# Historical Textiles and Their Characterization

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# PREFACE

This book focuses on gaining new insights into research on and the application of methodologies for the determination of the composition and degradation of historical textile materials. It presents a broad range of examples that can be found during the conservation and restoration of historical materials—from historical textiles on mummies to metal fibers and pearls.

Moreover, the book highlights the importance of a multidisciplinary approach as a part of complex tasks when only a relatively low amount of materials is available for analysis. In cases of the characterization of precious valuable and rare materials, only sensitive, selective, and reliable analytical procedures can be applied.

This book therefore presents sensitive and selective analytical procedures for the characterization of historical textiles, validated by certified reference materials. Current efforts to include optimized procedures and mathematical modeling in analytical chemistry, restoration and conservation, and materials characterization are also presented. These methodologies are applied to historical samples, where they have proved fundamental in unraveling the complex composition of samples with metalized yarns and pearls collected from historical samples.

As this book utilizes current scientific advances to better understand the principles of materials characterization, it is of broad general interest, but it will be of particular interest to the chemical, anthropological, and conservation-restoration communities. Moreover, it can offer particular support to interested audiences in historical materials preservation.

Historical textiles, as objects of particular value to cultural national heritage, belong to the group of the most sensitive materials that often need to be restored and preserved. The main reasons for damage to them include unsuitable climatic conditions, whether from light or from biological, physical, or chemical factors. The main goal of research into historical textile degradation and the need for restoration is to preserve the object and prevent its further destruction. The task with the greatest responsibility is to effectively clean objects of heterogeneous composition that contain fabrics combined with leather parts, bones, animal skin parchments, or wooden and metal parts. Before cleaning, proper material investigation needs to be performed in order to determine the morphology, chemical and physical composition, and all other properties of the materials investigated. Without proper materials characterization, it is not possible to preserve valuable objects. Only after obtaining a full and deep insight into the composition of materials can historical items be cleaned, conserved, and restored appropriately. For example, after characterization and cleaning, damaged textiles often need to be attached to a material of similar structure and color. In addition, during the restoration of significant works of art, it is necessary to replace the missing parts and reconstruct the material in a completely identical way, that is, using the techniques originally applied and using similar embroideries and colors. All this is impossible without chemical analysis and characterization.

The characterization of historical materials that are highly valuable works of art with the goal to return them to their original condition is a very time consuming and arduous task, but it is an important step in preserving cultural and historical heritage. Methods chosen in the characterization depend upon material properties and analytical tasks. Therefore this book presents the most prominent methods of historical textiles characterization, as well as different real complex case studies which combine the investigation of textiles with metals, organic binding media (resins, waxes, and proteins), mummies, jewelry, and so on by using different methodologies for characterization.

# ACKNOWLEDGEMENTS

This book is dedicated to my precious teacher(s) Gyurme Chokyi Sengye Rabjam Rinpoche and Dilgo Khyentse Yangsi Rinpoche, who are an eternal inspiration in becoming a better person, and to my first teachers, mother Renata Penzar and father Josip Penzar, as well as to all mentors and professors I was privileged to work over many years until now: Prof. Ilse Steffan from the University of Vienna in Austria, Prof. Lidija Ćurković, Croatia, Prof. Ljerka Bokić and Marija Kaštelan-Macan from the University of Zagreb, and many others.

Many results could have not been discovered without the efforts of multidisciplinary teams and collaboration with dear coworkers from different institutions and universities, so my gratitude goes to all of them.

My deepest gratitude goes to the people who are the closest to my heart, to Jure Rezić and Ernest Meštrović, whose patience and support helped me during writing this book.

Last but not least, this book is for you, dear reader, I hope you will find it useful, providing advice, support, and inspiration that will help you in your everyday work.

# CHAPTER I

# HISTORICAL MATERIALS AND DEGRADATION

## 1.1. Historical textiles

Although the original term “textile” comes from the Latin word *textere*, which means *to weave*, today the term is used for fibers and for all products made of them by any processing technology, that is, spinning, weaving, knitting, lace, release, needlework, and so on. This means that the term textiles includes all linear and flat textile products and products made from them. Recently, the word *textiles* has been introduced as a synonym for textile [1]. The production of textiles in the history of humankind dates back to the beginning of civilization and is conditioned by the primary human need to find protection from the cold. Cotton, wool, linen, silk, and other textiles of natural origin were used in ancient Egypt, silk production was mentioned in China as early as 3,000 BC, and carpets over 2,000 years old have been found in Asian tombs [2].

Today, tapestries, embroideries, folk costumes, church items, toiletry bags, fans, hats, wallets, flags, and many other decorative and artistic items are often the subject of various restoration and conservation interventions. During restoration works on historical textiles, it is necessary to first determine the composition of the textile material, which may be of plant or animal origin (wool, hair, silk, cotton, linen, jute, hemp, grass, nettle), and then it is necessary to determine all the other components on the material (like metal components or other items, Figure 1). Animal fiber is mainly composed of protein and is more resistant to destruction than plant fiber, which is formed mainly of cellulose. Flax and cotton, for example, are very susceptible to the action of bacteria in humid conditions and rarely remain preserved in archaeological sites.

