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Photo Oxidation of Paper Documents

A Literature Review

by JOHN B.G.A. HAVERMANS & JAVIER DUFOUR

INTRODUCTION

In order to extend the lifetime of paper-records and books, librarians and archivists will store them under a controlled environment when possible, even though, the deterioration process of the papers stored is still continuing. About 50 years ago serious deterioration was found on paper documents as a result of for example, the application of acidic materials such as rosin-alum sizing. To avoid this type of acid deterioration, standards have been developed to increase the durability of newly manufactured paper. Main changes in the paper manufacturing process are for example the use of alkaline compounds and the choice of the raw material. Although standards are now predicting the lifespan of paper, there is still no agreement to what qualities paper have to be tested, in order to be sure about its durability behaviour, especially to consider the environment where the papers would be stored. The wish of each librarian and archivist is indeed a controlled environment, however due to the high costs, the realization of such storage is not always feasible.

Air pollutants, airborne particles, present in these storage rooms, may stimulate the deterioration of the paper [1,2,3,4]. Recent investigations showed that for example SO_2, and NO_x will stimulate the paper deterioration, even if the paper stored is alkaline.

Another problem perceived is the deterioration of paper by light, not limiting only to the well known problem of the photo yellowing of cellulose materials and in special newspapers[5]. Due to restrictions in archives, libraries and museums, papers are well protected against light sources, which may emit a radiation causing the photo deterioration. Still the effects of the photo deterioration of paper should not be underestimated. Recent research showed for example that papers after deacidification became more sensitive towards photo deterioration[6]. There-

fore this paper will present a review on the theoretical backgrounds of the effect of light on the deterioration of paper.

PHOTO-DEGRADATION OF CELLULOSE

Photo-degradation and photooxidation of cellulosic materials have been widely investigated, both in presence and in absence of oxygen. If high temperatures are involved, cellulose degrades by thermal oxidation[7,8]. Initially, at increased temperatures, cellulose radicals may form, and these may react with oxygen to produce, for example, hydroperoxide radicals (see Fig. 1).

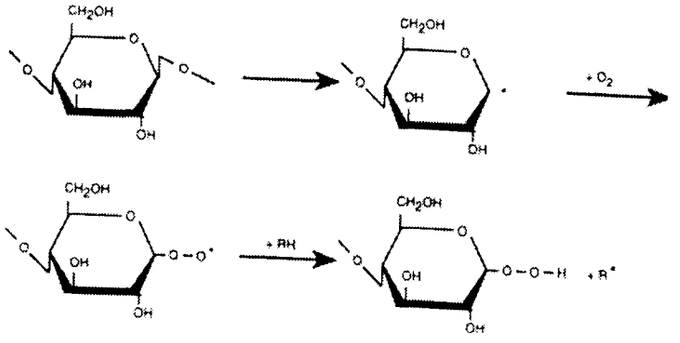

Fig. 1: Oxidation of cellulose and the forming of hydroperoxide radicals

As oxygen reacts preferentially in the amorphous region, thermal oxidation will somewhat enhance the fraction of microcrystalline cellulose. According to Havermans, due to thermal ageing both the crystalline fraction of the cellulose and the equilibrium moisture content will decrease[4].

Secondly, the hydroxyl groups present (C_6-alcohol group and C_2 and C_3 alcohol groups), and the reducing end-groups are easily oxidized[7,8,9], to give aldehydes and carboxyl groups. The ring structure of the glucose unit may remain intact. When the C_1-H or C_4-H bonds are attacked during oxidation, chain rupture will presumably result. Some major end products of this type of degradation include glucuronic acid, gluconic acid and aldaric acid. The thermal degradation of cellulose can also yield 1,6-anhydro-β-D-glucopyranose, and this reaction is used for a synthesis of this compound. This depolymerisation occurs rapidly if the material is exposed to microwave radiation[10] (Fig. 2).

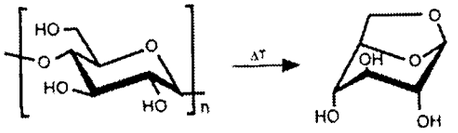

Fig. 2: Synthesis of 1,6-anhydro-b-d-glucopyranose from (1→4)glucans using microwave radiation (according to Straathof et al., 1988)

Dehydration reactions may also occur, and these may be classified as:

- intermolecular dehydration (cross-linking), and,
- intramolecular dehydration (formation of double bonds, monomers may dehydrate to give furan systems).

Dehydration reactions generally occur in an acid environment, hence this type of reaction is only of secondary interest in these investigations. depolymerization, where cellulose breaks up into smaller units under the influence of oxygen and increased temperature, mostly produces 1,6 anhydro-ß-D-glucopyranose, also known as levoglucosan. An outline of the oxidation products which can be formed is given in Fig. 3.

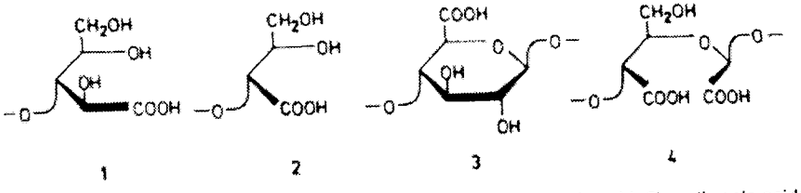

Fig. 3: Some carboxyl products formed after oxidation; 1) arabinonic acid; 2) erythronic acid; 3) glucuronic acid and 4) di-carboxilic acid structure.

The first attempts to study the photo-degradation were carried out by exposure to sunlight. Yellowing was found due to such exposure, but different results were obtained when the sunlight was glass-filtered. In this case, sunlight could bleach the papers. This phenomena were due to the different light spectra involved in the tests, since glass filters out the far UV, and to temperature effects[11].

Only light which is absorbed by a molecule is effective for producing chemical changes. With highly purified cellulose there is no absorption in the visible region,

but it also remains uncertain whether there is any specific absorption in the ultraviolet region, and if there is, what are the absorbing groups or chromophoric systems responsible[12].

Three degradation mechanisms can be differentiated: direct photolysis produced by wavelengths lower than 3400 Å, photosensitised degradation promoted by the presence of impurities or lignin, and photochemical initiation of free radicals[13].

