bands of carbonyl function group of all ancient fibers comparing with the standard new linen fiber, resulting of the oxidation of the hydroxyl group, reflecting the degradation of glycosidic linkages in the cellulose fibers.
- XRD results of ancient fibres have shown significant decreasing in the crystalline properties and crystallite size of all ancient linen fibre comparing with standard new linen, indicating an increase in the amorphous areas upon natural ageing. The results also have indicated that the sample of undyed linen tunic from The Italian mission's excavations of bani ebada at Al- Minya is amorphous, where as the peak at $2\theta=22.8°$ which assigned to the cellulose I of the linen is disappeared.
- SEM analysis of all ancient textile samples have showed that all of them are made of linen fibres and illustrate that the fibers appear severely damaged as breaking, tearing and the other fiber with broken ends appearance and many transverse cracks and longitudinal splits, consistent with loss of scale structure. Moreover, SEM photographs exhibit that there are various contamination, where as many soil particles were often found everywhere along the fiber surfaces, this evidence indicates that the fabric appear very dirty. All these degradation views probably indicate that the fibers had deteriorated over the long period of ageing
- FTIR, XRD and XRF results of ancient inorganic three pigments from a tomb at Al-Minya, New kingdom have illustrated that the red pigment is hematite, the yellow one

is Natrojarosite and the green pigment is a mixture of Egyptian blue, goethite and calcite.

- There should be further studies of the physicochemical characterization of Egyptian linen colored with pigments and organic natural dyestuffs before ageing, since the painting and dyeing process alone is also expected to slightly alter linen's properties.

Publications from this Ph.D. Thesis

1- H. El-Gaoudy, N. Kourkoumelis, E. Varella, D. Kovala-Demertzi, “The Effect of Thermal Ageing and Color Pigments on The Egyptian Linen Properties Evaluated by Physicochemical Methods,” Journal of Applied Physics A, Material Science & Processing, 105: 497-507 (2011).

2- N. Kourkoumelis, H. El-Gaoudy, E. Varella, D. Kovala-Demertzi, “Physicochemical Characterization of Thermally Aged Egyptian Linen Dyed With Organic Natural Dyestuffs”, Journal of Applied Physics A, Material Science & Processing, 112: 469-478 (2012).