Figure 1.1. Historical textile before cleaning, analysis, conservation, and restoration.

All textile materials are subject to deterioration under the influence of various factors, such as light, insects, microorganisms, and dirty air, which individually or together cause significant losses in the strength of the material and its elasticity. Due to the loss of strength, textile materials in many cases are no longer able to function in their original purpose, for example, as a support for the painted layer of a work of art. "Outdated" textile backings are a big problem for restorers, who in the past often resorted to dubbing. Nowadays, however, this process is no longer considered satisfactory. Since the early 1970s, targeted research has attempted to examine the various causes of damage and to develop new procedures for the conservation and restoration of textile media [3].

Oxygen in the atmosphere affects all organic matter, including textiles. In contact with atmospheric oxygen, the organic matter in the canvas oxidizes. The process is unstoppable and at best can be slowed down. The oxidizing fabric loses its elasticity and becomes brittle, a process that is further accelerated by contact with drying oils (e.g., linseed or poppy oil) that absorb large amounts of oxygen during the "drying" process.

Prolonged exposure to normal atmospheric conditions will cause the decay of the textile material. The rate of decay varies depending on the environment and the nature of the material itself [2, 3, 4, 5].

The main factors that accelerate the decomposition of textile material can be classified into three groups:

### 1. Organic substances:

Since the textile is of organic origin, it is susceptible to attack by moths, bacteria, mold, and fungi that require a high degree of relative humidity or even condensation. In the case of decomposition of cellulose by the action of microorganisms, the fibers lose strength and elasticity, become brittle and disintegrate over time. Decomposition is greatest in situations that favor the growth of these organisms, such as moisture, heat, stagnant air, and contact of these materials with nutrients.

### 2. Physical factors:

Excessive heat causes drying and exposure to ultraviolet radiation causes weakening of the material, as well as photochemical decomposition of the underlying dyes. These factors are particularly harmful when high atmospheric humidity and pigments act as catalysts and accelerate the decomposition of textiles. The oxidation effect has UV and visible light, as well as electromagnetic radiation of the visible and ultraviolet part of the spectrum, which leads to photo oxidation, so UV filters are used for protection. In the case of physical factors, the influence of moisture is also very important. Like any organic matter, textiles rot and decompose under the influence of moisture. Of all the species, cotton is the most resistant material, but only if it is constantly in water, as otherwise it decays even faster than other types. Moisture resistance is increased by careful cleaning of the fibers and removal of natural adhesive materials. The greatest difficulty and consequence of exposure to moisture on textiles is created by shrinkage during wetting, and later (greater or lesser) stretching during drying. The problem is the harmonization of individual materials that often behave in opposite ways in the same time interval; as the textile material tightens, the preparation stretches, and vice versa. The preparation contains binders prone to swelling, such as glue, chalk, and bolus (inorganic binders), while the fibers of the fabric swell by receiving moisture. As a consequence, when water condenses with moisture on contact with a textile substrate, the swollen glutoline adhesive creates a gel-like mass that has only limited mechanical strength. Stresses occur that can cause the painted layer to separate from the textile substrate. Wet cloth is also sensitive to greater cold—if wet fibers freeze, they become brittle. Ice, which has a larger surface area and volume than water, stretches the fibers from the weave.

**3. Chemical factors:**

Metals in direct contact with the canvas catalyze oxidation, which in old paintings is clearly visible at the edges over which they are stretched to the sub-frame (stretching edges), leading to a loss of color and corrosion [6]. Ocher preparations containing iron contribute to the accelerated deterioration of textile material. Exposure to harmful gases can also weaken the textile material. In some cases, these gases can interact with other substances in the atmosphere to turn into acids, which are the main cause of the decay of some textile materials. It should be noted that our civilization and industrialization contribute to the process of the accelerated decay of materials. Inorganic acids that enter the environment in exhaust gases (sulfuric and carboxylic acid) have a corrosive effect on cellulose. Depending on the location and equipment, the air in a museum or room where art objects are exhibited or stored also contains sulfur dioxide and dust particles. Sulfuric acid formed from sulfur dioxide destroys fibers. Dust particles that settle on the back of the material or in the gaps between the textile carrier and the sub-frame or coating accelerate the decomposition process. The microclimate of the space is very important in this process: because the thickness of the decorative frame in paintings or museum exhibits leaves a small air space between the wall and the museum object, there is a gradient in temperature and humidity. As a rule, the temperature behind the object is lower and the humidity higher. Climatic "inter-spaces" cause water to diffuse through the textile substrate and the image layer. This can cause cracks, separation of layers, and deformation. Patches on the canvas, inscriptions on the back, and similar materials increase the resistance to diffusion, which is one of the possible causes of their visibility on the face of the painting [3].