Direct photolysis

In direct photolysis, the rupture of the chemical bonds occurs by the absorption of light with a sufficiently high energy. The exact energy required will depend on the nature of the bond and the atoms involved. The cleavage of either carbon-carbon of carbon-oxygen bonds will require an energy of 80 to 90 kcal/mole. Removal of hydrogen atom require about 100 to 110 kcal/mole. This energy requirements will be met by ultraviolet light of wavelength 3400 Å or shorter, which corresponds to 84 kcal[14]. Actually, there is no doubt that wavelengths greater than 3100 Å are unable to photolyse pure cellulose directly[12]. In this way, a mercury vapour lamp emitting 2537 Å is capable of inducing photo-degradation processes.

Experiments using cotton cellulose and an irradiation of 2537 Å at 40° C, showed not only a decrease in the DP, but also the formation of aldehyde or keto-carbonyl groups[15] and carboxyl groups[16] as well as the formation of carbon dioxide, carbon monoxide and hydrogen. Also, the presence of acetaldehyde, propionaldehyde, acetone and methanol has been detected by Desai[17].

Many attempts have been developed for elucidating the reaction mechanism. It was concluded that the primary photolytic process consists of a chain scission between the anhydroglucose units and the formation of gaseous products is a secondary process[18]. However, the reaction mechanism is still quite uncertain.

Several groups have been proposed as chromophores for the primary absorption process. Studying the decomposition gases, carbon monoxide, carbon dioxide and hydrogen were observed[19]. An explanation of the source of hydrogen formation is the photolysis of alcohol groups according to reaction (1).

$$R\text{-}C\text{-}OH + Hv \rightarrow R\text{-}C{=}O + H_2 \qquad (1)$$

This can be a fact, that using unfiltered light from a mercury lamp (185 nm was used), the radiation could promote n → Rydberg transitions at lactol and hydroxyl oxygen centres.

Also, carbonyl and carboxyl groups formed during sample preparation, impurities or products of secondary photo-oxidative processes have been suggested[14].

Actually, it is generally accepted that the acetal group at the C1 position of the anhydroglucose unit exerts a chromophoric effect, which in high molecular weight polysaccharides produces a band absorption and thus induces direct photolysis reactions[12,20,21].

Anyway, in photooxidation processes, free radicals are involved as transient intermediates during the processes that subsequently lead to the formation of degradation or oxidation products. Kleinert reported in 1969 that peroxides were formed in cellulose after the irradiation with ultraviolet (UV) light in air or oxygen[5]. Hon concluded that the photooxidation of cellulose results in a decrease of the degree of polymerization of the cellulose, while chromophoric groups are formed. Also the author showed the formation of peroxide-type radicals using ESR spectroscopy[22]. However, the nature of the radicals depends on the irradiation spectra and the origin of cellulose[23].

The effect that acidity plays in this deterioration process is an important role. Wood cellulose was degraded using UV light. By means of UV absorption spectroscopy a bond was shown at 270 nm at pH 12, however at pH 2, this bond was absent[13]. Malondialdehyde has been proposed to account for this behaviour. Also volatile acids were formed, however the majority of the soluble fraction of degradation products is composed of neutral sugars like D-glucose, cellotriose and D-mannose.

The presence of moisture will greatly influence the radical formation, however it was shown that at about 5.7 % the yield of the radicals is at a minimum (the average moisture content of paper is generally 5–7 %).

Photosensitised degradation

As most of the commercially grade papers are of wood cellulose, there will be always a residue of hemicellulose (HC) and other impurities present in the fibres[4,24]. Besides, paper contains also an amount of fillers and other additives. If a photosensitiser (A) is present in the paper, the light will absorb and the energy will be transferred. In case of triplet energy transfer, the triplet state may transfer both energy and spin angular momentum according to reaction (2).

$$A(T_1) + B(S_0) \rightarrow A(S_0) + B(T_1) \qquad (2)$$

Generally triplet photosensitisers are used to produce other triplets, however there is one important exception. O_2 molecules exist in its ground state as a tri-

plet, and its lower state excited state is a singlet. Direct conversion of O_2 to this excited singlet state with light is again a forbidden process, but singlet oxygen can be produced using a triplet photosensitiser since the total spin is conserved during energy transfer. This singlet excited state O_2 can add in one step to, for example, conjugated systems.

If paper contains special components due to a post treatment like deacidification, the sensitivity towards oxidative deterioration can be enhanced. This is especially the case when compounds like ZnO or TiO_2 are being used. Both transition-state metals can promote the oxidative deterioration of cellulose, especially in the case of high alkalinity. It is known for example, that aldoses and ketoses undergo rearrangements in alkaline solutions. So paper made from wood cellulose, thus containing aldose groups, may show for example the Lobry de Bruyn-Alberda van Ekenstrein transformation[8]. Here firstly an enolisation of the aldose will take place to an 1,2-enediol, which can be converted to either of the two C-2 epimeric aldoses or to a ketose. Also aldonic acids can be epimerised by alkali. Strong alkali will convert the end groups in polysaccharides to various carboxylic acids. (1–4) linked polysaccharides (cellulose and hemicellulose), are degraded by an endwise mechanism, the peeling reaction. This reaction occurs during for example alkaline pulping. The reaction start with the isomerisation of the end group to a ketose in which the glycosidic bond is in the beta-position with respect to the carbonyl group. Since this structure is labile in alkali, the glycosidic bond is cleaved with the removal of the end group. This is called the beta-alkoxy elimination. The eliminated group is tautomerised to a 4-deoxy-2,3-glycodiulose. The peeling reaction is terminated by a so-called stopping reaction, where a direct beta-hydroxy elimination from the 4 C-3 position is taken place. The 3-O-substituted glycosides of (1–4) linked polysaccharides are rapidly stabilised in alkali through benzylic acid rearrangement because the beta-alkoxy elimination takes place much easier than the beta-hydroxy elimination. The cleavage of glycosidic bonds by alkali is usually slow in comparison with the acid-catalysed hydrolyses.

Photochemical initiation of free radicals

A different type of free radical, formed in irradiated cellulose was demonstrated by Phillips et al. using cotton cellulose[13]. Their results showed a maximum free radical concentration induced by light ranging between 3250 and 4000 Å (with a maximum at 3600 Å) and did not show absorption by any one specific chromophore. If an impurity in the purified cotton cellulose were responsible for the absorption, it could be reasonably expected that the impurity would have a more specific absorption than that observed.

It is suggested that the free radicals obtained in this study resulted from an intermediate state in which the electrons are in a excited band. Such radicals are unaccompanied by chemical changes. Thus, it was proposed a semiconductor-type model for excited cotton cellulose.

