



From Traditional to Laser Cleaning Techniques of Parchment Manuscripts: A Review

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HIGHLIGHTS

- Dirt and stains cause deterioration and big problem for the surface of parchment manuscripts.
- Traditional and laser cleaning techniques of parchment manuscripts are studied.
- All cleaning techniques have advantages and disadvantages, and all are required depending on specific criteria.
- Effective analytical techniques are very necessary to detect the suitable cleaning materials and techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

According to improper factors in museums, storages and libraries environments, surface deposits and different types of dirt can contaminate the surface of parchment manuscripts. The brittleness, hardness, corrosion, discoloration and stains from different sources are considered to be some of the deterioration forms resulting from the reaction between parchment and stains. This study aims to make a survey on different stains found on parchment, explain the forms and mechanisms of their deterioration, and explain the traditional and laser cleaning techniques used for stains removal.

Moisture, dusts, soot, blood, iron rust, adhesives residues and microorganisms stains are considered the most common stains on parchment manuscripts. This study confirms that mechanical cleaning, chemical techniques, cleaning with organic solvents, and laser cleaning have been used. Sometimes cleaning processes especially traditional cleaning can lead to pressure, irreversible damage, surface or molecular structural damage and denaturation of collagen. This latter can occur in advanced states of degradation. Laser cleaning is preferred for parchment because it is a contactless, chemical free and non-destructive procedure.

Analysis and investigation should be used for the evaluation of deterioration and conservation treatments. The study reveals that all cleaning techniques of parchment manuscripts have advantages and disadvantages and all are required, but the state of preservation and nature of stains will direct the selection of the suitable cleaning technique. Sometimes one or more techniques can be used for the removal of the same stains on the same manuscript.

1. Introduction

Parchment is a material derived from an animal source which has been used for centuries as a writing material for historical manuscripts, documents and works of art [1].

Parchment mainly consists of collagen fibres. Their molecular subunits are polypeptide chains with various amino acid side chains $Rx:(-NH-CHRx-CO-)n$ [2]. Type I collagen is a fibrous protein with a well-known basic unit consisting of three highly abundant amino acids, which are glycine, proline, and hydroxyproline [3]. The major constituent of parchment is the hydroxyproline amino acid polypeptide protein. Collagen structure consists of three individual protein strands in the α -helix conformation. These are rigidly held by strong hydrogen bonding interaction between the hydroxyl of the hydroxy-proline and the amino hydrogens of adjacent glycine units [4].

Parchment is a thin, flexible substance made from the skins of animals. Its color varies from chalky white through shades of cream to dark buff. The darker shades are often due to accumulated dirt, but can also occur due to handling [5].

Dirt is defined as a material which is in the wrong place.

The conservator always needs to remove material dirt without removing material which is in the right place. This process is frequently complicated by the fact that the substance of the object may be very similar to the dirt [6].

Some authors discussed the problems caused by stains on documents and manuscripts. Ritzenthaler [7] said that embedded dirt or stains can obscure textual information on manuscripts and should be brought to the attention of a conservator. Chahine and Rouy [8] discussed the problem of stain on parchment and they confirmed that the cleaning of parchment should be completely safe, that means preserving the inks, the structure of the material and the coatings, if any was applied on the surface during manufacture. Bilmes et al. [9] said that surface dirt can occur due to handling, wear, moisture, stains of grease and soot. Many documents have also ink or graphite pencil writings and marks, which must be eliminated or removed. Piñar et al. [10] stated that the microbial alterations detected more frequently on ancient parchments have red or purple maculae, with darkly pigmented purple stains. Piñar et al. [11] explained that various stains and a

thick layer of grime; at the outer edges of parchment manuscripts were deposits of a gritty substance that resembled sand. Campagnolo et al. [12] reported that smoke stains and soot, particles and dust affect the document's legibility by obscuring text and reducing contrast. Giacometti et al. [13] mentioned different sources of stains such as red wine, tea, soot from smoke, oil and blood stain. They also reported that blood stains look similar to iron gall ink as haemoglobin is rich in iron, which should contribute to the difficulty of separating the ink used in writing from bloodstains. Sakr et al. [14] stated that manuscripts can get contaminated from different types of microorganisms, which form stains with different colors depending on type of microorganisms. El-Shamy [15] explained that the main effects of microbiological deterioration on parchment are due to the presence of different stains, and loss in tensile strength.

There are different traditional techniques used for the cleaning of parchment. Mechanical cleaning (dry cleaning) is often required before any further intervention in a liquid medium, because superficial dust could migrate deeper inside between fibres. The mechanical treatments are generally time consuming, especially when the parchment is very dirty, sometimes too aggressive, and in addition not completely effective [8]. Mechanical cleaning leads to the formation of pressure by using scalpels, erasers and poly vinyl chloride erasers leading to irreversible damage of the surface appearance of parchment manuscripts [16].

Wet cleaning by using water or water mixed with other solvents, and organic solvent cleaning are commonly used in the cleaning of parchment. These techniques may lead to surface or molecular structure damage. The use of water or solvents can lead to hydrolysis of the collagen bonds resulting in gelatin for-

mation "gelatinization" [16]. The use of ultrasonic waves in the cleaning of parchment gave good results but it can be dangerous on powdery deteriorated inks, and it can also be harmful to very deteriorated and fragile parchment by disrupting the fibres [8].

The nano-second laser cleaning of parchment manuscripts has been proposed as an alternative for traditional methods that include mechanical scratching and use of an eraser or solvents. Laser cleaning technique has several advantages such as its being contactless, chemical free and non-destructive, providing a high accuracy successful cleaning [16-17]. Elnaggar et al. [18] confirmed that traditional mechanical and chemical cleaning methods may cause disruption of the fibres or chemical change. They also said that laser cleaning could offer an advantage due to its selectivity, precision and minimal material handling.

Analysis and investigation play an important role in the detection of the state of preservation of parchment manuscripts. Many authors have used analysis and investigation techniques for the evaluation of parchment deterioration and conservation treatments [19-34].

The authors found that there are some factors that contribute to the challenges encountered in the effect of stains and cleaning of parchment manuscripts as follows:

- There are few specialists in the conservation of parchment manuscripts.
- Lack of application of ethics and goals of parchment cleaning.
- Lack of specialized training in the treatment (specially the cleaning process) of parchment manuscripts in museums, historical or cultural libraries programs. These types of manuscripts are often treated by conservators from allied specialties, who might not fully understand them, or may not

have the scientific background to fully grasp newly developed cleaning systems.