## 1.2. Textile fibres on historical materials

The fibers that make up the fabric should be identified before any processing of the material begins, especially if stain removal is required. Physical tests such as incineration (dry distillation) allow the rapid identification of the presence of animal fibers that do not burn but are extinguished with the rest of the clean charcoal, and during which a pronounced smell of burnt hair is created. Fibers of plant origin burn easily, into the fine ash. Many fibers can be easily identified using a microscope. Animal hair, for example, is identified thanks to its cuticles and medullar cross-sections. Simple dyeing tests allow conservators to distinguish between different types of fibers.

According to their structure, all fibers are polymeric substances—chain macromolecules made of various polymers that can be formed either naturally (natural polymers such as cellulose, protein, or natural rubber) or synthetically in industrial plants. Textile materials most commonly found in archaeological sites are natural polymers of plant or animal origin: linen, cotton, hemp, wool, and silk.

The size of the cellulose macromolecule is expressed by the average relative molecular weight and the average degree of polymerization. During plant growth, cellulose macromolecules orient themselves in parallel along the fiber axis and come to a close position, whereby the hydroxyl groups of adjacent chains are cross-linked by hydrogen bonds and thus form crystal regions in the cellulose fibers. In addition to cellulose, plant fibers also contain lignin in woody fiber ingredients, wax, starch, sugar, and proteins. All impurities except wax, negatively affect the durability of the material. Processing, combing and rinsing remove woody ingredients as well as natural adhesives, which increases the quality of the fabric.

**Flax** is a natural cellulosic fiber obtained from the stem of a plant originating from the *Linaceae* family, and which blooms with small blue flowers (Figure 1.2).

Figure 1.2. Flax natural cellulose fibers for historical textile restoration.

There are about 200 different species of this plant; the most important plant of the species for obtaining fiber is *Linum usitatissimum*. Flax fibers contain 65–90% cellulose and impurities: pectin, wax (which positively affects the fiber's resistance to moisture), starch, sugar, protein, lignin, and so on. This plant fiber is resistant to moderate alkaline conditions due to its cellulosic composition, but is easily subject to damage in an acidic medium. Strong alkalis decompose internal pectin at higher temperatures, so the technical fiber decomposes into elemental properties [1]. Flax fiber is usually lighter in color, somewhat greenish gray. The finest types of linen are lighter, silvery yellow in color. Under standard conditions, it contains 12% moisture. By receiving moisture, the fibers become thicker, shorter, and firmer. Linen canvas is the highest quality type of painted surface carrier [3]. Moisture penetrates easily inside the linen material and causes changes in both the dimensions and weight of the material and the overall strength. Flax does not absorb dyes very well and is usually used in the bleached or unbleached state [8].

**Cotton** is a plant fiber obtained from the seeds of a plant of the genus *Gossypium*, of the family *Malvaceae* (Figure 1.3). According to its composition, cotton is almost pure cellulose (82–89%, Figure 1.3) with a lower percentage of wax (0.4 to 0.9%), pectin (0.6 to 1.1%), protein (1.0 to 1.8%), organic acids (0.5 to 0.9%), and minerals and ash (0.6 to 1.5%); 7–10% moisture is absorbed on the fiber. This fiber is the widest and most widely used textile fiber in the world. Historical sources state that cotton textiles date from around 5800 BC in the area of present-day Mexico. In Europe it has only been used since the Middle Ages, where it was introduced by the Arabs via North Africa and Sicily.

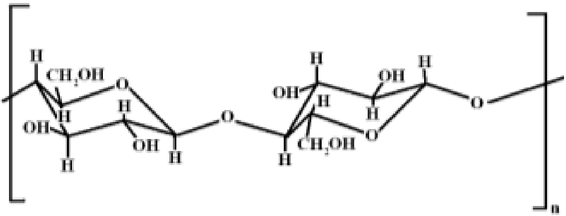


Figure 1.3. Chemical structure of cellulose polymers.

As the cotton does not have sufficient elasticity, the cotton cloth remains loose after stretching. An important property of cotton fabric is the fact that it tightens when wetting and applying the preparation, but stretches when it dries.

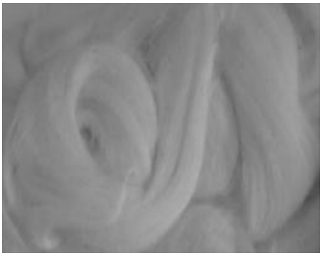
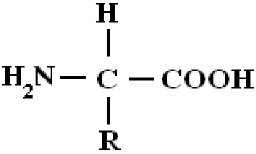


Figure 1.4. Cotton natural cellulose fibers for historical textile restoration.