PHOTO-DEGRADATION OF GROUNDWOOD-CONTAINING PAPERS

The presence of lignin promotes the formation of free radicals and chemical oxidation when wood cellulose is exposed to ultraviolet light. For example high yield mechanical and or chemimechanical pulps are susceptible to photo-oxidative reactions which cause the pulps to become discoloured and loose brightness. The energy responsible for the initiating of the chromophore forming reactions is that absorbed 290 and 400 nm in the UV spectrum[25]. Specially, the 330–385 nm region of the sunlight spectrum causes the largest amount of yellowing. Window glass that filters most UV-B radiation in sunlight can therefore still transmit wavelengths that can cause considerable amounts of yellowing or brightness reversion[26].

Yellowing of lignin-containing pulps occurs and the changes have been attributed to the formation of keto, aldehyde and carboxylic groups. Lignin is suggested to take up the role of sensitiser. Radicals formed on the cellulose backbone and the nature and concentration of such radicals varies with the lignin content. Recently, it has been proposed that guaiacyl-glycerol-β-O-4-guaiacyleter groups in lignin undergo hydrogen abstraction from the benzylic carbon by light induced peroxyl or alkoxyl free radicals to form ketyl free radicals. These ketyl radicals undergo rapid cleavage of the β-aryl ether bond to produce phenoxy free radical and an enol which tautomerises to the aromatic ketone[27]. In the presence of air, these phenoxy radicals can form quinones, which act as chromophore[25,28,29,30]. The rapid formation of o-quinones during the early phase of irradiation, followed by a dramatic reduction of these species at later phase, has been detected. These o-quinones react with neighbouring lignin groups creating other more complex chromophores which do not have quinoid character[31]. However, the nature of the radicals and the following reactions depends on the external atmosphere.

Whether the irradiation is carried out in the absence of oxygen, the produced free radicals combine to increase molecular weight. On the other hand, the presence of oxygen inhibits the condensation, probably due to the combination of light induced carbon-centred free radicals with oxygen to form peroxy free radicals[32].

The yellowing or brightness reversion of high-lignin pulps upon light exposition is the biggest obstacle to the use of these pulps when no discoloration is required. Some solutions have been proposed to solve this problem as the use of

additives which absorb UV radiation and free radicals scavengers[33,34]. However, many articles have been published showing that the responsible reactions of colour reversion are not the same reactions that decrease the mechanical permanence of paper[35,36]. These papers were excluded from the standard for permanence due to their apparent instability, but this was due to the acidic papermaking conditions used for their production[37,38,39,40]. Thus, the high quality lignin-containing pulps can be used as components for papers that will maintain physical properties during long term storage, because the produced yellowing does not affect the readability[41].

Post-Irradiation Effects

The post-degradation effect due to UV irradiation is known from many years ago. Launer and Wilson observed that paper irradiated under conditions that would result in bleaching (3300–4400 Å), yellowed after storage for 15 months[42]. The yellowing was greater in the areas which had been irradiated than in the areas which had been blanked from irradiation. Stillings and Van Nostrand[43] also found a post-irradiation effect using cotton linters and a quartz mercury arc. The irradiation was carried out in nitrogen atmosphere. When the samples were stored in oxygen, degradation continued for some time. The post-photoageing degradation could be deferred by storing the samples in nitrogen. Launer and Wilson did not find the effect of the oxygen and attributed the observations of Stillings and Van Nostrand to the presence of near ultraviolet irradiation in their source. This post-ageing effect is greatly accelerated by increasing the temperature.

The nature of the post-irradiative changes depends largely on the history of irradiation. When the materials are irradiated in vacuum or in the presence of inert gases, these delayed changes were greater than those produced when the sample is exposed in the presence of oxygen. The post-irradiation changes are progressively diminished as the duration of the exposure in the presence of oxygen is increased[14].

All these facts indicate that the radicals formed during the irradiation of cellulose are the responsible ones for the post-degradation effect. These effects are due to the subsequent interaction between these radicals and the oxygen in the surrounding atmosphere leading to further degradation. The mechanism is given below.

$$RH_2C\cdot + O_2 \rightarrow RH_2C\text{-}O_2\cdot \qquad (3)$$

$$RH_2C\text{-}O_2\cdot + RH_2C\text{-}H \rightarrow RH_2C\text{-}OOH + RH_2C\cdot \qquad (4)$$

This mechanism explains why the post-degradation is inhibited in nitrogen atmosphere. Propagation reaction (reaction 3) can not be produced in absence of oxygen.

Conclusions and Recommendations

This literature review on the oxidative deterioration of cellulose and paper shows, that under no circumstances may this degradation type be ignored. Although the presence of direct light can be avoided often during consulting archival documents and books, there will still be a risk of forming initiators causing further deterioration. The extent of this risk is however until now unknown. Alkali compounds may promote the oxidative deterioration, however, this deterioration type is from a lower degree than that of the acid hydrolyses type. Therefore it is to be recommended to carry out research on the effects on the oxidative and alkaline deterioration of paper, especially for naturally aged papers which are deacidified. Furthermore it has to be considered if the present accelerated ageing methods for paper will be valid for promoting both types of degradation mechanisms.

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Summaries

Photo Oxidation of Paper Documents. A Literature Review

The problem of the photo yellowing of cellulose materials and in special newspapers is well known. Due to restrictions in archives, libraries and museums, papers are well defended against light sources, which may emit a radiation causing the photo deterioration. Still the effects of the photo deterioration of paper should not be underestimated. This paper presents a review on the theoretical backgrounds of the effect of light on the deterioration of paper and shows, that although the presence of direct light can be avoided often during consulting archival documents and books, the risk of forming initiators causing further deterioration should not be ignored. The extent of this risk is however until now unknown. Therefore it has to be recommended to carry out research on the effects on the oxidative and alkaline deterioration of paper, especially for naturally aged papers which are deacidified.

Photo-oxydation du papier. Un rapport littéraire

Le problème du jaunissement du papier et en particulier du papier journal sous l'influence de la lumière est un phénomène bien connu. Grâce aux réglementations en vigueur les objets déposés dans les archives, les bibliothèques et les musées sont protégés des sources de lumière qui sont susceptibles de provoquer une radiation causant la détérioration du papier. Cependant il ne faut pas sous-estimer la détérioration du papier induite par la lumière. On présentera un aperçu sur les arrière-plans théoriques du phénomène et on montrera que, même si on évite d'exposer les documents et les livres que l'on consulte à l'incidence directe de la lumière, il ne faut cependant pas ignorer qu'un risque de détérioration existe toujours. A l'heure actuelle il n'est pas encore possible de mesurer l'ampleur de ce risque. C'est pourquoi de nouvelles recherches s'imposent sur la détérioration oxydative et alcaline du papier, en particulier en ce qui concerne les vieux papiers qui ont été désacidifiés.