- Insufficient understanding of constituents of parchment documents and manuscripts by many conservators.
- Unfamiliarity with advanced cleaning options developed in other fields of conservation that can be applied to parchment manuscripts and are safe at the same time.

This study aims to:

- Do a survey on the stains types found on parchment manuscripts.
- Describe the deterioration forms resulting from different stains.
- Explain the mechanism of parchment deterioration caused by stains.
- List traditional methods in the cleaning of parchment manuscripts and their important disadvantages.
- Explain laser cleaning process of parchment and their advantages and disadvantages.
- Produce effective methods of analysis and investigations that should be used to examine parchment surfaces and assess the effects of stains, cleaning materials and methods on parchment properties, considering both ethical and practical perspectives.

2. Types of stains, their formation, deterioration and removal using traditional techniques

2.1. Stain caused by water (wetness stain)

It should be mentioned that researchers have written about the problems caused by water, but they have not written about the water stain on parchment manuscripts. Reyden [35] defined water as a broad stain caused by movement and deposition of discoloration products carried in an aqueous solution and distin-

guished by a dark, curvilinear tide-line along the point of evaporation. Reyden also explained that water itself is a colorless liquid that does not stain a material.

Walsh [36] reported that the conservators have a major role in assessing the conditions in which the manuscripts are located in high relative humidity or in the case of direct water contact.

The authors thought that there are some sources, from which the water can cause stains on the surface of parchment manuscripts, some of these sources are as follows:

- In the case of poor storage, there are some ceilings that induce water that falls on the manuscripts.
- Storage archival materials directly below water and sewage pipes or above active drains in case they leak [37], or other accidents resulting in severe water damage [38].
- Water damage can come from external sources such as rivers, storms, and overflowing drainage systems [39].
- Water, after fire, is considered the greatest threat to archival and museum collections [40].
- Stains caused by water or excessive moisture can also be obtained with wet cleaning application by water or water mixed with an organic solvent without a good mechanical cleaning of some of the soil and dirt on the surface.
- It was reported by Paper conservation Catalogue [41] that some traditional paper conservation techniques such as cleaning may result in irreversible changes of an artifact when applied to parchment. Additionally, because of its animal origin, parchment sometimes tends to react to treatment methods in unpredictable ways.

Larsen [42] reported that water can cause some physical and chemical deterioration to the components of parchment manu-

scripts, which includes parchment sheet itself, the inks, pigments, and dyes. Manfredi et al. [43] stated that water is the only binding agent, which forms intermolecular bonds that join the fibres by means of hydrogen-bond bridges. Možir et al. [3] informed that long-term degradation of parchment is a reflection of breakdown of the collagen structure, caused by water and other factors.

Hansen et al. [44] explained that water affects collagen in several different ways. Water plays a direct role in the chemical changes of collagen through hydrolysis, salvation of free radicals, hydrogen bond stability and the rate of gelatin formation. FitzGerald [31] reported that moisture causes gelatinization and mold growth while a dry environment leads to irreversible embrittlement. Gelatinization is the process that turns parchment collagen into water soluble gelatin and this occurs as a reaction due to substantial fluctuations in heat and moisture, and results in the irreparable break down of parchment fibres. Gelatinized parchment is usually very stiff, discolored and translucent and in the leaf edges, where they are the most exposed to heat, denaturation occurs at the shrinkage temperature.

Hansen et al. [44] explained the gelatinization process of parchment. Collagen consists of amino acids, which include three similar strands of a protein containing large amount of glycine, alanine, proline, and hydroxyproline. The spatial configurations of repeated triple amino-acid sequences including glycine, alanine and hydroxyproline or proline cause the helical conformation between the strands. A triple strand of the protein is intertwined in an alpha-helix termed tropocollagen. Water molecules are intimately connected with the hydrogen bonding holding the triple helix together. Additionally, chain-breaking of a macromolecule by hydrolysis results in molecular weight decrease. This is another mode of

protein deterioration that may occur through denaturation. For collagen, this might be by interaction with water and is designated gelatinization (Fig. 1). By heating collagen in water, the water molecules can gain sufficient energy to compete for the hydrogen bonds maintaining the triple helix configuration.

Problems caused by water or excessive moisture are as follows: expansion of the object more than its original dimensions; increased discoloration and darkening of skin already damaged by microorganism and insects; solubilizing of media and softening resulting in offset onto adjacent materials (felts, blotters, etc.); changes of surface preparations and coatings; removal of the lime and / or chalk resulting in a translucent appearance similar to rawhide; in difficult cases of water exposure, realignment of the fibre bundles to a random pattern (rather than parallel to the surface) resulting in a stiff, horny, translucent skin; translucency resulting from overly damp skin being dried under no tension at all; gelatinization of an already degraded skin [41]. FitzGerald [31] said that parchment resembled a solid block which may be due to exposure to heat and water damage (Fig. 2).

2.2. Dust and soot stains

Dust and soot are considered dangerous sources of solid particles on manuscripts. Suspended particles are minute solid particles suspended in air.

Dust: Dust is one of the major components of atmospheric pollution. It is composed of fine dry particles or any finely powdered substance of earth and any other matter in the air. The various sources of dust in museums, archives and libraries are wind, traffic on road, shoes, hands and garments of staff and visitors, carpet, construction materials, etc. [45]. Accumulation of these dust particles cause disintegration and discoloration of

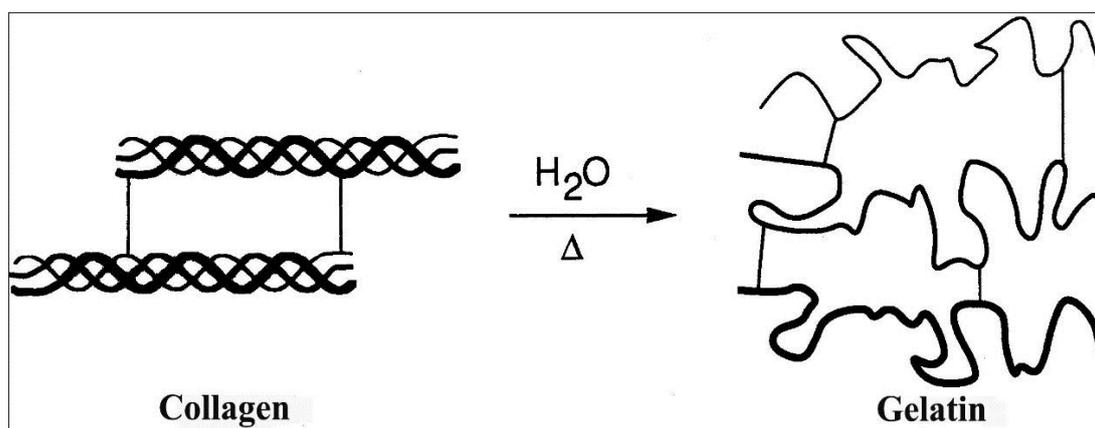


Fig. 1: Denaturation of collagen [44]