Moreover, cotton fibers can also tolerate moderate alkaline conditions, but change greatly under the influence of acids. It does not transfer moisture like flax and has pronounced absorption properties, thanks to which it also has the property of good dye uptake [3].

Natural fibers of animal origin (wool, hair of various animals, and silk) are made of proteins whose macromolecules are composed of amino acids (Figure 1.5).



$$\mathrm{H_2N}-\underset{\substack{|\\ \mathrm{R}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{C}}}-\mathrm{COOH}$$

Figure 1.5. General formula of α-amino acids.

**Wool** is a natural protein fiber obtained from the fleeces of sheep. It is made up of the protein keratin (the most common amino acids are serine, glycine, leucine, arginine, glutamine, tyrosine, and cystine) [1]. Wool fibers better absorb moisture and receive dyes from plant fibers due to both their chemical and morphological structure. Wool fiber is not a solid fiber, and it is significant that in its wet state it loses even more strength (Figure 1.6).

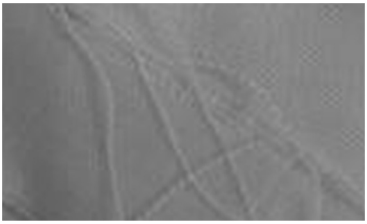


Figure 1.5. Wool as natural protein fibers for historical textile restoration.

**Silk** is a thin and shiny natural fiber obtained by un-wrapping the cocoons of silkworms. We distinguish between two types of natural silk, cultivated and wild silk, which have almost identical chemical composition: they contain 70–82% fibroin, 18–30% sericine, 0.1–1% fat and waxes, and 1–1.4% pigment and ash [1]. Silk is as strong as steel wire of the same diameter [10] but is very sensitive to light and will be damaged if exposed to ultraviolet light.

The fabric that serves as a mechanical carrier of an image or as a base for another work of art (flags, banners, etc.) affects not only the durability but also the appearance of the work of art. The chemical and physical interactions of the components of the system used should be taken into account [11]. We can reliably come to a conclusion about the mutual chemical influences of different painting materials on the basis of knowledge about the components present on the textile material, so the analysis of these substances is very important.

In the case of conservation and restoration work, detailed documentation is first prepared on the material that needs to be processed. It is necessary to make an analysis of the material itself so that it is subjected to analytical procedures: after the physical-chemical analysis, the degree of damage to the external and internal structure of the object is determined. The structure of the tissue and the nature of the changes are then examined. Yarn analysis is performed and the condition of the object is determined with the help of micro photographs. Art and technical forms and elements in binder, decoration, and cut are examined. Proper preservation procedure includes careful documentation of the detected condition, cleaning and rinsing, replacement of necessary parts, sterilization, and proper storage and protection from undesirable atmospheric factors [13, 3].

Proper treatment of textiles usually requires the use of flat heated substrates and holders and other parts that can support sensitive textiles during rinsing, washing, and drying. Dust carries with it organic and mineral particles that settle on fabrics [14]. Alkaline reactions (from pH 7–9) caused by dust favor the development of fungi on the fabric. Most dirt can be removed from the textile material by rinsing in deionized water, with the addition of 0.4 to 1% ammonium hydroxide solution, and if necessary it is possible to add 1% neutral nonionic detergent (such as Lissapol N). During washing, some white materials can be bleached in 4% hydrogen peroxide solution. Sodium silicate and meta silicate can be used as stabilizers to be added to control peroxide decomposition. Stains caused by copper corrosion should be treated with 1–5% ammonium hydroxide solution. Stains caused by corrosion of silver should be treated with potassium cyanide and then iodine, and washed with sodium thiosulfate. Textiles with iron stains should be washed with 5% hydrochloric acid, 5% oxalic acid, 10% hydrofluoric acid, 5% EDTA, 5% acetic acid, 5% lactic acid, and 2–10% ammonium citrate. In doing so, oxalic and hydrofluoric acids are most effective for removing iron stains from archaeological textiles. After any chemical treatment, intensive rinsing in deionized water removes all residual chemicals that can cause further destruction of the textile material over time. Textiles that cannot be cleaned with water (e.g., textiles containing water-soluble dyes) are recommended to be treated with organic solvents such as perchlorethylene or trichlorethylene and kerosene (white spirit). Although the disadvantages of cleaning with these solvents are pronounced (high treatment costs and the problem of the toxicity and flammability of these chemicals), there are many advantages to cleaning with organic solvents: they do not soften textile fibers as water does, which reduces the risk of material shrinkage and loss of shape; if they can only be treated this way, organic solvents are more efficient at removing grease, they are also mostly volatile so they dry quickly.

