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Thermoanalytical methods: a valuable tool for art and archaeology

A study of cellulose-based materials

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Cultural Heritage Special Chapter

Abstract In this study, some results of previous studies concerning papyrus and paper, with special regard of artistic and archaeological materials, are reported and discussed. A historical introduction of such cellulose-based materials and of their use from the antiquity is presented first. The diagnostics and conservation aspects are discussed. The role of thermal analysis for a precise characterisation of these materials is illustrated. Complementary methods of investigation, such as optical microscopy, electron microscopy, X-ray diffraction and various types of spectroscopy are also considered. In addition, alteration or restoration processes may be usefully monitored by means of reflectance spectrophotometric measurements.

Keywords Cellulose · Papyrus · Paper · Thermal analysis · X-ray diffraction

Introduction

With the ever-expanding world of knowledge on cellulose-based materials that is not only of interest in the artistic and archaeological fields, it is a hard task to think of writing a comprehensive article on this subject. The author made every effort to collect the different problems concerning the cellulose-based materials, also considering that the interest should not just limited to archaeological findings. We have also to reflect on the fact that it appears limitative to consider wood, waterlogged or not, papyrus and paper and do not include other materials such as textiles, canvases, paint wooden panels, which have often comparable conservation problems. The author will limit the present paper to a discussion of the application of thermal analysis methods to only two cellulosic materials: papyri and paper. The main purpose of this work remains to encourage in-depth studies regarding the use of thermoanalytical techniques in the diagnostics of historical, archaeological and artistic materials.

Papyrus

A survey of the literature regarding the production and preparation of papyrus sheets and their use in antiquity must start from Pliny the Elder's Naturalis Historia. In the volume XIII (71–82) some interesting notations are given.

> Papyrum ergo nascitur in palustribus Aegypti aut quiescentibus Nili aquis, ubi evagatae stagnant duo cubita non excedente altitudine gurgitum, bracchiali radicis obliquae crassitudine, triangulis lateribus, decem non amplius cubitorum longitudine in gracilitatem fastigatum, thyrsi modo cacumen includens, nullo semine aut usu eius alio quam floris ad deos coronandos.
>
> Praeparatur ex eo charta diviso acu in praetenues, sed quam latissimas philyras. Principatus medio, atque inde scissurae ordine. Hieratica appellabatur antiquitus religiosis tantum voluminibus dicata, quae adulatione Augusti nominem accepit, sicut secunda Liviae a coniuge eius: ita descendit hieratica in tertium nomen.

Different types of paper are therefore described.

> Texitur omnis madente tabula Nili aqua. Turbidum liquoris glutinum praebet. In rectum primo supina

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> tabulae schida adlinitur longitudine papyri quae potuit esse, resegminibus utrimque amputatis, traversa postea crates peragit. Premitur ergo praelis, et siccantur sole plagulae atque inter se iunguntur, proximarum semper bonitatis deminutione ad deterrimas. Numquam plures scapo quam vicenae.
>
> Magna in latitudine earum differentia: XIII digitorum optimis, duo detrahuntur hieraticae, Fanniana denos habet, et uno minus amphitheatrica, pauciores Saitica, nec malleo sufficit; nam emporiticae brevitas sex digitos non excedit. Praeterea spectatur in chartis tenuitas, densitas, candor, levor.

The last sentence characterizes actually the main properties that papyrus leaves must present to be a good writing media.

The history and use

Ancient sources (Herodotus, Theophrastus and Strabo) remind us of different places to grow the papyrus plant: Ethiopia, Palestine, Babylon and Egypt. These sources also talk about various uses of this plant. In these texts, we can find different terms, depending on the use of the plant: *byblos* for making the paper and *papyros* for all other uses. Papyrus was a material of great importance for the dissemination of culture in Greece, Egypt and, in general, the ancient world. Plini the Elder wrote about Egypt as the home of papyrus. The author wrote about the preparation of the leaves that could be used singly or glued together to form a roll. The factories suitable for the construction of the sheets of papyrus were located in the growing areas of the plant because the papyrus had to be worked while it was still fresh. The sheets of paper were produced with the marrow of the plant extract from the stem and cut into strips as thin as possible. These strips were stretched next to each other on a table with the margin superimposed; this was followed by laying a horizontal layer first and a vertical layer second so that the strips met through the layers at right angles. The sheet was then pressed and exposed to the sun for the exsiccation.

After this process, the sheets (*kollemata*), usually about 20 sheets total, were connected to form a roll of varying length, called *tomos.* The roll of the Ptolemaic period (III–I BC) was shorter than the roll of the Roman period (I BC–III AD). Rolls, once built, were treated with various substances, for example propolis or egg whites, before they were ready to accommodate writing. The sheets were often covered with protective substances, such as cedar oil, which kept out, with its smell, insects and rodents that could damage the roll. The roll, thus formed, was used usually first on the front i.e., the side where the fibres ran parallel to the writing, and later were re-used on the reverse side. A wooden rod (*omphalòs*) was usually placed inside the roll as a support that was used to facilitate the withdrawal and then reading. A blank sheet for protection could be placed at the beginning and at the end (*protokollon* and *eschatokollion*) of the roll. The writing on the scroll was placed in columns (*selides*) of differing width and height. The number of rows (*stichoi*) in the column could vary from roll to roll, but the number remained constant within the same roll. The ancient Egyptians used a slender reed (Juncus Maritimus) with the end cut, which formed an acute angle, and then chewed the end to obtain a fine brush. Starting from third century BC, the Greeks used a cane stem that was bigger, and the end was cut at the tip where a crack was then made. With this kind of pen, they continued to use the same ink used by the ancient Egyptians; one such ink consisted of carbon black and diluted rubber that did not cause damage to the papyrus and was considered the best ink.

The papyrus was also used in Greece. It was probably imported into Greece in the seventh century BC. This date has been supported by the Naukrati foundation and the trade relations between Egypt and Greece that were established by Psammetic I (656–609 BC). Papyrus had spread to Greece when Egypt opened its borders to the trade settlements of the Greeks at the time of Psammetic I.

In Egypt, the production, consumption and export of papyrus paper became abundant in the Hellenistic period (III BC) when the manufacture and sales were controlled by the State. This monopoly would continue into the Roman age in the first century AD; to protect their monopoly, the imperial authorities ordered the eradication of the papyrus plant in most of Egyptian territories, limiting the crop to a few districts.