Lichtinduzierte Oxidation von Papier. Ein Literaturbericht

Das Problem der Vergilbung von Papier, insbesondere Zeitungspapier unter Lichteinfluß ist wohlbekannt. In Archiv, Bibliothek und Museum gelten Vorschriften, die die Objekte vor Lichtquellen schützen, welche eine von ihnen ausgehende Oxidation bewirken können. Dennoch sollten die Folgen des lichtinduzierten Abbaus von Papier nicht unterschätzt werden. Es wird ein Überblick über den theoretischen Hintergrund des Phänomens geboten, und es wird gezeigt, daß, auch wenn direkter Lichteinfall beim Einblick in das Objekt vermieden wird, dennoch die Gefahr besteht, daß ein weiterer Abbau ausgelöst wird. Das Ausmaß dieser Gefahr ist bislang freilich nicht bekannt. Es sind deshalb weitere Forschungen angebracht zum oxidativen und zum alkalischen Abbau von Papier, besonders für alte Papiere, die neutralisiert wurden.

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Properties of Paper in Naturally Aged Books

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INTRODUCTION

An examination of eighteen books, naturally aged for more than one hundred years has been carried out to investigate the effects of natural aging on the paper. The purpose of the study was to determine if there was any relationship between the properties of papers in books which had been artificially aged and those which had been naturally aged. In addition it was hoped that this study might provide some evidence which would assist in drawing comparisons between the microenvironments created within books and those within books which have been shrink wrapped.

In 1980, chemists at the Research and Testing Office at the Library of Congress undertook a study comparing the deterioration of papers under accelerated aging conditions, 90° C and 50% relative humidity, with and without shrink-wrapping[1]. Two books were tested: one half of each was shrink wrapped and the other unwrapped. After aging, the paper was tested for pH, acid content, brightness and folding endurance. From the results, they concluded that shrink wrapping significantly increased the rate of degradation of paper. The chemists left it to custodians and conservators to decide whether the physical protection afforded by the shrink wrapping would compensate for any possible increased rate of deterioration.

Researchers at the National Archives and Records Administration, Washington, recently investigated the effect of shrink wrapping on simulated bound volumes[2]. Four volumes were made using 50 sheets of new paper and old bindings. Each volume was cut in half; one half was artificially aged as is; the other was shrink wrapped and then aged. Aging conditions were 70 °C and 65% relative humidity. The brightness, folding endurance, pH and viscosity of paper in each half book was measured. Apart from brightness, the results showed little difference between how paper in the wrapped and unwrapped books aged. The researchers found that the brightness of paper in the wrapped bindings decreased more than the paper in the unwrapped volumes. Testing was performed on the first six pages, the last six and the middle twelve papers. Position was found to have a small but

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Table 1: Details of the books used in the study.
a: Books with a significant strength difference between the middle and outer pages

no.	Title	pages	size (mm)
2	Henry Connel, Jr.: The NSW Magesterial Digest. Sydney: John Sands 1866	463	220x140
4	Alexander Bain: The Emotions and the Will. London: Longmans, Green & Co. 1875	342+23	222x140
5	John William Draper: History of the Conflict between Religion and Science. London: C. Kegan Paul & Co. 1878	217+17	187x125
7	Alexander Oliver: The Statutes of NSW Vol I A-J. Sydney: Thomas Richards 1879	667	240x155
8	Alexander Oliver: The Statutes of NSW Vol II K-W. Sydney: Thomas Richards 1879	681	240x155
10	W. Robertson Smith: The Old Testament in the Jewish Church. Edinburgh: A & C Black 1881	248+17	194x130
11	H.P. Blavatsky: Isis Unveiled Vol I Science. New York: J.W. Bouton 1882	345	232x150
12	H.P. Blavatsky: Isis Unveiled Vol II Theology. New York: J.W. Bouton 1882	377	232x150
14	A. Liversidge & R. Etheridge (Eds): Report of the 1st Meeting of the Australian Association for the Advancement of Science. Sydney: ANZAAS 1889	359+49	216x140
15	W. Baldwin Spencer (Ed): Report of the 2nd Meeting of the Australian Association for the Advancement of Science. Sydney: ANZAAS 1890	407	216x140
16	J. Hector (Ed): Report of the 3rd Meeting of the Australian Association for the Advancement of Science. Sydney: ANZAAS 1891	333	212x140

definite effect on brightness; the middle being slightly brighter than those at the front or back of the volume. However, position had no apparent effect on any other properties.

Staff at the Library of Congress have studied the accelerated aging of paper within microenvironments[3]. Brief details of later work were presented at the International Seminar on Research in Preservation and Conservation held in New York in 1991[4]. At this seminar it was reported that paper in the centre of piles of acidic paper deteriorated more rapidly at 90 °C and 50 % relative humidity than did single sheets of paper. This was attributed to the retention of degradation products within piles of paper and, by extrapolation, within books also.

Table 1: Details of the books used in the study.
b: Books without a significant strength difference between the middle and outer pages

no.	Title	pages	size (mm)
1	John Henry Pepper: The Playbook of Metals. Sydney: Routledge, Warne & Routledge 1862	259	183x120
3	Max Muller: Introduction to the Science of Religion. London: Longmans, Green & Co. 1873	226+17	188x125
6	John Jacob Holtzapffel: Turning and Mechanical Manipulation Vol IV. London: Holtzapffel & Co. 1879	314	222x140
9	Herbert Spencer: The Data of Ethics. London: Williams & Norgate 1881	175+10	215x140
13	John Jacob Holtzapffel: Turning and Mechanical Manipulation Vol V. London: Holtzapffel & Co. 1884	341	220x140
17	R. Tate, E.H. Rennie, W.H. Bragg (Eds): Report of the 5th Meeting of the Australian Association for the Advancement of Science. Sydney: ANZAAS 1894	364	212x140
18	Rev W.M.M. Cooper: Flagellation & the Flagellants. A History of the Rod. London: John Camden 1874	292+21	190x120

The finding that paper in the middle of a pile deteriorates more rapidly than loose paper is contrary to the commonly held belief that the most deteriorated pages in books tend to be near the front and back covers. This raises the question of whether the findings from the accelerated aging studies could be a result of the elevated temperature and humidity conditions that are required for accelerated aging, and of the temperature and moisture gradients throughout the books that may accompany such aging. To determine if the weaker centre pages were simply an artefact of the accelerated aging process, we examined the strength of papers throughout naturally aged books. This paper reports the findings of our study.