## 1.3 Consolidation of historical textiles

During conservation and restoration works, it is very often necessary to reinforce sensitive textile material by attaching it to a mesh base made of polyester, cotton material, glass fibers, or other material. Due to the lack of alternative solutions, until the early twentieth century weakened or destroyed textile supports were treated using fabric patches, adding edges or duplicating images. Duplication was a universal method for treating all types of damage, regardless of their size and extent. However, the discovery of modern synthetic adhesives for material restoration has led to a change in the way textile media is treated. Particularly sensitive textile materials are sometimes placed between plastic or glass surfaces. In most cases, thermo-stable adhesives (polyvinyl acetate, polyvinyl alcohol, acryloid B-72, or their emulsions) are used as a coating that is then thermally bonded to the textile. All damage and protrusions on the material must be additionally fixed with glue to prevent additional extraction of fibers. Various synthetic resins are also available to the preservative to consolidate the textile material, with emulsions and water-soluble resins being preferred because they do not dry as quickly so the preservatives have more time available to treat the material.

The resins most often recommended for the restoration and conservation of textile material are the following:

1. Polyvinyl alcohol (very soluble in water, dries with minimal shrinkage)
2. Polyvinyl acetate (V7, may shrink fibers due to resin shrinkage during drying)
3. Etulose (i.e., ethyl-hydroethyl cellulose, water soluble, very flexible)
4. Polymethacrylate
5. Acryloid B-72, 5% solution in toluene

### *1.3.1 Treatment of tears and holes*

In general, the space around a tear or hole will be stretched and deformed as a result of the relaxation of mechanical stress. Before this area is stabilized, it should be leveled and when this is done, depending on the extent to which the canvas is stretched, the edges of the crack when joining will overlap. The tear is then stabilized with Japan paper, smoothed and further treated. If the textile backing is stretched too much, the overlap is removed with a scalpel. There may be tears on the materials with which the edges can no longer be joined. After leveling between the two sides of the tear, a hole/gap remains. In extreme cases, the restorer will try to tighten the shrunken canvas along the tear with weights and wetting.

The process is not entirely simple as it can lead to the formation of fine cracks in the painted layer. When the edges of the tear are placed together again, they are fixed on the front with Japanese paper or sewn on the back. The tears are restored by sewing the torn threads, while the holes are filled with a piece of cloth. In case of large damages after the treatment of tears and holes, the textile material must be duplicated. Fabrics suitable for patches are those whose structure corresponds to the original wearer. Gauze and old canvas can also be used for patches. The patches are glued with glutoline glue, a mixture of flour and water, wax, lead white, synthetic resin or wax glue.

*Maruflage* is a term used today for a method of joining a textile material to a solid surface. *Maruflage* is used when there is great damage to textile carriers, unusual painting shapes, or protection from damage and deformation of the painted layer is required. Rigid supports more effectively stabilize a textile item made of duplicating material. Duplicate materials should be stable as they are exposed to light and air pollutants. They should be as strong as possible, possess isotropic characteristics (spread and contract equally in all directions), show minimal reactions to changes in humidity, and blend well with adhesives. Each duplicating cloth must be washed, leveled and free from irregularities. To flatten it, it must be tensioned on a frame that is larger than the original image. These canvases usually weigh 300–450 g/m$^2$. Canvases were the only materials for duplication and patches until the 1970s [3].

### *1.3.2 Disinfection of historical textiles*

For successful treatment against moths and insects, infected textile materials should be placed in closed containers containing thymole crystals. The crystals should be evaporated so that the container is held above the bulb, and then a 0.5–1% solution of Lysol should be applied to the textile material by spraying. This treatment will remove most of the problems. Carbon disulfide can also be used instead of thymole crystals. The disinfectant solution can be prepared in the laboratory by mixing a 0.1% solution of Dowicide 1 (orthophenyl phenol), 68% ethanol, and 30% deionized water. This solution is effective for removing most bacteria, fungal spores, and surface molds.

Fungicides are used to control fungal tissue diseases. It is very harmful to store textile items in plastic bags and bags in damp rooms. The item can be exposed to protective chemicals in several ways: by immersion in a bath or, for example, by spraying objects. In addition, protection can be carried out by heating the object at a temperature of 60–70°C for about 30 minutes or by disinfecting with an IR lamp.

### *1.3.3 Preservation and protection of historical textiles*

Textile materials should be stored in conditions that limits exposure to atmospheric pollutants and ultraviolet rays. Relative humidity should be a maximum of 68% because an environment with relative humidity above 70% encourages the appearance of moths. Ideally, textiles should be stored in dark rooms with a low temperature of $10^0$C and low relative humidity (<50%). All rooms should be airy, well ventilated, and clean and well and properly lit. Dust should be removed from the room where the items are located. Moths and other insects should be repelled using para-dichloro-benzene inside the warehouse. This is very important for all woolen materials [15, 5].