Even in Rome, the use of papyrus paper contributed greatly to the cultural and literary development that began in the third century BC (the term *charta* was common for a roll of papyrus).

During the establishment of the library in Alexandria, Egyptians, at the time of Ptolemy Philadelphus, had a near monopoly on the cultivation and manufacture of papyrus paper. In the period following the conquest of Alexandria by the Romans, papyrus was exported throughout the Mediterranean world. That papyrus made it to the borders of the empire was evident at Dura-Europos, which was on the banks of the Euphrates River in Mesopotamia, where papyrus replaced parchment from 165 AD with the appearance of the Roman garrison and disappeared from the area in 256 AD when the garrison was withdrawn.

Although there have been findings outside of Egypt that were of considerable importance, e.g. the discoveries of papyrus in Ercolano, Derveni in Macedonia or at Dura-Europos in Mesopotamia, it must be said that Egypt was the land that gave the greatest amount of material. There were a few factors that favoured the preservation of a large number of papyrus fragments in Egypt.

1. The main factor was related to the dry climate of that particular land.
2. Another factor was dependent on the socio-political situation. After the conquest of Alexander the Great (331 BC), Egypt became one of the largest centres of Greek culture.
3. Another factor was the foundation of the Library of Alexandria (297 BC) by Ptolemy Soter, which became the largest library in the known world, and reached a capacity estimated at around 400,000 volumes.

The library of Aristotle (IV BC), passed to Theophrastus, then to Nele and then to Epicurus (IV–III BC) who, upon his death, left it to Hermon, was rich with antiquities and important material. Although the library of the school of philosophy was nothing more than a room containing schoolbooks, it was the first model of a library in the Greek world.

The Library of Alexandria was not only a place for the collection of texts in Greek and later Latin, it was also an important cultural centre where people worked together in the so-called ‘Alexandrian philologists’ to fix the text, preparing issues and comments (*ekdoseis* and *hypomnemata*).

Also of importance was the library found in the Villa of the Papyri in Herculaneum, owned by Lucius Calpurnius Piso Caesoninus, father-in-law of Caesar, protector and friend of Philodemus of Gadara, Epicurean philosopher of the period of II–I BC. Between the two generations of Herodotus and Thucydides which determined to be the time of transition from oral culture to the civilization of the book, the role of this library was simply a place to fix and preserve texts.

The real civilization of the book actually began with the Alexandrian age: books began to appear accompanying texts, especially the classics, with a series of signs, starting with accent marks, to help the reader.

Middle and upper Egypt, a place where there was greater preservation of the papyri, was once an area seething with life, being both culturally and politically active. This area was also where the sand of the desert retained much of the light fragments from the ruins of houses, or *kimân* (heaps of wastes) or even graves and archives and what remained of private and public libraries. The findings of that time appeared at the end of 1700, warranting no more than a ‘scholarly curiosity’. Discoveries during this period included documents like the *Charta Borgiana*, a II century AD documentary text that contained a list of the names of workers who had participated in the construction of canals and dams in 192 AD.

Between the years 1752–54 the excavations at Herculaneum began on the orders of Charles III of Bourbon; it was here where, in the interior of the Villa of the Papyri, there were about 2,000 carbonized papyrus scrolls found. These rolls would have to wait 40 years before being published. Oxyrhynchus, one of the towns in the Fayum, has not yet distributed their material. The excavations of Grenfell and Hunt Oxy in 1896–97 continued to bring even more material to light.

Ancient iconographic pictures allowed a better understanding of the manual operations of extractions of the papyrus plants in the appropriate stage of maturation (Fig. 1), as shown, for example, in the mural paintings of Mastaba of Akhethotep and Ptahhotep, a double tomb situated on the west side of the Step Pyramid at Saqqara, dating at the end of Dynasty V. Another example was depicted in the Mastaba of Ti (1473–1458 BC) in Thebes. A scene of papyrus gathering was also depicted in the tomb of Senby’s son, Ukh-hotep, at Meir, Middle Kingdom [1]. All of the images depicted colourful carved images of gathering papyrus and its different uses.

The characterisation

The characterisation and specification of complex materials, such as papyrus, which was used for many purposes and often tastefully decorated, could be achieved by means of complementary methods of investigation, such as macro and microscopic observation, electron microscopy, thermal analysis, X-ray diffractometry and various types of spectroscopy. The results from these methods allowed us to uncover the fabrication methods, historically relevant information, the ensemble of materials used and the refinement techniques of natural resources. In addition, deterioration and alteration processes could be monitored and conservation and restoration procedures could be improved. Several studies were recently carried on [2–7], revealing the important role played by thermal analyses, in addition to other analytical techniques.

The papyrus plant, *Cyperus papyrus* L. (Cyperaceae), is a triangular stemmed reed, which grows to a height of between 1.5 and 3 m and is topped with a bushy cluster of

Fig. 1 Papyrus gathering

fine green, thread-like strands with small flowers on the end. The quality of the papyrus leaves depends upon a number of factors, such as the geographical area where papyrus plants grow, the harvesting and the layer of stem pith used in manufacture. For the study of ancient papyrus, some modern papyrus sheets and papyrus plants were considered first (Fig. 2).

Optical and electron microscopy

Coming from both the Botanical Garden of the University of Genoa and the Ciane River, in Sicily, near Siracusa, different sections of papyrus plant stalks, taken 20 cm from the top of the plant, were examined under a scanning electron microscope (SEM) and optical microscope (OM). The results were compared with those obtained from fragments of ancient papyrus leaves. The lignified parts of both the plant and ancient papyrus sheet fragments were either red (using acid flouroglucine) or blue–green (using Toluidine Blue) and were observed under polarised light microscopy. Calcium oxalate crystals and starch granules were also detected. From these observations of papyrus fragments from different origins, specifically Egyptian and Greek-Roman, it was clear that the ancient Egyptian paper was richer in starch when compared to the Roman paper. It could be assumed that the Egyptian papyrus contained a large quantity of starch, a material that naturally occurs in the plant as a food reserve. It was, in fact, preferably found in the residuals of the vascular bundle sheath. Microscope observations were compared with the results obtained by thermal and calorimetric analyses (TG and DSC). The thermal curves were different depending on which part of the plant was used to manufacture the papyrus sheets, which influenced the amount of cellulose and lignin present (Figs. 3, 4, 5). Moreover, the Egyptian and Greek–Roman papyri were also different in thermal behaviour.