THE BOOKS

Eighteen books published between 1862 and 1894 were obtained from the clearing centre at the National Library of Australia. All were non fiction, hardcover and in good condition. Their storage history was not known. The books are listed and described in Table 1.

The spines were cut from the books using a guillotine. Five samples of ten adjacent pages were taken from each book (front, front section – halfway between the front and middle, middle, back section – halfway between the middle and the

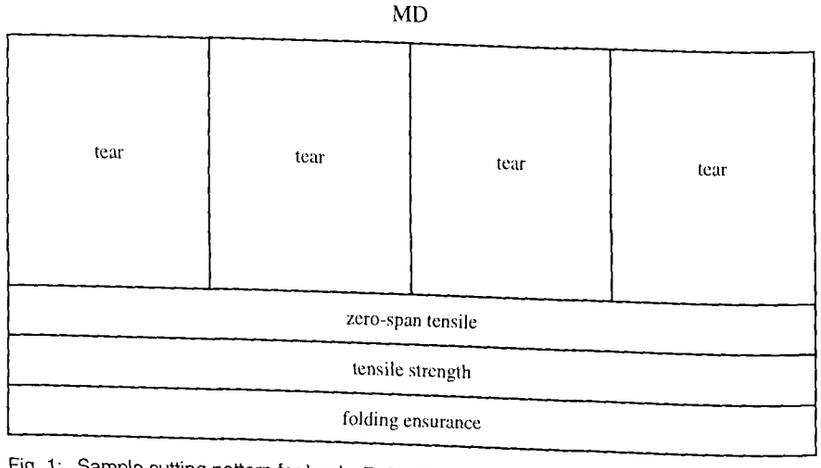

Fig. 1: Sample cutting pattern for books 7, 8, 11, 12, 14, 15, 15, 17

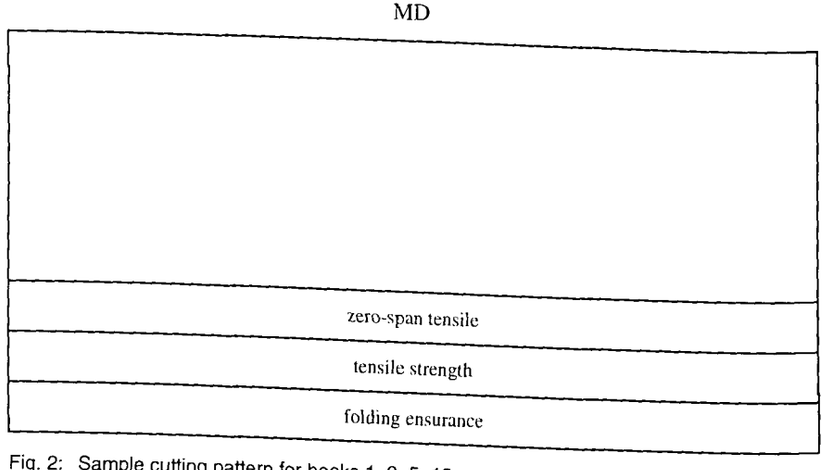

Fig. 2: Sample cutting pattern for books 1, 3, 5, 18

back, and back), designated A–E respectively. Unless the papers were visually different, we assumed that only one type of paper was used in each book. Obviously-different endpapers were not included in the front and back samples. Some books (numbers 3, 4, 5, 9, 10, 14 and 18) had different paper at the end of the book, generally for advertisements or illustrations. Only four samples were possible from these books; sample E was not taken.

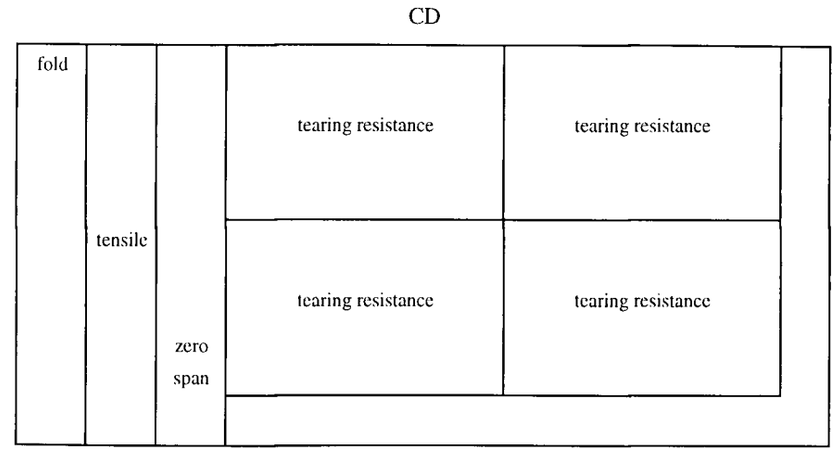

Fig. 3: Sample cutting pattern for books 2, 4, 6, 9, 10, 13

The specimen cutting pattern for books 7, 8, 11, 12, 14, 15, 16 and 17, which have the machine direction (MD) of the paper parallel to the spine, is illustrated in Fig. 1. The remaining books with the machine direction parallel to the spine, books 1, 3, 5 and 18, were too small to have pieces for tearing resistance cut from them; the specimen cutting pattern for these books is shown in Fig. 2. Fig. 3 illustrates the cutting pattern for books 2, 4, 6, 9, 10 and 13 which has the machine direction of the paper perpendicular to the spine.

THE TESTS

The samples were tested in the machine direction for folding endurance, tensile strength, stretch and zero-span tensile strength. Tearing resistance in the cross direction (CD) was determined on paper from all books except books 1, 3, 5 and 18. For each test, the direction of testing was that in which the property was greatest, as this would better highlight any differences between papers (in the weaker direction, the properties may have been reduced to such low levels that distinguishing between them is not possible).

Physical testing of the above properties was performed at the Division of Forest Products, Commonwealth Scientific and Industrial Research Organisation, Melbourne, Australia. All paper samples were conditioned for at least twenty-four hours at 23°C and 50% relative humidity according to AS 1301 414m-86[5].

Folding endurance, internal tearing resistance, tensile strength and stretch were tested using the relevant Australian Standard methods[6,7,8]. Zero-span tensile tests were conducted on wet samples according to the instrument's instruction manual[9]. The results for each ten-page sample were averaged for each test and statistical analyses of variance performed. The average results are listed in Table 2.