Fig. 2: Solid block phenomenon of parchment which is due to the effect of water and heat [31]

manuscripts by chemically reacting with the writing materials since they contain sharp particles like silicon, acidic gases and metallic ions. Manuscript collection of some museums and libraries which are situated near the coastal area is also affected by salt dust such as common salt (NaCl), magnesium chloride ($MgCl_2$) etc., that are not active chemical agents yet, they damage the manuscript collection. Dust causes physical or chemical deterioration to manuscript collections by abrasion and chemical reaction respectively [45].

Soot: Soot is a black flaky or powdery substance of carbon particles which is produced by imperfect combustion of coal, wood, oil, etc; it causes damage to manuscripts [45]. Smoke resulting from incomplete combustion produces tiny particles of carbon in the air. When deposited, these particulates are identified as soot (Fig. 3). Organic and inorganic materials produce different types of smoke residue or soot [46]. Soot sticks onto the surface of the manuscript and causes discoloration. Furthermore, it becomes very difficult to remove it as it chemically binds to the fibres of the manuscripts.

The mechanism of dust and soot deterioration

- Suspended particulate matters attract moisture, which in turn give rise to chemical reaction. Acidic gaseous contents like sulphur dioxide (SO_2), nitrogen dioxide (NO_2), carbon dioxide (CO_2) of the particulate matters are converted to sulphuric acid (H_2SO_4), nitric acid (HNO_3) and carbonic acid (H_2CO_3) respectively in the presence of moisture and metallic ions such as copper and iron which catalyze the chemical reactions. These acids can cause denaturation of collagen fibre of proteinaceous material like parchment by hydrolytic reaction in

which water is introduced to these polymeric chains through the amorphous region. Manuscripts become discolored and brittle due to the effect of suspended particulate matters. The legibility of written contents of manuscripts is also affected by the deposition of particulate matters.

- The suspended particulate matters are hygroscopic in nature, they settle on the surface of the manuscript collection, they absorb moisture and increase the moisture content of the writing materials and influence the mold growth. It may also cause abrasion by physical damage on the surface of the manuscript.
- Rain from an undetected leaking roof had mixed for centuries with dust to form encrustations upon a great number of manuscripts, many of which resembled to bricks.

2.3. Blood stain

Giacometti et al. [29] explained that blood stains aren't uncommon in historical manuscripts, and historical texts can even be written in blood. Moreover, blood looks almost like iron gall ink, as both haemoglobin and iron gall are rich with the same color-carrying iron oxides, which contributes to the problem of separating ink from blood stains. In criminology, multispectral imaging has been found of assistance when dating blood stains at crime scenes. Blood stain can occur in historical documents, that appear as brownish stains which might sometimes obscure the text. Unlike paper documents, parchment cannot be washed during conservation and stains are thus not usually removable. They explained that from the experimental study on blood stain on parchment, it had been absolutely clear that the blood has made the parchment red like meat, and ob-

scured the writing to imaging under both transmissive and reflective lighting.

Blood stain can result from human beings, as follows:

- Handling: Although rare, it happens that blood staining is caused by a person accidentally injured.
- Storage : In case of a storage room with windows and doors improperly sealed that do not prevent the entry of insects and rodents, which may suffer any wounds that lead to the presence of drops of blood on the manuscripts [48].

2.4. Iron gall ink stain

Corregidor et al. [49] mentioned that the main components of iron gall ink, besides iron (II) sulfate, are tannic acid, Arabic gum, and water. Gall oaks and gall nuts are the two types of galls containing gallotannic acid and gallic acid, which were used as tannic acid sources. Additionally, commercial tannic acid powder was also used.

Boyatzis et al. [50] explained the deterioration of aged parchment marked with laboratory iron gall inks. They explained that hydrolysis of collagen in the acidic environment that resulted from iron gall ink, may degrade collagen fibrils, seriously altering their conformation; and therefore their secondary and tertiary structures. They proved from their experimental study that no actual change in shrinkage temperatures in ink-free areas was observed, but ink areas showed considerable decrease upon ageing, especially in formulations containing no gum Arabic. In addition, calcium sulphate crystals in both inked and ink free parchment areas were observed through elemental micro-analysis; their presence was assigned to ion migration from inked areas to adjacent ink-free regions of the specimens. Their results also proved changed in the chemical composition of parch-

ment and sign of deterioration of the material, including gelatinization under acidic hydrolytic conditions induced by the ink environment.

Albro et al. [51] explained the aspects of deterioration of documents and manuscripts that can be obtained as a direct result of iron gall ink corrosion. They informed that cracks are clear through the ink and documents. Losses are holes in inked areas of documents. Delamination happens at an inked layer of documents splitting or peeling away from the main body of the documents. Discoloration shows diffuse, darkened areas of documents surrounding ink applications.

Yusupova [52] mentioned that other frequently encountered damages are: decay and deterioration of manuscripts, written in acid ferrogallic inks; fading of non-water-resistant and ferrogallic texts; the falling off of texts and colour layer of miniatures; appearance of fragility and transparency; pigment spots of different colour and intensity, different losses, ruptures and cuts.

2.5. Microorganisms stain

Sakr et al. [14] reported that microorganisms (fungi and bacteria) plays an important role in deterioration of parchment with irreversible degradation with different stains derived from different sources of microorganisms. They also explained another aspect of biodeterioration of parchment is the structural damage by secretion of a wide range of enzymes in particular collagenase enzymes that could decompose complex collagen such as parchment into short chain of free amino acids soluble in water that could be used as a carbon source by colonizing microorganisms for their growth and colonization, thus reducing mechanical properties of colonized objects, and in the advanced state of deterioration, these objects may turn into powdery form.