Fig. 2 Papyrus plants in the Botanical Garden at the University of Genoa

Thermal analysis

Two thermoanalytical techniques were applied.

DSC was performed using a Mettler-Toledo® Instrument DSC 821^{e}. Samples (0.5–1.5 mg) were loaded into aluminium pans with lids and heated to 625 °C at a heating rate of 10–1 °C min^{-1} in an oxygen flux (100 mL min^{-1}) and in static air. An empty aluminium pan was used as a reference, and the heat flow between the sample and reference was recorded.

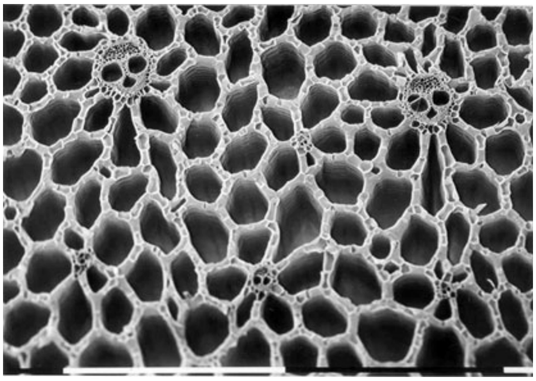


Fig. 3 SEM photograph of the central part of the papyrus plant coming from the Ciane River (Siracusa, Italy). Transverse section. Marker is 1 mm

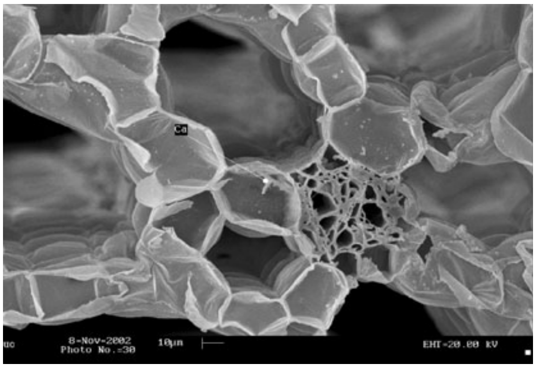


Fig. 4 SEM-EDX image showing several calcium oxalate crystals inside the papyrus plant tissues

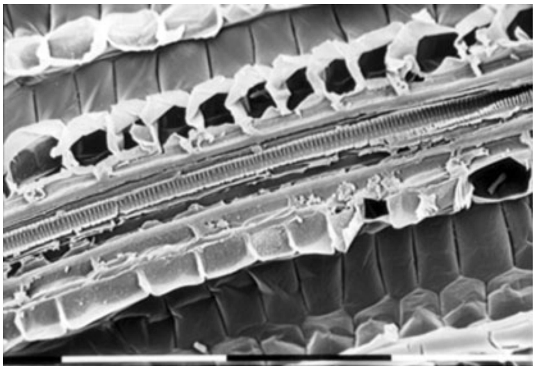


Fig. 5 A SEM photograph of the central part of the papyrus plant coming from the Ciane River (Siracusa, Italy). Tangential section. Marker is 1 mm

In addition the DSC 821, a TG–DTA apparatus STA 409 (Netzsch) was used. Samples, between 5 and 10 mg, were heated over a temperature range from room temperature to 800 °C at a heating rate of 5–10 °C min^{-1} in oxygen at a flow rate of 100 mL min^{-1} and static air. Al_2O_3 was used as a reference material.

Microscope observations were compared to the thermal and calorimetric results. In modern papyri, TG and DSC curves showed a different behaviour depending on the parts of the plant used to manufacture the sheets (see the thermogram of Fig. 6); the difference in the shape of the curves could probably be explained by the different amounts of cellulose, hemicellulose and lignin present in the different portions of the plant. In every DTA and DSC thermogram, the first broad peak was assigned to the decomposition and combustion of cellulose and hemicellulose, and the second narrow peak was due to the combustion of the residual lignin. This behaviour was very similar to the results found by Wiedemann and co-workers [2–4] and was discussed in depth by Basile [5]. A useful comparison for the peak assignment method also was found in the work of Tsujiyama and Miyamori [8], though the different experimental conditions led to a shift in the characteristic peak temperatures.

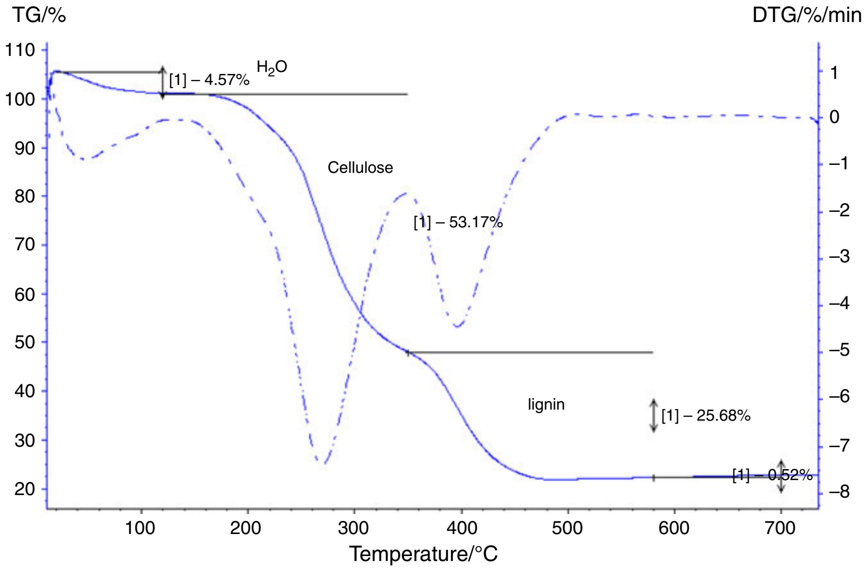
When considering archaeological papyrus fragments, different thermal behaviour was observed between Egyptian and Greek–Roman papyri, as remarked by [7]. The first peak, assigned to the cellulose thermal decomposition, occured at a slightly different temperature (259.0 and 255.6 °C for the Egyptian and Greek–Roman papyri, respectively), and there were some differences in the shape of the curves (the Egyptian curve seemed to be the sum of at least three effects); the second peak, assigned to the lignin thermal decomposition, fell at a remarkably different temperature (421.0 and 405.2 °C for the Egyptian and Greek–Roman papyri, respectively) and had noticeably different areas (i.e., the state of the conservation and quantity of lignin). The small differences in the shapes of the curves have also been related to the differing starch content and constituent clay minerals.