The remaining tests, apart from the fibre analysis, were conducted at the National Library of Australia. The pH of paper from each book was determined by the cold extraction method specified in AS 1301.421s-91[10]. Pages immediately adjacent to those tested for physical properties were used in the pH determinations. The results reported in Table 2 are the average of three determinations for each section (A–E) of each book.

Table 2: Average results of mechanical and pH tests performed on paper from old books. NB: For each book, the results for A–E are the average for each section of the book; the number in bold is the average of these results and represents the average result for the entire book.

sample no.	folding endurance (double folds)	zero-span tensile strength (kg/15mm)	tearing resistance (mN)	tensiletrength (N/m)	stretch (%)	pH
1	**7.2**	**9.2**	**–**	**3400**	**1.4**	**4.8**
1A	6.6	9.1	–	3400	1.4	4.8
1B	6.5	8.9	–	3300	1.4	4.9
1C	8.2	9.6	–	3500	1.4	4.8
1D	8.1	10.1	–	3400	1.5	4.9
1E	8.2	9.7	–	3300	1.4	4.7
2	**1.7**	**5.0**	**280**	**2500**	**1.3**	**4.6**
2A	1.5	7.0	370	3300	1.1	4.5
2B	1.0	5.1	270	2500	0.90	4.7
2C	1.7	3.3	250	1600	2.1	4.6
2D	1.3	5.1	270	2500	0.84	4.7
2E	2.6	4.9	260	2500	1.6	4.5
3	**4.5**	**8.8**	**–**	**4100**	**1.4**	**4.6**
3A	3.6	8.7	–	3700	1.4	4.6
3B	4.7	9.1	–	4200	1.4	4.6
3C	5.0	8.9	–	4300	1.4	4.6
3D	4.7	8.7	–	4200	1.4	4.6
3E	–	–	–	–	–	–

Table 2: continued

sample no.	folding endurance (double folds)	zero-span tensile strength (kg/15mm)	tearing resistance (mN)	tensiletrength (N/m)	stretch (%)	pH
4	**–**	**2.3**	**110**	**1900**	**0.55**	**4.3**
4A	–	3.7	180	2000	–	4.6
4B	–	1.8	77	1900	0.55	4.2
4C	–	1.8	79	2100	0.55	4.2
4D	–	2.0	88	2000	0.60	4.3
4E	–	–	–	–	–	–
5	**1.8**	**7.0**	**–**	**3100**	**1.3**	**5.7**
5A	1.8	7.2	–	3200	1.4	5.2
5B	1.6	6.8	–	3200	1.3	5.4
5C	1.8	6.3	–	2900	1.2	6.3
5D	2.0	7.7	–	3200	1.3	5.7
5E	–	–	–	–	–	–
6	**1.8**	**6.7**	**220**	**2600**	**1.2**	**4.6**
6A	2.0	6.4	230	2500	1.2	4.6
6B	2.3	6.8	220	2500	1.3	4.6
6C	1.6	6.6	210	2500	1.2	4.6
6D	1.5	6.5	210	2500	1.2	4.6
6E	1.7	7.0	220	2700	1.1	4.6
7	**1.6**	**5.1**	**180**	**2600**	**1.3**	**5.3**
7A	1.7	4.8	180	2000	1.4	5.3
7B	1.3	4.7	170	2000	1.3	5.2
7C	1.2	4.3	160	1700	1.1	5.2
7D	1.6	5.5	210	2200	1.2	5.1
7E	2.1	6.0	220	2400	1.4	5.7
8	**1.5**	**5.0**	**180**	**2200**	**1.3**	**5.0**
8A	1.5	5.1	190	2100	1.3	5.1
8B	1.6	7.1	180	2500	1.3	4.8
8C	1.3	4.2	150	1900	1.1	4.8
8D	1.7	5.4	190	2300	1.4	4.9
8E	1.5	5.3	190	2100	1.3	5.2

Table 2: continued

sample no.	folding endurance (double folds)	zero-span tensile strength (kg/15mm)	tearing resistance (mN)	tensiletrength (N/m)	stretch (%)	pH
9	**0.5**	**2.9**	**120**	**2100**	**0.8**	**4.7**
9A	0.70	3.2	130	2200	0.9	4.7
9B	0.50	2.8	110	2000	0.7	4.6
9C	0.50	2.8	110	2200	0.8	4.6
9D	0.40	2.7	110	2000	0.7	4.8
9E	–	–	–	–	–	–
10	**0.3**	**3.9**	**170**	**3500**	**0.99**	**4.4**
10A	0.80	5.2	230	3700	1.3	4.4
10B	0	3.5	160	3400	1.0	4.3
10C	0.25	3.5	150	3200	0.81	4.3
10D	0.25	3.6	150	3500	0.91	4.4
10E	–	–	–	–	–	–
11	**0.6**	**3.1**	**130**	**2000**	**0.66**	**4.3**
11A	1.0	3.7	190	2200	0.81	4.5
11B	0.33	1.9	91	1800	0.54	4.2
11C	0	1.7	93	1700	0.55	4.2
11D	0.33	2.0	98	1900	0.57	4.2
11E	1.0	3.8	200	2200	0.82	4.6
12	**0.6**	**2.4**	**130**	**1900**	**0.64**	**4.3**
12A	0.80	3.2	180	1800	0.80	4.4
12B	0.25	1.7	94	1800	0.54	4.2
12C	0.38	1.6	97	1800	0.52	4.2
12D	0.33	1.7	97	1900	0.56	4.3
12E	0.90	3.6	200	2100	0.80	4.5
13	**1.8**	**6.4**	**230**	**2400**	**1.1**	**4.8**
13A	1.8	5.8	220	2500	1.0	4.8
13B	2.5	8.5	270	2600	1.1	4.8
13C	1.5	6.1	240	2600	1.1	4.7
13D	1.5	6.3	210	2100	1.1	4.7
13E	1.8	6.3	240	2400	1.1	4.8