Lech [53] informed that parchment is subject to the process of biodeterioration. This process occurs by microbial enzymatic degradation of organic components of these materials, which in the case of parchment is mainly collagen. Microorganisms can cause changes on the surface of documents, such as stains or discolorations, and can lead to weakness of the structure of the material and increase its brittleness until complete destruction. The most dominant fungi that can be found on organic materials such as parchment include *Alternaria*, *Aspergillus*, *Cladosporium*, *Chaetomium*, *Penicillium*, *Phoma*, *Stachybotrys* and *Trichoderma* genera. She also confirmed that microbial activity in an environment depends not only on their species-related properties, but also on external factors, such as temperature, humidity, pH or light exposure, ventilation pollutants (such as Ozone (O₃) and Volatile Organic Compounds).

Piñar et al. [10] said that when biodeteriorates, parchment becomes rough, assumes a diffuse staining and a porous appearance, and sometimes becomes perforated. They also showed that the microbial alterations detected more frequently on ancient parchments have the following characteristics: red or purple maculae, with nucleated peripheral halo, isolate or coalescent (Fig. 4).

2.6. Adhesive residue stain

There are some types of adhesives that their residue can appear on historical manuscripts such as parchment. Some of these adhesives are rubber based adhesive, starch, protein adhesives (such as hide glue), gum Arabic, tape adhesive, etc, [54]. Adhesive stain can appear on the surface of parchment (Fig. 5) especially with increasing moisture in surrounding environmental conditions [55].

3. Cleaning techniques of parchment

The cleaning processes are considered complicated by the fact that the substance of the object may be very similar to dirt [56]. It is also very important process for the following reasons:

- Reduce or stop the potential for damage to parchment manuscripts, which can cause decrease of pH value, abrasion, and degradation;
- Reveal the aesthetic reasons when it interferes with the visibility of the imagery or information [57].
- Improve the readability of parchment documents or manuscripts.
- Increase the chemical stability [56].
- Cleaning is a necessary preliminary to a further treatment, as when preparing a surface before coating or joining, consolidation, etc. [56, 58].

There are many questions that need to be considered for conservator when undertaking or deciding on a cleaning treatment. Some have already been raised in describing the nature of dirt itself but there are many others which are related to questions of conservation ethics and historical study. Faced with a dirty object you need to ask (and answer) the following questions [6]:

- Why clean?
 - Is it dirt? Should some or all of it remain?
 - Is the dirt causing damage?
- Can the object tolerate being cleaned?
 - What are the physical and chemical properties of the object and dirt?
 - What will affect the dirt without affecting the object?
- What is the effect of cleaning?
 - What will be the appearance of the object surface after cleaning?
 - Will the stability of the object be affected?

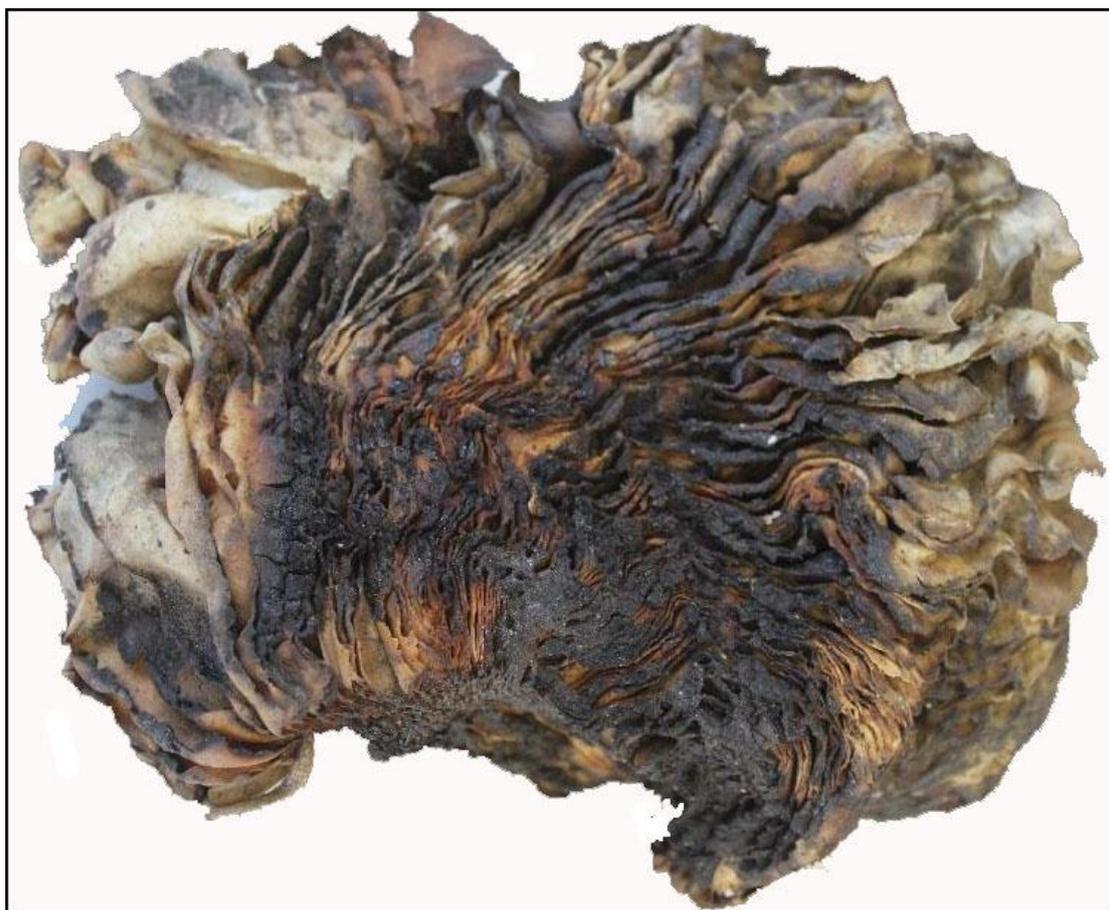


Fig. 3: Soot distorted parchment documents as a result of the heat of the fire [47]



Fig. 4: Microbial stains on ancient parchment [10]



Fig. 5: Moisture staining and brown adhesive staining along split spine fold of parchment [55]

- How often will the object need cleaning in future?
- How can you clean the object?
 - Is there an appropriate treatment?
 - How does the treatment work?
 - Is the treatment safe both for you and also for the object?
 - When do you stop?

The authors confirm that there are some techniques that have been used for the cleaning of parchment documents and manuscripts. These techniques have some advantages and disadvantages, and there are differences between them.

3.1. Surface cleaning

Surface cleaning is the action of removing dust and other deposits from the surface of an object without the use of liquids.