## 1.4. Binding media on historical materials

The bonding material is the material that serves to strengthen the colored pigment and inorganic filler on the material, thus creating a solid and durable surface [2]. Each coating must meet many requirements, the most important of which are the requirements for transparency of the coating, glossy or matte appearance, and appropriate protective properties [10]. Various natural materials meet the necessary conditions and have historically been used as a binder: proteins, carbohydrates, resins, and waxes and mixtures thereof. The true composition of a complex binder was often a closely guarded secret of the individual artist. Glues obtained from animal or fish organs, skin, or bones have been mostly used as binding materials on paper and as substrates in paintings [4]. Egg white was used to lighten the manuscript and as a binder for gold leaf [16], and egg yolk as a binder for tempera [2]. Casein can be found on coatings of colored furniture, textiles, and wall paintings [4].

**Carbohydrates** are organic molecules that are very widespread in nature, and are therefore used as binders, adhesives, and additives in all water-soluble art materials. The most commonly used are vegetable gums (gum Arabic, gum traganath, cherry gum), simple sugars and honey, or dextrin.

**Waxes** contain chain carbohydrates, acids, alcohols, and esters. They can come from a variety of sources: plants (carnauba wax, candelabra, or Japanese wax), animals or insects (beeswax, spermaceti, lanolin), and minerals and fossilized materials (ceresin, earth wax, or paraffin). They are used as waterproof materials, binders, and fillers in paintings and other works of art [4].

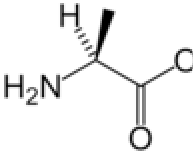
**Resins** are dried and hardened secretions from plants or trees that are made of isoprene parts and can be: monoterpenoids (turpentine oil, camphor, rose oil), sequiterpenes (shellac, elemi), diterpenes (canada balsam, rosin, sandarac, copal, kopaiba) or triterpene resins (dammar and mastic) [18]. Resins differ greatly in their properties such as appearance, odor, hardness, solubility, color, and color fastness [2]. They are mostly used as coatings on paintings and furniture, musical instruments, and gilding, or as components of complex bonding materials [4, 19, 20].

**Proteins** are organic molecules of high molecular weight, greater than 10,000 Daltons. They consist of sequences that form 22 amino acids interconnected by a peptide bond, which are characteristic of each protein. Proteins can be broken down into amino acids by hydrolysis [17].

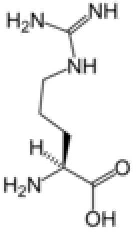
**Protein binders** have been used since the time of ancient Egypt. Amino acids appear as monomeric units of protein in many natural materials found (eggs, glue, and casein) that have been used as a binding material. In order to be able to determine the amino acid composition of a protein, it is necessary to break the polypeptide chain by hydrolysis. Although this results in partial destruction of the indole ring in tryptophan and loss of ammonia from the side chain of amide groups in glutamine and asparagine, and significant formation of glutamic and aspartic acid, it still allows the protein binder to be determined on the basis of the identification of other characteristic amino acids.

Amino acids are weak carboxylic acids that contain an amino group (-$NH_2$) [24]. Only those amino acids in which the amino and carboxyl groups (-COOH) are attached to the same carbon atom are biologically important [8]. Amino acids serve as starting materials for various other compounds needed by the body (enzymes, hormones, pigments) [25]. Essential are those that the body not only can synthesize but also must receive through diet [26–29].

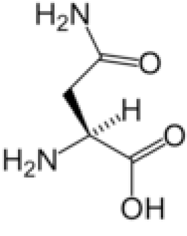
Amino acids are classified according to the position of the amino group on α, β, and γ amino acids. Amino acids that make up proteins can be divided into three different groups: amino acids that have polar but non-ionized side chains (glutamine, serine, threonine, tyrosine, and cysteine), amino acids that have acidic side chains (aspartic acid and glutamic acid), and amino acids that have basic side chains (lysine, arginine, and histidine) [30]. The chemical reactions of amino acids correspond to their functional groups: acylation (typical amino group reaction) and esterification (carboxyl groups). All amino acids (Figure 1.6) are amphoteric in nature, and their mutual differences in acid-base properties are very important for the functioning of proteins and peptides, as well as for the analysis of amino acid mixtures that we want to separate due to their proton-donor and acceptor properties [30].