X-ray diffraction

X-ray diffraction methods were in agreement with the results found by the thermal methods. The role of this technique will be discussed in detail in the section on paper.

It was remarkable that the morphological features of the papyrus plant were still visible in ancient papyrus sheets [7], even if they looked deformed due to manufacturing and ageing. OM and SEM analyses highlighted different lignin contents in the various portions of the papyrus plant, which agreed with the experimental results obtained by DSC and

Fig. 6 TG and DTG curves obtained for a central portion of the papyrus. The analysis was performed in static air at a rate of 10 °C min^{-1}



TG analyses. Moreover, SEM and EDX analyses of the modern and ancient papyrus sheets showed that the different manufacturing methods (and also in many cases, its origin) caused the curves obtained by thermal and calorimetric analyses to behave differently. In conclusion, experimental data demonstrated that DSC and TG analyses, combined with electron and optical microscopy, in addition to X-ray diffraction, were useful tools for the study of ancient papyri.

The analysis performed allowed for the accurate characterisation of methods for obtaining additional information concerning papyrus. Of particular interest were studies carried out by [5], which led to the data on the temperature achieved at Herculaneum during the eruption of Vesuvius in 79 AD. In fact, the rolls of papyrus found partially burned in Herculaneum have shown, through a study of calorimetric and thermal gravimetric analyses, that the local temperature, as a result of volcanic eruption, did not exceed 300–320 °C. Another interesting aspect was that papyri with different kinds of manufacturing present different conservation problems, which was already noted many years ago by Geraud [9] and Wattenbach [10]. In particular, the Roman papyri were thicker than the Egyptian papyri (this led Davy [11] to assert that the Roman papyri were two sheets glued together). Moreover, glue and whitening substances used in the manufacturing process have prevented the rolls from reaching the same degree of carbonation. This was evidenced by the lighter colour and by the marks left by moisture that led to a series of damages.

The studies carried out by Humphrey Davy

Davy [11], at the time of the discovery of Herculaneum, was extensively involved in the problems concerning the papyri. A series of experiments were conducted by heating fragments of papyrus and analysing the gas evolved. Other observations were made regarding the colour of the leaves.

> Various specimens of papyri were heated to dull redness in a small covered crucible of platinum to which air had no access. Some of the chestnut and most perfect specimens lost nearly half their weight, and the very black ones, and those containing the large quantity of white ashes, all lost more than one-third….. When the whole of the carbonaceous and vegetable matter of the papyrus was destroyed by slow combustion, the white ashes remaining, which were principally carbonate of lime and lime, proved to be from 1/10 to 1/20 of the original weight of papyrus;…. and a larger quantity was insoluble in acids. Ammonia was found in the products of all the papyri that I distilled,….from which it is probable that it arose principally from decomposed glue, used in the manufacture of the ink….

However, Davy was convinced that 'the operation of fire is not at all necessary for producing such an imperfect carbonization of vegetable matter….The results of the action of heat upon the different species of papyri, proved likewise, that they had never before been exposed to any considerable degree of temperature' [12].

With regard to the ink used in the ancient Egypt had already been analysed by Davy [13] and consisted of a suspension of carbon particles in shellac; '….the ancient ink was composed of finely-divided charcoal suspended in a solution of glue or gum…'

Conclusions

In sheet manufacture, the patterns for thermal analysis of a typical papyrus plant are different in the different parts of the papyrus when optimal age conditions are used [7].

The methods of calorimetry and thermal analysis showed that the proportions of the main constituents of the papyrus (cellulose, lignin and minerals) vary with the age of the plant, manufacturing processes and environmental effects.

DSC investigations, which were micro-destructive in the conservation of materials, contributed effectively to identify a number of additives used in the manufacture of papyrus leaves.

The set of measurements could provide a characterisation that was as complete as possible of the material, its manufacture, its condition and its deterioration over time.

Paper

The paper consisted of two main components: cellulose and additives. Cellulose, made from linen rags, cotton rags and wood pulp, and additives, consisting of dyes, fillers and binders.

The oldest papers, which consisted entirely of cloth cellulose, had a very good permanence (the property of a material to maintain and preserve its chemical and physical characteristics over time) when stored in an appropriate environment.

The invention of movable type for printing gave an incredible boost to paper production with the consequence of shortages in raw materials.

To be durable, a material must also be stable. A book or a document would last a long time only if the characteristics of the materials they contained were likely to ensure that they do not deteriorate over time.

The causes of deterioration of library materials may be chemical, physical or biological. In this paper, the chemical and physical causes, grouped for clarity in external physical–chemical factors (environmental) and internal physical–chemical factors to the paper were examined.

External factors

1. Climate-environment (high temperatures, humidity, temperature changes and humidity changes, light and radiation and some particular types of weather)
2. Air pollution (dust, soot and smoke, mist, sulphur dioxide and sulphur trioxide, hydrocarbons, ozone, nitrogen oxides, ammonia and amines, hydrogen sulphide, chlorides of marine origin, etc.)
3. Use (mechanical stress, bad storage, grease and perspiration, stains, accidents, vandalism, theft, etc.)
4. Disasters (wars, fires, earthquakes, floods, etc.)
5. Improper restoration (restoration that was wrong or unnecessary)

The main degradation factors have been:

Temperature

An increase in temperature can accelerate all degradation reactions through oxidation by the atmospheric oxygen, causing yellowing and brittleness in the paper.

The increase in temperature also favours the negative action of other factors, such as that of water: the reactions of hydrolysis are in fact greatly accelerated by an increase in temperature. To remain in good condition in storage, but also during consultation or in exhibitions, the temperature should be between 18 and 22 °C.