Surface cleaning, is equally to as dry cleaning. It's a mechanical cleaning method used to reduce superficial soil, dust, grime, insect droppings, accretions and etc. Sometimes, it is an initial pro-

cess that precedes cleaning and many other treatments applied for the removal of different stains found on the surface of parchment manuscripts, all sizes of soft hair or synthetic brushes, bristle brushes, "bench brushes." Designate brushes can be used specifically for surface cleaning. Some mechanical removal tools can even be used like scalpels, tweezers, spatulas, needles, wood and metal probes, cotton swabs and pads (dry and dampened) [57]. Munn [59] mentioned that a low suction vacuum might be considered in the surface cleaning of vellum. Hassel [60] said that vacuum cleaner, scalpel, erasers, moist cotton swabs are used in the surface cleaning of parchment documents.

Popular methods in the first half of the last century included the use of pellets of sticky bread, rolled or pressed on the surface; wiping with cotton wool or chamois leather moistened with water; or swabbing with benzene [61-62]. Kite and Thomson [62] said that dry cleaning is important for the cleaning of proteinaceous materials such as parchment. It can

be applied by using a good brush vacuuming, which is effective and required. They also mentioned that smoke sponges, Wishab erasers (sulphur and chlorine free). Groomstick, and glass bristle brushes (used rarely in certain circumstances they may be the only treatment that works to remove stubborn surface deposits and soils) have been used for the cleaning of proteinaceous materials.

The surface of parchment is prepared to achieve specific characteristics; therefore, special attention to the effects of surface cleaning is necessary to avoid damage or altering the surface of this skin. There is usually no problem with surface cleaning, when the surface of parchment is hard and shiny in the same manner as paper [57].

When the surface of parchment is smooth (because it has been pumiced), the closed, glazed character becomes open and velvety because the grain or flesh sides fibres of the skin are only attached on one end, creating a nappy texture. The abrasive nature of surface cleaning can be problematic by actually teasing the fibres away from the skin. It is more difficult to remove eraser crumbs from the different fibres that make up the surface nap [57].

The surfaces of parchment skins may have been coated with a white substance like gesso. Medieval parchment makers used a mixture of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and chalk (CaCO_3) to coat the skins while drying, and scribes used the same mixture for illumination with egg tempera colors. It is necessary to make careful examination under the microscope for parchment documents, which were also prepared overall with a white ground, because this process can help determine the suitability of dry cleaning these surfaces. A haloing effect around words may have been produced by a palimpsest [an original historic erasure made by scraping the surface of the skin to re-

move ink]; this haloing could be disturbed by surface cleaning. Parchments can be surface cleaned with cotton swabs dampened with ethanol : water (1:1). This can remove shine, which may not or may be desirable [57]. Abdel-Maksoud [28] used vinyl block eraser to remove the blur that resulted from the use of marking pen found on a parchment document. He also used a soft brush and sponge rubber to remove the dust from the surface.

Wet methods have been replaced by using alcohol solutions applied locally with cotton buds, which introduce more controlled cleaning with less risk to the surface and to the highly hygroscopic collagen fibre.

Vest [63] stated that the choice of surface cleaning depends on the structure of the surface of the parchment, the adhesion of the ink to the parchment surface and the state of preservation. She also informed that dry cleaning methods are usually excluded if the parchment is in an advanced state of deterioration or the adhesion of the ink to the surface is poor.

3.2. Wet cleaning technique

Vest [63] reported that wet cleaning methods include, among others, the use of saliva, Industrial Methylated Spirits (possibly mixed with water), and ethanol (96%(v/v) with water). The solution is applied on cotton wool swabs and causes less mechanical pressure than the use of erasers. Nevertheless, after drying, the surface can suffer from damages such as transparency or a change from a smooth to a more rough surface. These changes could also be seen by the naked eye. Another major problem associated with water-based treatments of parchment is that a visually intact fibre structure can be transformed into a gelatinous substance by contact with water, and iron gall ink corrosion may cause other irreversible damages.

Wet cleaning was used for the removal of some stains such as paste or residues of adhesive animal glue. The removal of water soluble adhesives such as paste and animal glue needs to be thorough to avoid stiffness and cockling, but not so thorough that the lime is removed from the skin. It is better to use less water when removing paste or glue. When the grain layer has been pumiced, it is very likely to go transparent when wet, particularly if pressure is applied. Working under a microscope is a good idea. Water and ethanol is often helpful in varying concentrations. Heat is disastrous; it will congeal the fibres and make the skin shrink. What cannot be removed at this time can be removed during the humidification process when the adhesive will often swell [59].

3.3. Cleaning with organic solvents

Wet methods have been replaced with alcohol solutions applied with cotton buds, which give more controlled cleaning with less risk to the surface and to the highly hygroscopic collagen fibres like parchment.

Some conservators replaced surface cleaning by using organic solvents especially for moldy parchment. They used cotton swabs dampened with an organic solvent such as ethanol to remove mold growth. This method may be more effective than dry cleaning in some cases, and may be preferred because of the reputed fungicidal property of the solvent. Degraded and moldy parchment may benefit from "washing" with alcohol on the suction table prior to consolidation.

It should be mentioned that the use of solvent will not prevent mold growth in the future. Mold removal should be achieved before any other treatment step to prevent further contamination. Cleaning with solvents is very important, and it can precede consolidation, humidification, or pressing, because all these treat-

ments will make the removal of mold growth more difficult or impossible. Mold-damaged parchment is subject to mold reactivation if it is left in a humidity chamber or damp pack too long.

3.4. Bleaching process

It should be noted that although there have been examples of the use of bleaching agents to remove or reduce discoloration in parchment, these are not common. Lemon juice, hydrogen peroxide, onion juice, and complex mixtures involving ammonia, soaps and chloramine B are included in the bleaching method. In the field of manuscript conservation there has been a gradual trend to minimize the bleaching processes as conservators know very well about the risks in their application, and perhaps because it has been recognized as unnecessary or inappropriate to 'brighten' items simply in order to access text that is already legible. Equally, the use of solutions to intensify faded inks appears to have been abandoned. Although such chemical methods were still being explored as late as 1981 [62]. It was recommended that bleaching materials are very harmful to parchment.

3.5. Laser cleaning of parchment

For the first time in 1978 excimer and Nd:YAG laser cleaning of paper, parchment, and textiles by John Asmus was applied, where 350 nm radiation from excimer and 355 nm third harmonic of YAG radiation yielded were tested as comparable results. Since then from this time many experimental studies for the devolvement of laser cleaning technique have been performed in this field. During the eighties, the technological level of the laser devices increased significantly, Kautek and his co-workers were the first who developed the workstation of laser cleaning programmed [64-65].