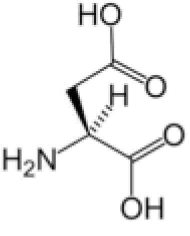
Alanine



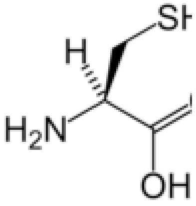
Arginine



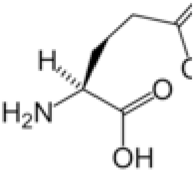
Asparagine



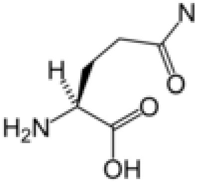
Aspartine acid



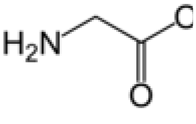
Cysteine



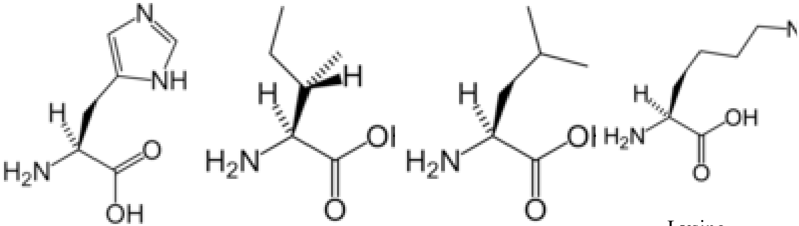
Glutamin acid



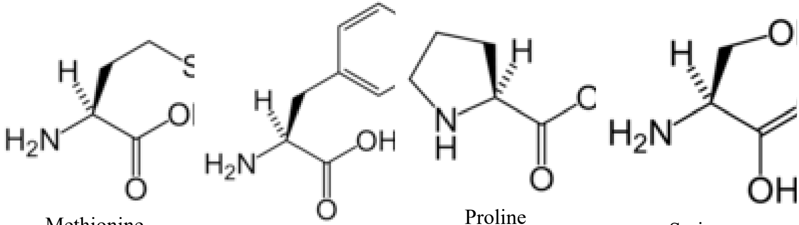
Glutamine



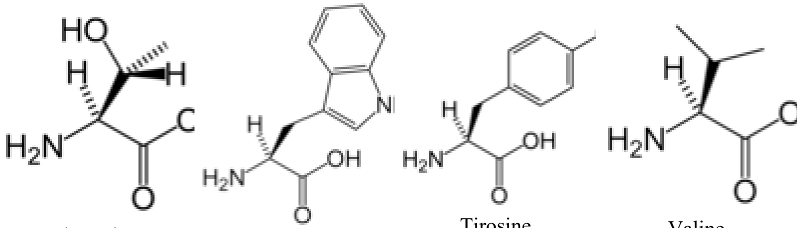
Glycine



Hystidine Isoleucine Leucine Lysine



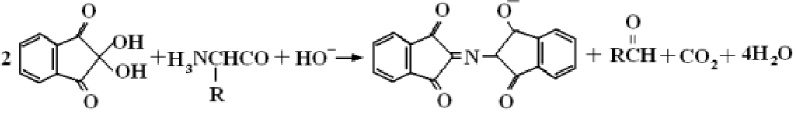
Methionine Phenylalanine Proline Serine



Threonine Triptophean Tirosine Valine

Figure 1.6. Aminoacids detected in historical materials from protein binders.

The presence of amino acids can be detected by the formation of a purple color with the reagent ninhydrine, which is often used to detect fingerprints [30]. All primary α-amino acids produce the same purple component as is presented in the following reaction:



Nynhidrine + aminoacids Purple color (Ruhemans purple

Amino acid analysis is often performed today by ion exchange chromatography based on acid-catalyzed hydrolysis of peptide-linked amides [30–39]. The peptides were hydrolyzed by heating in 6 M hydrochloric acid for 24 hours. The resulting mixture of amino acids is separated by ion exchange chromatography: at the outlet of the column they are mixed with ninhydrin and, depending on the intensity of the color or signal, are determined electronically. Unknown amino acids are identified by comparison with reference materials. This procedure can be performed automatically in an amino acid analysis instrument that has excellent sensitivity and can determine peptide samples in amounts of 10–5 to 10–10 g [30, 40, 41]. In addition to ion chromatography, paper chromatography [42, 43], inverted-phase thin-layer chromatography [44–48], high-performance liquid chromatography [49–53], and thin-phase thin-layer chromatography [44, 54–57] are of great importance in the analysis of amino acids and proteins and other analytical methods [58–61].

In addition to natural binders, which in history could only be used, today on historical textile materials can be found mixtures with new materials used in restoration and conservation work. From a conservation-restoration point of view, it is very important which bonding material is used on the textile material. Drying oxidizing oils act on textiles like water; there is shrinkage, but also darkening and partial transparency. When the oil dries, the canvas spreads again, but does not lighten—it becomes yellow-brown and loses transparency. As it ages, it darkens even more and transmits tanning to spreads. At the beginning of the drying process of fatty oxidizing oils, the oil absorbs oxygen and moisture from the air and increases the volume, which at this stage causes the fibers in the fabric to expand and shorten. In the next stage, it releases moisture and reduces the volume, leaving the fibers unevenly elongated. The drying process can take more than 10 years. Not all fatty oxidizing oils act equally on canvas; more harmful are those that are poorly cleaned, hot pressed, and slow drying. Linen is the most resistant to the influence of oil, while jute is not resistant due to the larger amount of woody materials. Turpentine oil evaporates quickly, so it does not affect the shrinkage and stretching of the fibers in the fabric. Alcoholic varnishes have the least harmful effect on canvas, which is why they are often mentioned for the protection of the reverse of a painting, but they have the disadvantage of yellowing over time [22]. Natural fabrics have excellent hygroscopic properties. The fiber in the fabric contains between 6 to 12% moisture. As moisture is lost, the fibers stretch and become loose. At a relative humidity of 20% to 95%, untreated canvas will shrink to 6.5%, while glue-impregnated canvas will spread between 1.5% and 5% [23, 3].