Humidity

It is useful to recall some practical definitions:

Absolute humidity ‘p’ is the mass of the water vapour contained in the unit of volume (or mass unit) of moist air at a given temperature. Absolute humidity at saturation ‘P’ is the mass of the water vapour contained in the unit of volume (or mass unit) of moist air when, at a given temperature, the moist air can not absorb more steam; that is, the maximum amount of water in the steam, which may be contained in a m^3 of air at a constant temperature. The moisture saturation depends on the temperature, and it increases with increasing temperature. Relative humidity is the ratio in percentage between the absolute humidity and humidity at saturation:

$$\mathrm{RH} = \frac{\mathrm{p}}{\mathrm{P}} \cdot 100$$

At saturation, p = P, and the relative humidity is 100%. For example, a pure cotton paper in a conditioned environment with 50% RH contains 5–7% in mass of water; if the paper is carried in an environment with 80% relative humidity, it will absorb more water, while in an environment with 30–40% RH, it will tend to lose water.

The condensate water can cause stains, gore, solubilisation of inks, pigments and defacement of the ligatures. It has been recommended that for proper preservation, a relative humidity between 45 and 55% should be maintained. Ideal environmental conditions, if any, should be achieved by varying the temperature and moisture very slowly. The effects of high humidity have been particularly evident on organic materials (papyrus, parchment, paper, wood, leather, etc.) that have a cellular structure and are hygroscopic. Excessive humidity causes swelling and deformation, which causes hydrolysis of cellulose, collagen skins and parchments. It also favours the attachment and growth of microorganisms that can cause considerable alteration or complete destruction. However, moisture that is too low hardens the skins and parchments and dries bindings. Certain variations in the temperature and humidity, including those due to changes in temperature from day to night, cause distortions and curvatures in the media, which can lead to the separation of pigments and inks.

The main effects of important gaseous compounds, with the exception of ammonia and volatile amines that have a basic reaction, have been the decrease in the pH of the material. Particular attention has been reserved for the gaseous compounds of sulphur and nitrogen oxides. Hydrogen sulphide, which can be either naturally occurring or introduced into the air from industrial discharge, reacts with metals and forms compounds generally dark in colour and therefore can produce changes in the pigments of miniatures, watercolours and gouaches. Sulphur dioxide, SO_2, forms sulphur trioxide, SO_3, by oxidation; in the presence of moisture, it may form sulphuric acid and then attack many materials, especially those of organic origin, such as paper and leather. The process of oxidation of sulphur dioxide to sulphur trioxide is catalysed by the heavy metals such as iron and copper and their ions. The absorption of SO_2 promotes acid hydrolysis of cellulose and other organic components of the paper, which quickly leads to depolymerisation of the material, and then to its destruction. The degradation of paper caused by absorption of SO_2 has been very marked if the paper contains lignin and when manufactured cellulose degradation is poor. Nitrogen oxides, NO and NO_2, are formed in the combustion process above 1200 °C in the presence of air. These gaseous compounds can cause damage to materials because they also induce acid, resulting in acid hydrolysis. Therefore, they have been harmful to paper, textiles, leather and some organic pigments. The ozone (the concentration in the air can be as high as 1 ppm in exceptional cases) has a specific action on organic materials, attacking them, splitting the double bonds and forming oxidized groups, aldehydes and ketones. The oxidizing action of ozone has been particularly strong on wet paper, causing major damage in a short time.

Internal factors

1. Intrinsic instability of the materials often worsened by the manufacturing processes (the evolution of manufacturing processes through the centuries has led to a product with features always less suitable for storage)
2. Tanning (for leather and parchment) that has been performed poorly
3. Inks and other acid substances
4. Impurities (metals: iron, copper, etc.) causing catalytic reactions of degradation.

Unfortunately, the huge demand for paper in the centuries after the invention of printing with movable type has caused a decline in the demand for quality.

In the above figure, a paper working machine as depicted in ‘Recueil de planches sur les sciences, les arts liberaux et les arts mechaniques’ at the end of the XVIII century is drawn.

Modification of fibrous substances

At the end of the eighteenth century, the discovery of chlorine and the increased demand for raw materials due to the invention (in the first decades of the nineteenth century) of the paper machine led to the use of straw, paper pulp, mechanical wood and finally to the preparation of chemical pulp, semi-chemical pulp and ultimately the modern high-yield pulp. All chemical extraction treatments of cellulose from wood, eliminating the non-cellulosic components, have been quite energetic treatments, performed at high temperatures that degrade the fibre. Furthermore, the process of bleaching the chemical and mechanical pulp has used mainly oxidizing compounds, such as chlorine and derivatives and peroxides, which in addition to modifying the molecule of cellulose, have oxidized and therefore created acid groups and also have left acid residues that cause the hydrolysis of β-glycosidic bonds of cellulose.

The stability of mechanical wood pulp has been very low because other substances in the wood, mainly hemicellulose and lignin, were much less stable than the cellulose; through degradation, these substances produced coloured acid groups that degrade the cellulose as well as the entire fibre.

Hemicellulose, whose structure is mainly amorphous, is easily accessible to various reagents and rapidly degradable; bonds in the hemicellulose consist of glucoxilans glucomannans and have a hydrolysis rate 6 to 10 times faster than that of the β-glycosidic bonds of cellulose.

Development of refining techniques

Highlighted in a study by Barrow [14] on the quality of paper in books printed from about 1500 until the first half of the 1900s, starting from the end of 1600s, there was a considerable worsening in the mechanical properties of paper, particularly concerning the resistance to the double fold. At the end of the seventeenth century, systems refineries encountered a major breakthrough with the invention of the refiner called ‘Hollander’, which reduced the refining time with great economic advantage but produced a paste with worse characteristics. In the following centuries, other methods of refining have tried allowing a ‘continuous process’, always with the aim to speed the process of making paper. At the end of the 1800s, the conical refiner was invented that led to the modern disc refiners; all of these systems have been drastic in regards to the degradation of the fibres.

Modification of the sizing technique

The sizing, which was necessary to make the felt of cellulosic fibres suitable for writing, was not present with mucilage, or rather vegetable gums or starches, until the first major innovation made by the masters of Fabriano in the twelfth century. The invention of sizing with gelatine allowed for nearly dry paper by virtue of soaking it in a lukewarm solution of the adhesive. With the exception of biological damage associated with the biodegradability of these products, sizing starch or gelatine had no major problems with chemical stability.