Excimer laser was the first type that has been used in the conservation of culture heritage. Q-switched Nd:YAG laser became the most common laser for cleaning of organic materials especially for paper and parchment manuscripts in the infrared and visible range (1064nm, 532nm). It should be mentioned that the use of laser cleaning can be also a great risk on collagen (the main constituents of parchment fibres), besides its risk on inks and pigments constituting the graphics or the drawing applied on documents and manuscripts. There have been many studies on laser cleaning in the past decades, some of these studies have succeeded and others have failed [66].

3.5.1. Ablation threshold in laser cleaning of parchment

The removal of stains layers depends on the ablation threshold fluence F_{th} of the substances to be removed. Therefore, fluence levels must lie below the ablation threshold of the parchment fibres, F_{p-th} . Therefore F must exceed the threshold for the removal of the contamination matter, F_{c-th} , and be lower than the morphological modification threshold, F_{p-m} , as well as the photochemical or chemical conversion threshold, F_{p-chem} (Fig. 6) [67].

A good understanding of the phenomena that occur when laser radiation interacts with a substance is a key element for the success and optimization of any laser cleaning procedures. In general, if it had been assumed that radiation having fluence, that is, energy per unit area, F_0 , interacts with a substance. Part of the energy could be absorbed by the material (F_{ab}), part is also scattered (F_{sc}), and part could also be transmitted (F_{tr}). A picturing of those processes is shown in Fig. 7 [68].

The overall energy balance is given by this equation:

$$F_0 = F_{ab} + F_{sc} + F_{tr} \quad (1)$$

In turn, the absorbed fluence F_{ab} may eventually cause thermal effects (F_{th}) or photochemical modifications (F_{ph}) within the material, and part of it may be reemitted as fluorescence or phosphorescence (F_{fl}). These processes are described by this equation:

$$F_{ab} = F_{th} + F_{ph} + F_{fl} \quad (2).$$

3.5.2. Types of laser used in the cleaning of parchment manuscript:

3.5.2.1. Excimer laser

The gas laser (excimer) emits in the UV region, at different wavelengths, but according to the parchment sensitive nature, all literature preferred to use $\lambda = 308 \text{ nm}$ (XeCl). Using excimer laser in cleaning dust and soot contaminants from ancient parchment, exhibited a high chemical stability of the parchment chemical structures, and the fibre structure showed no changes analogous to conventional methods [23, 69].

3.5.2.2. Nd: YAG Laser

Nd: YAG laser cleaning is the standard laser system for organic materials especially for parchment, it emits on the near infrared region (NIR) at $\lambda=1064 \text{ nm}$ (ω) and three other harmonics 532nm, 355nm and 266nm [17].

Nd:YAG laser cleaning on parchment at 1064nm radiation could remove iron products effectively without any surface damage [70].

The cleaning of dirt and dust can be done by using Nd: YAG Q-Switched laser at 1064 nm (infrared), and 532 nm (green) showed cleanliness surface of parchment manuscript so that there is no photothermal effect on the fibre structure of parchment [71].

Nd:YAG laser at wavelength 1064 nm gave high effectiveness for removing of insect excrements and defilements of calf historical parchment [72]. Kennedy et al.

[73] investigated using Nd: YAG Q-Switched laser at three different wavelengths: 1064 nm (infrared), 532 nm (green) and 266 nm (ultraviolet) for cleaning dirt and dust from parchment by several fluence levels. It shows that laser cleaning of parchment is an effective way for removing surface dirt. They found that laser cleaning at UV wavelengths is not ideal for use in a conservation context because of photochemical interaction of UV laser beam with components of parchment. They concluded that laser cleaning at 1064 nm or 532 nm is not harmful to the collagen structure within parchment at the fluency levels that have been studied there. They also recommended that laser cleaning at 1064 or 532 needs further studies to be adopted in cleaning up historical materials.

3.5.2.3. Er: YAG Laser

It is the most recent laser tested for the cleaning of parchment manuscripts, that emitting at $\lambda=2.94 \mu\text{m}$ by adding water (it is considered a wet method) [74-76]. The aim of adding water or other hydroxylated liquids is to increase the Er:YAG laser pulse efficiency on the surface, but also the hygroscopic nature of parchment may have an effect on the -OH bonds of the chemical structure of parchment. It should be mentioned that this method should be applied carefully and it will be difficult to use it for removal of superficial contaminations [75].

3.5.3. The use of laser cleaning for removal of different stains from parchment manuscripts

3.5.3.1. Dust and soil stains

Femtosecond (fs) laser irradiation (Ti: Sapphire laser) using the fundamental and second harmonic emission (795 and 398 nm), and nanosecond (ns) laser (Nd:YAG laser) was used at the second and third harmonic of the fundamental

emission (532 and 355 nm) for the cleaning of ancient parchments. The result has demonstrated the possibility of elimination of carbonaceous contamination from the specimens [77].

Q switched Nd:YAG laser at three different wavelengths: 1064 nm (infrared), 532 nm (green) and 266 nm (ultraviolet) have been considered successful tool in cleaning dirt and dust contaminations from parchment manuscript by different degree of cleaning and different thermal effect [17,73].

3.5.3.2. Iron rust stains

Papanikolaou et al. [70] clarified that Q switched Nd:YAG laser at 1064 nm employed for the cleaning of iron rust products from parchment manuscript was successful without any thermal effects on the fibre structures. However, more studies are required to apply this technique to archaeological materials

3.5.3.3. Glue stains

Kautek et al. [16], used an ultraviolet excimer pulsed laser at 308 nm for cleaning glue spots from parchment sheet of music, which was part of a choir book dating before 1500 A.D. by ablation method.

3.5.4. Advantages and disadvantages of using Laser techniques

3.5.4.1. Advantages of laser cleaning

There are some advantages for the application of laser cleaning on parchment. It is used for the preservation of historical parchment, it has low environmental impact, versatility and reliability, localized action, the laser cleans only where directed [78]. The following advantages are summarized as follows:

- 1- Contactless tools, which offered no mechanical scratches or harmful stress of the fibres [70].

- 2- Selectivity, so the restorer can determine the cleaning procedures time [18].

Localized action, allowed defining operative fluence ranges ensuring effective discriminations between contaminations to be removed and the layers underneath to be uncovered and define the degree of cleaning process to ensure the safety of the surface without damage of the fibre structure [79].