Table 2: continued

sample no.	folding endurance (double folds)	zero-span tensile strength (kg/15mm)	tearing resistance (mN)	tensiletrength (N/m)	stretch (%)	pH
14	**0.5**	**2.5**	**100**	**1800**	**0.81**	**4.3**
14A	0.80	3.8	150	2000	1.0	4.4
14B	0.50	1.6	95	2000	0.91	4.3
14C	0.40	1.6	66	1500	0.58	4.2
14D	0.40	2.0	86	1800	0.75	4.3
14E	–	–	–	–	–	4.3
15	**0.6**	**2.3**	**100**	**2000**	**0.82**	**4.2**
15A	0.80	3.4	110	1800	0.82	4.3
15B	0.50	2.3	81	2000	0.79	4.2
15C	0.40	1.5	70	1900	0.71	4.1
15D	0.50	2.1	86	2100	0.80	4.2
15E	0.90	2.8	140	2300	0.98	4.4
16	**2.2**	**5.3**	**280**	**2600**	**1.8**	**5.0**
16A	3.3	6.9	350	2900	1.8	5.2
16B	1.7	5.0	250	2600	1.6	4.8
16C	1.7	3.4	240	1700	2.5	4.9
16D	1.2	4.1	220	2640	1.5	4.8
16E	3.3	7.2	340	3000	1.9	5.4
17	**0.9**	**1.7**	**110**	**1700**	**0.9**	**4.6**
17A	0.80	2.1	140	2500	0.85	4.7
17B	1.1	2.2	130	2500	0.81	4.6
17C	0.70	1.2	83	1300	0.91	4.5
17D	0.60	1.6	83	1000	0.79	4.3
17E	1.1	1.4	130	1200	1.1	4.9
18	**1.2**	**4.9**	**–**	**3000**	**1.2**	**4.8**
18A	1.7	5.0	–	2700	1.2	4.8
18B	1.1	4.9	–	3000	1.2	4.9
18C	1.0	4.8	–	2900	1.1	4.8
18D	1.2	4.9	–	3100	1.3	4.8
18E	–	–	–	–	–	–

Table 3: Results of tests used to further characterise the paper. The first group of books are those with a significant strength difference between the middle and outer pages; the second group of books showed no such difference.

book no.	g/m²	lignin *	Al ions **	rosin ***	starch ****	carbonates +	fibre content ++	gelatine +++
2	74	x	√	√	√	√	esparto, (cotton & flax-type)	√
4	76	x	√	√	√	√	esparto, (cotton & flax-type)	?
5	95	x	√	√	√	√	esparto	?
7	73	x	√	√	√	√	esparto, cotton)	?
8	73	x	√	√	√	√	esparto	?
10	111	x	√	√	√	√	esparto	√
11	69	x	√	√	x	√	wood, cotton	√
12	72	x	√	√	x	√	wood, cotton	√
14	71	x	√	√	√	√	esparto, (wood)	?
15	64	x	√	√	√	√	esparto, (wood)	?
16	86	x	√	√	√	√	esparto	?
1	77	x	√	√	x	√	cotton, (wood)	?
3	102	x	√	√	√	√	cotton	?
6	86	x	√	√	√	√	cotton, (esparto)	?
9	80	x	√	√	√	√	esparto	?
13	87	x	√	√	x	√	cotton, (esparto)	?
17	76	√	√	√	√	√	wood	?
18	74	x	√	√	x	√	esparto, (cotton & flax-type, wood)	?

* phloroglucinol
** alizarin S
*** Liebermann-Storch & Raspail
**** iodine

\+ hydrochloric acid
++ the bracketed fibres are less than about 10% of the total fibre
+++ hydroxyproline

A number of additional tests were conducted on the paper from each sample. The results of these tests are summarised in Table 3. The phloroglucinol, alizarin S, Liebermann-Storch and Raspail, and iodine spot tests described by Browning[11] were used to test for the presence of lignin, aluminium salts, rosin and starch respectively. Hydrochloric acid was used to test for the presence of carbonate. The surface pH of the front paste-down sheet (i.e. the paper stuck to the inside front cover) and of the inner surface of the boards (i.e. the surface exposed after the boards were split) used for binding was determined using T 529 om-82[12] and are reported in Table 4. The grammage of the paper was determined using AS 1301 405s-92[13]. The presence of gelatine in the paper was determined using the hydro-

Table 4: Surface pH of boards and endpaper. The first group of books are those with a significant strength difference between the middle and outer pages; the second group of books showed no such difference.

book no.	surface pH of paste-down sheet	surface pH of inside surface of board after splitting
2	5.5	7.5
4	6.1	9.4
5	5.4	8.6
7	4.0	7.5
8	3.7	6.8
10	5.4	8.8
11	4.2	6.3
12	4.2	8.2
14	4.1	8.0
15	4.6	8.5
16	4.3	6.9
1	4.2	6.9
3	4.0	7.0
6	4.7	7.8
9	5.7	7.7
13	5.9	8.6
17	4.1	6.9
18	5.4	8.5

xyproline test[14]. This test is based on the reaction of Ehrlich's reagent with hydroxyproline produced by alkaline hydrolysis of collagen. The method is specific for glue or gelatine; other nitrogenous materials do not interfere.

Qualitative fibre analyses were conducted at Amcor Research and Technology, Melbourne, Australia on a single paper sample from each book. ISO 9184-1[15] was used except the Norval Wilson stain was used and samples were obtained by tearing small strips from the edges of pages to avoid ink printed areas.

DISCUSSION OF RESULTS

The results of this study indicate that the centre pages of eleven books (see Table 1) were weaker than the outer pages. In the remaining seven books there was

no significant difference between the strength of the middle and outer pages. There was no immediately apparent reason why the two groups of books should show different results. However the overall tensile, fold and zero-span tensile strength of paper in books with weaker centre pages was less than that of paper in the other group of books. The results of the zero-span tensile testing suggest that the weakness is due to poor fibre strength rather than weak interfibre bonding. It may be that when the paper in the second set of books deteriorates to similar strength levels, paper in the centre of these books will also be significantly weaker than paper nearer the covers.

Additional criteria were checked in an attempt to identify physical or chemical differences between the two sets of books that may affect the strength of the pages. The following were considered: number of pages in the book, date and place of publication, fibre composition, grammage and the presence of calcium carbonate, starch, aluminium, rosin, gelatine and lignin. The details of these criteria are listed in Tables 1–4. Fibre analysis indicates that the fibres in the paper of all but two of the books with weaker centre pages were predominantly esparto (the other two books contained wood and cotton fibres). However, none of these criteria clearly differentiated between the two groups of books.

A possible cause of the difference between the two groups of books is the conditions under which the books have been stored for the past 100 years. Unfortunately, as no details of their storage history are known, this factor cannot be checked. Exposure to differing storage conditions remains a possible cause of the different aging pattern of the two groups of books.

Barrett, with the assistance of researchers at the Institute of Paper Science and Technology, examined handmade papers from the 15–19th centuries[16]. On the basis of appearance, he described half of these papers as being in excellent condition and half in poor condition.