The degradation of glues based on starches could produce acid compounds that result in the degradation of cellulose, especially in paper sized with gelatine, which necessitated protection against unlawful acts of environmental pollution. The trouble began in the seventeenth century when alum was added to the gelatine to improve the yield. Natural alum is aluminium and potassium double sulphate, which has an acid reaction that accelerates the degradation of cellulose in the presence of moisture.

The situation worsened when, in the first half of the nineteenth century, people began to use the so-called sizing paste, which was used in the preparation of ‘soap’ by the dissolution of rosin (obtained from the resin of coniferous trees) with hot alkali; the mixing of this alkaline solution with the frothy and fibrous mixture caused the precipitation of rosin on the fibre with the addition of alum. From a practical point of view, it was obtained the advantage of working more quickly and using a cheaper product than gelatine, but it had the disadvantage in that it needed to be applied hot. Unfortunately, with this type of sizing, the piece of paper is 'born' acidic: the precipitation of the rosin in the finely divided fibres occurs at a pH of about 4–4.5. In the following decades, when natural alum, due to economic reasons and advances in the chemistry of aluminium, had been replaced by aluminium sulphate, a paper even more sour was obtained. In fact, the aluminium sulphate used in the paper mill, obtained from the treatment of bauxite, was always impure because of the presence of sulphuric acid.

Inadequate tanning processes (for leather and parchment)

The conservation of leather always had special importance because it was not only used for the cover of a bound book but also for furniture or other special items of use.

For all the various uses, the leather must be shaped; leather did not prevent the imprint of engravings and allowed for good adhesion to a layer of gold or other metals. For these reasons, it was used as bookbinding leather, tanned with tannins, the so-called vegetable leather, which, unlike the chrome leather that was too elastic, keeps 'the form'.

The deterioration has been undoubtedly due to excessive acidity inside the leather, which to be strong must have an acid pH; however, the pH should not be less than 3.5. The action of buffers, such as lactate or potassium citrate, had been used for leather successfully tanned with vegetable tannins, but it was not recommended for chrome leather. For the conservation of the scrolls, the problems were caused by defects in manufacturing: an excess of lime made the rolls whitish, dry, rough, inelastic and greedy for water; the hair side could turn brown, while the flesh side could turn white and dry. However, a lack of lime made the leather fat and oily. The most serious damage to the parchment was essentially biological. In a humid environment, the attack of microorganisms was facilitated, while in an environment too dry, curl and deformation occurred.

Acidity of the paper, ink or other acid impurities

The acidity, whatever the origin, was the main cause of chemical degradation: the hydrolysis of the β-glycosidic bonds in cellulose increased with decreasing pH, thus reducing the degree of polymerisation. The bonds in hemicellulose were even more sensitive, making them more accessible to various reagents (water, oxygen, etc.). The oxidation of lignin produced acidic compounds that increased the acidity of the paper, which in turn promoted the hydrolysis of the cellulosic components.

An important source of acidity, which caused extensive damage to library collections and archives, was the acidity of the ink, the so-called gallo-tannate of iron, which could cause perforation of the cellulose support. The oldest inks prepared with carbon black or other carbon particles dispersed in mixtures of arabic gum or other ligands had no problems with acidity and thus preserved the rolls or, in some cases, allowed for easy removal after the loss of binding power. The ink, called iron gall, ferro-gallo-tannics or iron gallo-tannate, was undoubtedly less penetrating and more easily removed with respect to the cellulose support. Because of this, it was possible to revive their properties with chemical treatments, or have them read by appropriate photographic systems, even when the old writing had faded or abraded.

These inks were prepared by reacting ferrous sulphate (green vitriol or *copperas*) with tannins extracted from items such as wood, leaves and gallnuts. From this, a black powder was obtained and dispersed in wine, vinegar and arabic gum, which in addition to keeping the dust in suspension provided the right consistency for preparation and adhesion. From the reaction between Fe^{+3}, resulting from the oxidation of ferrous sulphate, tannic acid and phenol groups formed a black-coloured complex that was very stable, and sulphuric acid. Due to the presence of sulphuric acid, this type of ink was a 'born' acid.

The situation worsened in the mid-1800 when the patent Leonhardi (an ink called "alizarin ink") was fabricated where the iron complex formed by the reaction described remained dissolved in a solution of a mineral acid.

The inks were made with black smoke and soot and were dispersed in linseed oil, which was either raw or cooked. The linseed oil easily underwent oxidation, which produced acidic compounds that had an adverse effect on the conservation of paper. Modern printing inks (printing, lithography, offset) have a more complex composition, containing resins, mineral oils, drying agents, pigments and solvents, making their stability to ageing and their influence on the print media not completely clear. The presence of transition metals certainly has had a negative impact, while in some cases the need to operate in an acid environment at pH 4–5 has been equally harmful.

Metallic impurities catalysing the degradation reactions

The presence of specific metal ions in the paper, especially transition elements (iron, copper, cobalt and manganese), has a negative effect on the conservation of paper. These ions may be in the paper because they were present in the water used for manufacturing, in the wood pulp, dyes or inks. One source of impurities has been derived from the use of recycled paper.

The ions of these metals were catalysts of the main degradation reactions of the paper i.e., oxidation, hydrolysis and the cross-linking. It appeared that the transition metals accelerated the oxidation of cellulose using atmospheric oxygen with a free radical mechanism and the formation of peroxides. These metal ions also catalysed the oxidation of sulphur dioxide to sulphur trioxide and then promoted the production of sulphuric acid in the paper. In conclusion, the ageing of library materials has been a natural evolving process that has been both spontaneous and irreversible. The process cannot be stopped, and the rate of degradation can only be slowed by minimizing or eliminating all the concomitant reasons that accelerate the process.

The miniature

The use of vegetable gum, such as what was found in paint binder, was due to demands for more aesthetic inks; it softened the colours in the rubber and included items such as egg white, that despite having less elasticity, showed a higher gloss and improved colour quality in pigments. In general, vegetable gum was dissolved in the rubber of all the colours that people wanted for achieving a brighter tone, while the egg white was added to the colours that people wanted for achieving more opaque tones. To use the egg tempera, it was beaten and filtered to make it soluble. Then, to preserve it, a few amount of realgar was added.