- 3- Chemical free, no chemicals used in cleaning stains which may have district reaction with the chemical structure of parchment manuscript.

3.5.4.2. Disadvantages of laser cleaning

Laser cleaning technique has minimal side-effects. The disadvantages are summarized as follows:

- 1- Laser cleaning technique has thermal effect, so it can damage fibre structure of parchment manuscript.
- 2- Laser cleaning may lead to discoloration and degradation induced by photothermal reactions especially for parchment manuscript which is considered a very fine and very sensitive material [17].

4. Analysis and investigation

There are many analysis and investigation techniques that can be used for the evaluation of cleaning materials and methods. These techniques can be applied for the experimental studies. The conservator should determine his choice of the method of analysis or examination according to the objective of his need from the experimental study. The conservator can apply some or more of the following analytical techniques:

4.1. Visual examination

Visual examination is very important to describe the forms of deterioration resulting from different stains. It is used for the

evaluation of the cleaning process used for stains removal. It can also be used (by the critical eye of the conservator) to detect the effectiveness materials and methods that should be used in the stains removal.

4.2. Optical microscope

Optical microscope can be used for investigation of the surface morphology of parchment, and at the same time to evaluate the effectiveness of the techniques and materials used in the cleaning process. The effectiveness of optical microscope is very limited, since small magnifications can be obtained.

4.3. Scanning electron microscopy in combination with energy dispersive X-ray microanalysis (SEM-EDX).

This method is considered a micro-destructive sampling technique because of the limited and precious nature of the objects under study. This method allows the investigation of the surface morphology of stained or cleaned parchment. Sometimes, it can detect the composition of the stains (by the identification of elements) and help to choose the correct technique and materials used for stains removal [32-33].

4.4. Transmission electron microscope (TEM)

The authors suggest that this method can be used to detect the depth of the stain through the fibre structure of parchment. It can also be used to evaluate the effectiveness of the cleaning techniques and materials used for removal of stains through fibre structure. This method was used for different purposes by Puchinger and Stachelberger [24], Puchinger et al. [25].

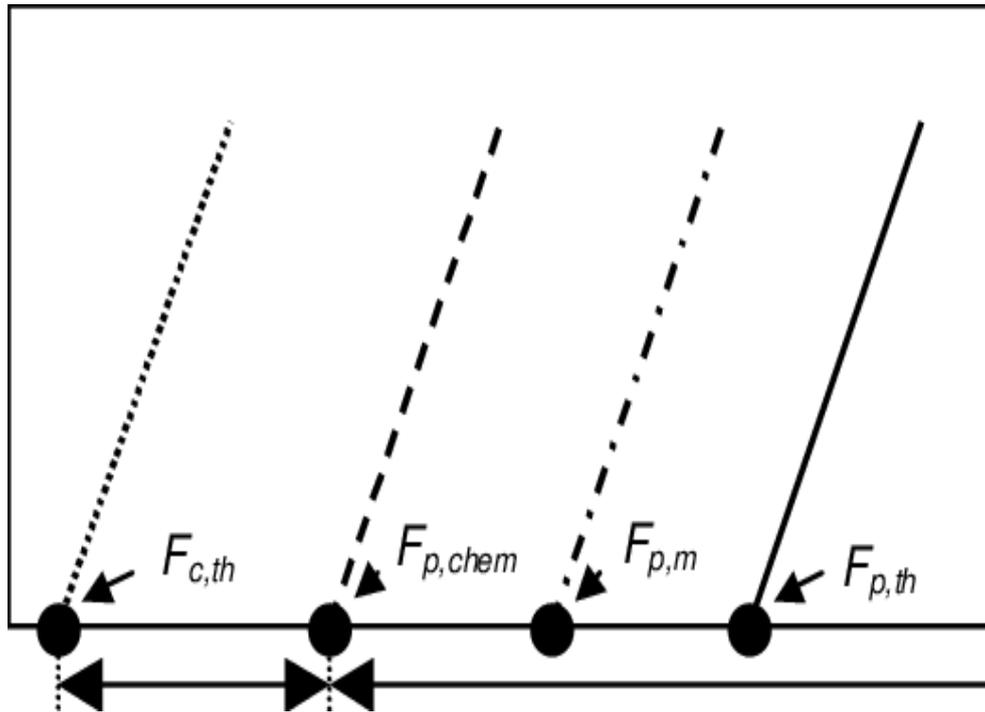


Fig. 6: Important thresholds in laser cleaning of parchment [67]

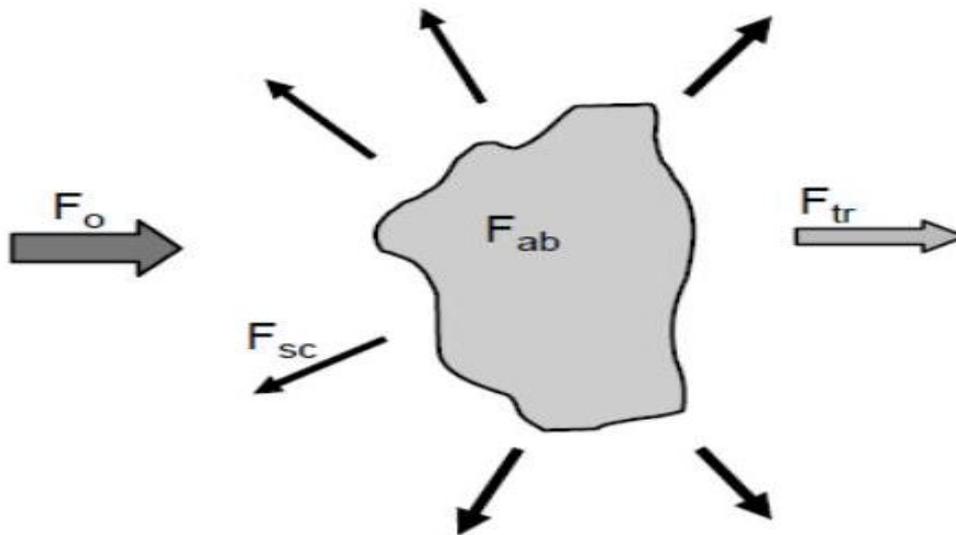


Fig. 7: A simple scheme of processes that may take place when incident radiation of fluence, F_o interacts with a material. F_{ab} , F_{sc} , and F_{tr} are the absorbed, scattered, and transmitted parts of the radiation, respectively [68]

4.5. Determination of hydrothermal stability by the micro hot table method

The hydrothermal stability is a fine measure of the state of deterioration of the parchment, moreover, using the micro hot table method in a small fibre samples gives detailed information on the hydrothermal stability of the parchment fibres. A small sample of fibres from the corium part of the parchment is soaked for 10 minutes placed on a microscope slide with a concavity and covered with distilled water and a microscope slip. The slide is placed in the micro thermo cell and heated at a rate of 2°C/min. The shrinkage activity is recorded by observation through a microscope with a suitable magnification or by video recording [20, 30].