A list of binding media on historical materials is presented in Table 1 of the appendix at the end of this book.

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# CHAPTER II.1

# METHODS FOR THE CHARACTERIZATION OF HISTORICAL MATERIALS: SPECTROSCOPY AND DETERMINATION OF CHEMICAL COMPOSITION

## 2.1. The elemental composition of textile fibers

Historical textile materials are made of cotton, flax, or hemp and contain different elements. Their content varies significantly between many parameters, such as the time of the year of production, the soil, the amount of water used during producing, and, particularly, the chemical and physical parameters used [1–7]. The elemental composition of textile fibers is determined by using selected instrumental spectroscopic methods, such as flame absorption spectrometry (FAS or AAS), graphite furnace absorption spectrometry (GF-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or mass spectrometry (ICP-MS), to name only a few. Nevertheless, in order to obtain a full insight into the elemental composition of historical textile materials, the first step is to transform them from solid form into a liquid sample that can be introduced to the spectrometer. The digestion of materials can be performed by using wet digestion methodologies, the microwave digestion system, or dry mineralization procedures, as is shown in Figures 2.1, 2.2, and 2.3, respectively.

Figure 2.1 presents the protocol for the open system wet digestion of historical textile fibers. The sample is weighed (0.5 g) into the laboratory glass, heated on the hot plate with the addition of 10 mL of concentric nitric acid and 10 mL of hydrogen peroxide. The solutions were evaporated until dry and then diluted up to 10 mL using 1M of nitric acid. Therefore, the samples were prepared in 10 mL volumetric flasks before spectrometric investigation. Figure 2.2 presents the microwave digestion protocol with nitric acid; the sample is weighed into the microwave vessel, heated under pressure up to 250°C with the addition of 7 molar nitric acid and after 20 minutes the solid sample is digested, followed by preparation in 10 mL volumetric flasks before spectrometric investigation.

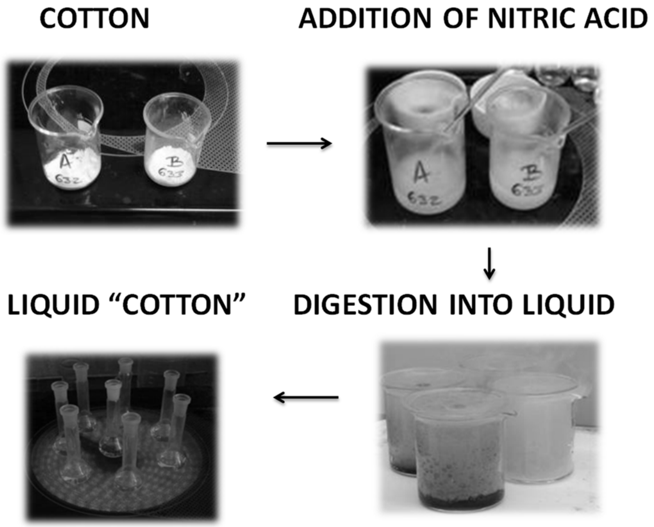

Figure 2.1. Open system wet digestion of historical samples by using 7 molar nitric acid and heating on a hot plate.

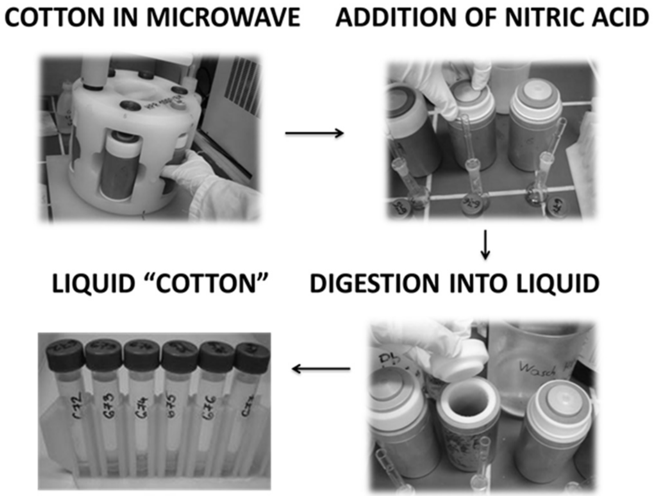

Figure 2.2. Microwave digestion of historical samples by using nitric acid and a closed microwave system.