The evaporation of water produced a very stable and durable paint film but was sometimes fragile. Often the actual binder was added as plasticisers in order to prevent cracking the paint film. Historically honey, sugar and glycerine were used as binders (Figs. 7, 8, 9).

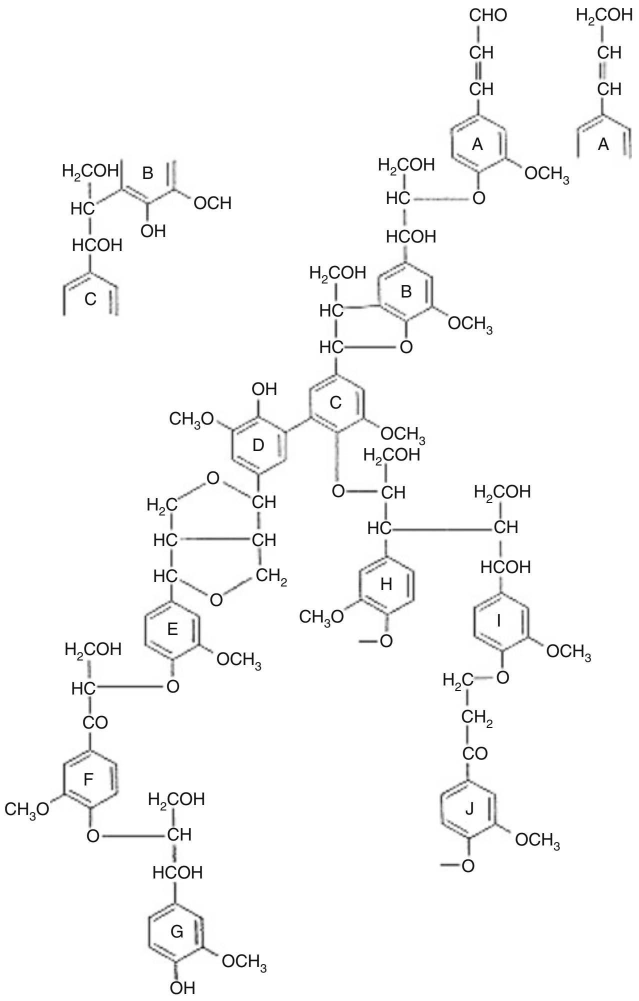


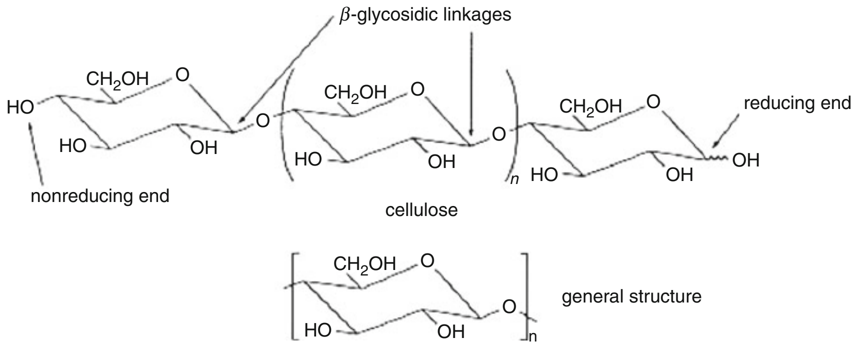
Fig. 8 A type of lignin

The characterisation

Crystallinity value

In order to find the crystallinity value for cellulose, X-ray diffraction for different paper samples (in Fig. 10, the

Fig. 7 Cellulose chain



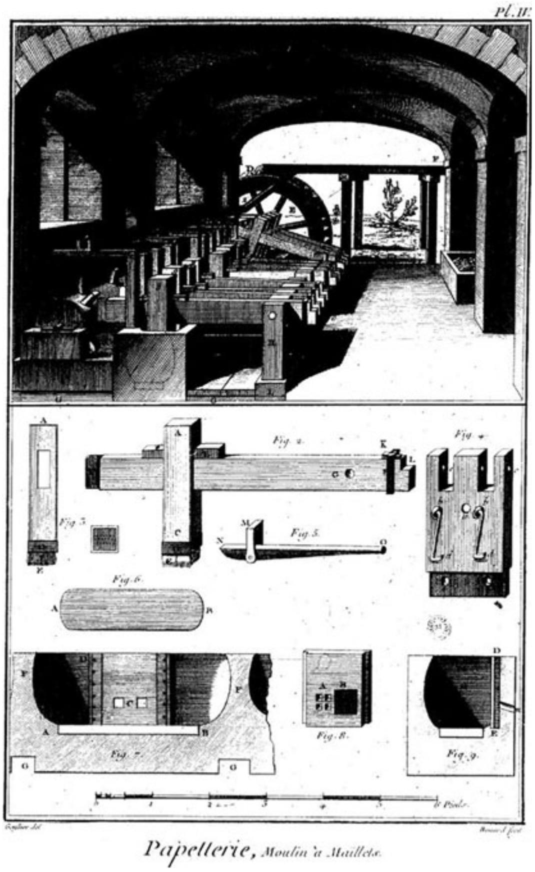


Fig. 9 A paper working machine of 1700s (Source: gallica.bnf.fr/ Bibliothèque Nationale de France)

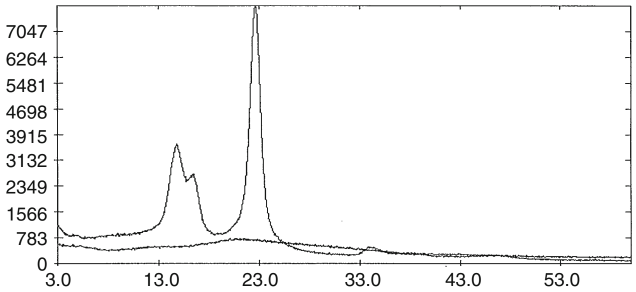


Fig. 11 Wide angle X-ray diffraction pattern for Whatmann pure cellulose paper compared with amorphous cellulose. Counts in arbitrary units versus 2θ

Fig. 12 SEM photograph of artificially degraded Whatmann paper

result for Whatmann pure cellulose paper is shown) were compared to a reference sample treated with dimethylacetamide and 7% LiCl and then precipitated in water in the amorphous form. For the acquisition of data, Ni-filtered CuKα radiation was used with a step of 0.05° and acquisition time of 5–20 s. From the ratio between the height of the (002) peak and the height in the correspondence of the amorphous curve, the percentage of crystallinity was obtained [15, 16] (Fig. 11).