4.6. Amino acid analysis

The method of amino acid analysis is particularly useful to characterize the oxidative breakdown of the parchment corium collagen by the determination of low values of the basic amino acids, and increasing values of the acidic amino acids [20]. It can be said that this method can determine the effect of different stains on the parchment corium collagen.

4.7. Energy dispersive X-ray fluorescence (EDXRF)

The authors suggested that this method can be used to detect the elements found on parchment surface that are a result of some stains, and to detect remains of elements detected after the cleaning process. Wouters et al. [26] informed that due to its mobile configuration, the analysis could be executed in a non-destructive manner by placing the object close to an X-ray molybdenum tube.

4.8. High-performance liquid chromatography (HPLC)

This method of analysis can be used to identify the adhesive stain in order to help the selection of suitable cleaning material and method which can be used for the removal process. The application of this technique can be done according to Wouters et al. [26]. Since they reported that after the sample preparation, the materials component can be identified according to the retention time, and the ultraviolet-visible (UV-VIS) spectrum.

4.9. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR can be used to analyze the effect of stains on collagen in parchment. It can also follow the changes in the function groups especially for collagen after using cleaning materials and methods. According to Abdel-Maksoud et al. [32] Mid infrared (MIR) spectra can be recorded with vertex 70 spectrometer (Bruker Optics, Billerica Inc., Massachusetts, USA) attached to room temperature DLa TGS detector. The spectral range can be 600 – 4000 cm⁻¹ and the resolution can be 4 cm⁻¹ with 16 scans.

4.10. Colorimetry

Each color can be measured using spectrophotometer according to [34] (Opti-match 3100, SDL company, England) from 400 – 700 nm. The color changes were recorded by the CIE L*a*b* system, where L* represents the brightness from 0 (black) to 100 (white), a* represents the red (positive value) or green chromatic coordinate (negative value), and b* represents the yellow (positive value) or blue chromatic coordinate (negative value). The total color change (ΔE^*) was calculated according to the equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where ΔL^* , Δa^* , and Δb^* are the differences of initial and final values of L^* , a^* , and b^* . This method can be used to determine the change of the color surface resulting from stains or from using cleaning materials and methods.

4.11. Microbial contamination study

The biodeterioration of proteinaceous materials is detected by stained spots, loss in tensile strength, and hydrolysis of the proteinic compounds [80]. The isolation and identification of fungi or bacteria species can explain the deterioration mechanisms and can define how to remove the microbial stains and how to select the suitable pesticides that should be used in the disinfection process.

4.12. X-ray diffraction

The authors conform that this method can be used to analyze the stains found on the parchment surface, in order to identify the compounds that form these stains. This will help the conservators to make a very good plan for stains removal.

4.13. Atomic absorption

The authors found that atomic absorption can be used for the identification of elements that can be found in some stains. It will help the conservators to select the cleaning materials and methods for stains' removal.

4.14. pH value measurement

pH value can be measured to determine the effect of stains or cleaning materials on parchment. pH measurement can be done according to Wouters [19]. pH measurements can be performed directly on the aqueous extract with a pH meter provided with a combination electrode.

4.15. Mechanical properties

Mechanical properties are used in the experimental studies (not for historical manuscripts) for the evaluation of the

effect of stains and cleaning materials on parchment. Mechanical properties can be measured according to ISO 3376 [81]. Samples can be taken from adjacent zones of a skin. These samples were 90 mm long, the free length between jaws of the testing machine was 50 mm, and the width of the free length was 10 mm. Six samples can be taken, three perpendicular to the backbone and three parallel to the backbone. The three results averaged for each direction. The samples should be measured after conditioning for 48 hours at 20⁰C and 65% relative humidity according to ISO 554 [82].

5. Conclusions

1. There are different types of stains that can be found on the surface of parchment manuscripts such as stains caused by water, dust, soot, blood, iron gall ink stain, microorganisms, and adhesive residue stains.
2. The embedded dirt or found of stains derived from different sources on the surface can obscure textural information, and affect inks, pigments and dyes on the parchment manuscripts.
3. The parchment properties can be effected after short or long term of exposure to dirt or stains, but this depends on the nature of parchment, nature of stains and surrounding environmental conditions.
4. Cleaning process is a vital process in the treatment of parchment manuscripts. It often precedes different treatment processes such as disinfection, consolidation, humidification etc., since it prepares the surface to accept the conservation materials and allow for more penetration through the fibre structure. It also reveals the aesthetic value of the manuscripts.
5. There are many analytical techniques that can be used in the exper-

imental studies to evaluate the cleaning process of parchment. Some of these analyses are shrinkage temperature measurement, amino acids, X-ray diffraction, Energy dispersive X-ray fluorescence, FTIR, microscopes, etc.

6. The effectiveness of nondestructive (portable instruments) or micro-destructive (such as shrinkage temperature) analytical techniques should be done before the cleaning of parchment in order to detect the best materials and techniques which will be used in the cleaning process, especially if parchment manuscripts suffer from oxidation or hydrolysis processes.
7. All the cleaning techniques of parchment manuscripts have advantages and disadvantages, and all of them are required, but it depends on the state of preservation and nature of stains that define the selection of the suitable cleaning technique. Sometimes one or more techniques can be used for the removal of the same stain from the same manuscript.
8. The use of mechanical cleaning appears to be the safest intervention for the object and conservator.
9. Cleaning by organic solvents is better than wet cleaning, especially for parchment manuscripts which suffer from hydrolysis or oxidation processes.
10. The use of bleaching process should be avoided and excluded during the cleaning process of parchment manuscripts.
11. Nd: YAG laser cleaning is preferred for the cleaning of parchment stains when it emits on the near infrared region (NIR) at $\lambda=1064$ nm, 532nm, 355nm and 266nm.
12. Appropriate precautions should be adopted when cleaning moldy

parchment both to protect the conservator and to avoid contaminating the work environment.

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