Degradation of the fibres and of the paper sheet

In Fig. 12 it is shown the acidic degradation effect on the cellulose fibres, as it results from the electron microscopy observation.

Other examples of paper degradation are shown in Figs. 13, 14, 15 and 16. The discoloration of the paper may be usefully monitored using reflectance spectrophotometry.

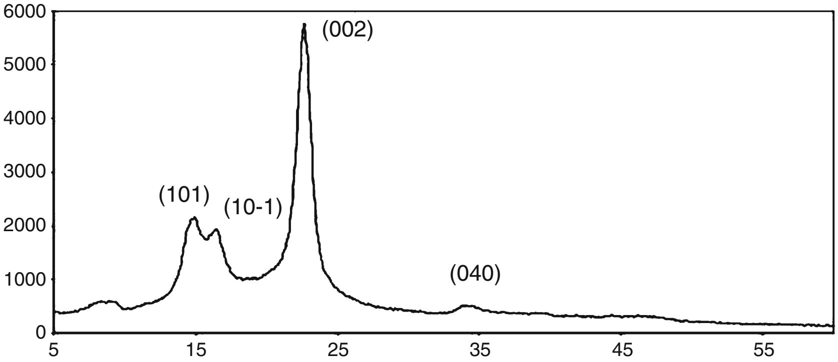


Fig. 10 Wide angle X-ray diffraction pattern for Whatmann pure cellulose paper. Counts in arbitrary units versus 2θ

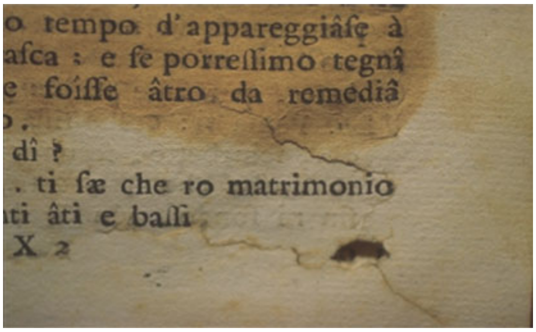


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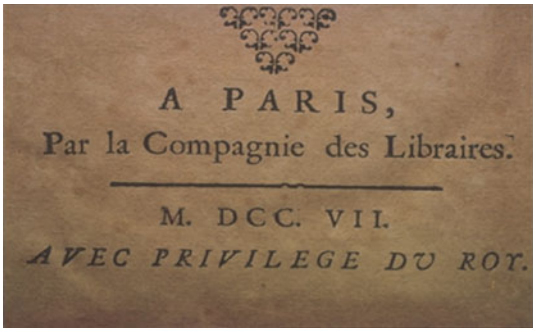
Fig. 13 The gore effect of water and ink acidity on a 1700s book's sheet



A PARIS,
Par la Compagnie des Libraires.
M. DCC. VII.
AVEC PRIVILEGE DU ROY.

Fig. 14 The effect of intrinsic acidity on a 1700s book

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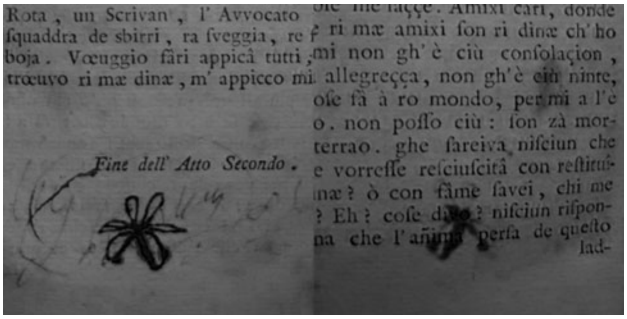
Fig. 15 The effect of humidity and intrinsic acidity on binding of a 1700s book

In several experiments, the effect of cellulose oxidation on thermal stability was studied by thermoanlytical methods. For artificial ageing sodium periodate was used [17].



Rota , un Scrivan , l' Avvocato
ſquaddra de sbirri , ra ſveggia , re
boja . Vœuggio fâri appicâ tutti ;
trœuvo ri mæ dinæ , m' appicco mi
Fine dell' Atto Secondo .

me façce . Amixi cari , donde
ri mæ amixi ſon ri dinæ ch' ho
mi non gh' è ciù conſolaçion ,
allegreçça , non gh'è ciù ninte ,
oſe fà à ro mondo , per mi a l'è
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Fig. 16 The effect of acidic ink on the reverse page of a 1700s book

Cellulose paper (Whatman no.1, chromatographic grade) was oxidised with 0.1 M sodium metaperiodate several times for 0–11 days at room temperature, and the paper was then analysed with FTIR before and after chemical treatments (reduction, further oxidation or alkaline hydrolysis). The results obtained from wide angle X-ray scattering (WAXS) were compared with the deconvolution of infrared data in order to obtain the crystallinity values. The cellulose oxidation in isolated domains by periodate was verified, which led to a significant decrease in crystallinity. In particular, alkaline hydrolysis (β-alkoxy fragmentation), followed by a mild acid treatment, removed the oxidised groups and recovered most of the crystallinity of cellulose.

Using simultaneous differential thermal analysis and thermogravimetry, the effects of different oxidation degrees on paper stability were also studied [18]. The conversion of 1,2-dihydroxyl groups to dialdehyde through periodate oxidation was determined and followed using thermal and calorimetric analyses.

Paper consolidation

This step of studies was followed by a series of tests regarding the graft of co-polymerisation using several monomers on the reactive sites obtained on cellulose using different oxidation methods. Also in this case the results of grafting were followed by means of thermal analyses [19, 20].

Kinetic studies

From the kinetic point of view the pyrolysis reaction of cellulose was described in term of Arrhenius equation [21, 22].

Conclusions

The set of analyses performed allowed for the accurate characterisation of paper, for its degradation and for its consolidation. Thermal analysis, also in this case, is a useful tool to follow the deterioration over time and to prevent it, pointing out the degradation mechanism and its possible causes.

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