A number of tests were used to characterise both groups of papers and to draw conclusions about the reasons for their present conditions. One of these tests was the detection of gelatine. Both infra-red and ultra-violet techniques were used to determine gelatine quantitatively. A correlation was found between the paper condition and gelatine content – historical papers in good condition contain significantly more gelatine that paper in poor condition. In the present study, the hydroxyproline test was inconclusive for most papers but indicated the presence of gelatine in books 2, 10, 11 and 12. These four books contained some of the stronger papers and all exhibited weaker centre pages. The infra-red spectroscopy technique used in Barrett's study was attempted but not successful in quantifying the gelatine content of the paper in the old books in our study. Differing gelatine contents remain a possible reason for the differences between the two groups of books.

Shahani has suggested that the centre pages of some books are weaker because the degradation products are retained within the book[4]. This hypothesis needs to be tested by identifying the degradation products and investigating the nature of the microenvironment created within books.

Passaglia[17] used mathematical modelling to study the protective mechanisms provided by storage containers but reached no conclusions regarding the interaction of the external environment with paper in a book.

Shahani[3] reported that when temperature and relative humidity are cycled, the relative humidity within books does not change significantly. Whether this is due to a buffering effect of the paper in the book, to the creation of a partially closed microenvironment, or to a combination of both was not determined.

Parks et al[18] studied the degradation products of paper in a closed environment with and without pollutants. The were able to tentatively identify a number of organic acids that are thought to be mobile degradation products of paper. However, these studies do not provide sufficient data to characterise the nature of the microenvironment nor the degradation products, and further research is required.

An alternative explanation for the differing degradation pattern between the two sets of books is that the outer pages of one group of books have been protected against degradation from a part of the environment that they do not share with the inner pages. One possible factor is the boards used in binding the books. Tests of the surface pH of the paste down sheet and of the inner surface of the board revealed little difference in pH between the two groups of books (see Table 4). However, given the complex array of materials used in or on the boards, factors other than pH may protect paper adjacent to them. It is interesting to note that, for all books, the pH of the end papers was on average three pH units below that of the inner surface of the board.

CONCLUSION

In the sample examined, a statistically significant portion of the books had centre pages weaker than the outer pages. No logical explanation for this observation has been found.

The observation that the centre pages of some books are weaker than the outer pages concurs to some extent with results from accelerated aging studies of the effects of shrink wrapping on the degradation of books. This indicates that the microenvironment created within a book is such that the centre of the pile deteriorates faster than the outside regardless of whether the book is shrink wrapped or not.

ACKNOWLEDGEMENT

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SUMMARIES

Properties of paper in naturally aged books

Artificial aging studies indicate that paper in books deteriorates faster than single sheets of paper, and that paper in the centre of a stack deteriorates faster than paper on the outside of the stack. The present study was conducted to determine if this was also true for naturally aged books. Mechanical tests were performed on paper from naturally aged books that were at least one hundred years old. The results of the testing revealed that the centre pages of a significant proportion of the books were weaker than pages nearer to the book covers. Additional chemical and physical tests have not distinguished between those books with weaker centre pages and the others. The results agree to some extent with those from artificial aging studies.

Propriétés du papier des livres vieillis naturellement

Des études réalisées sur le vieillissement artificiel du papier ont démontré que le papier contenu dans les livres se détériore plus rapidement que celui des feuilles de papier isolées; on observe le même phénomène pour les feuilles de papier empilées dans un tas: celles qui sont au milieu se détériorent plus rapidement que celles placées vers l'extérieur. Cette étude a été menée pour déterminer si ce phénomène se produisait également pour les livres vieillis naturellement. On a mesuré la résistance mécanique sur des livres vieillis naturellement qui avaient au moins cent ans. Les résultats des tests ont révélé que les pages centrales d'une proportion significative des livres étaient moins résistantes que les pages placées plus près de la couverture des livres. D'autres tests chimiques et physiques n'ont pas permis de constater une différence dans la résistance du papier entre les pages centrales et celles plus extérieures. Les résultats correspondent à peu près à ceux observés lors d'études sur le vieillissement accéléré.

Messungen an Papier in natürlich gealterten Büchern

Frühere Untersuchungen zur beschleunigten Alterung zeigen, daß Papier in Büchern schneller an Qualität einbüßt als einzelne Blätter, ebenso wie Blätter im Innern eines Stapels im Vergleich zu den äußeren. Jetzt wurde untersucht, ob dies auch für natürlich gealterte Bücher gilt. Es wurden die mechanischen Festigkeitswerte des Papiers aus mndestens hundert Jahre alten Büchern gemessen. Die Ergebnisse zeigen, daß in einer signifikanten Anzahl von Fällen die Blätter im Innern eines Buches schwächer sind als die näher bei den Deckeln gelegenen. Allerdings gibt es keinen korrespondierenden Unterschied bei anderen chemischen und physikalischen Meßwerten. Die Ergebnisse stimmen in etwa mit den bei beschleunigter Alterung beobachteten überein.

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Non Invasive Techniques for the Investigation of Foxing Stains on Graphic Art Material

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INTRODUCTION

Until now, it is generally believed that the yellow/brown stains, called foxing stains, present on the surface of a huge number of documents are onlydisgraceful. Many hypotheses have been raised concerning the origin of foxing: the diffusion of fungal metabolites into the paper may lead to discolouration of several colours including yellow/brown[1]. F. Gallo and collaborators brought to evidence and reproduced in vitro the fungal growth associated with the presence of iron in paper materials[2]. They showed that in some foxing stain areas the concentration of iron was higher that in the other areas. F. Gallo and I. Arai also identified more than 40 bacterial and fungal strains which were collected on foxed areas[3,4,5]. The presence of iron in papers since the XVIIth century may either produce rust due to the humidity content of paper or induce cellulose degradation associated with the degradation ofthe other materials as sizing agent[6]. A recent work of M.L. Florian[7] evidenced that the contamination would have occurred during the making of papers and the brown pigments would be due to membrane lipid oxidation in contact of proteins. I. Arai and collaborators showed that fungal growth may induce the hydrolysis of cellulose and gelatine (for gelatine sized papers)[8,9,10]. Free sugars and amino acids present in these areas may combine as Amadori compounds and finally produce fluorogenic compounds and then chromogenic endproducts. This hypothesis is the only one which is supported by chemical evidence of the extracted materials out of foxing stains. Organic acids (fumaric acid and malic acid), oligosaccharides (glucose to cello-trihexaoses) and amino acids have been found in these stains.

ANALYSIS OF FOXING STAINS: PREVIOUS METHODS

Foxing stains have been analysed using the following methods:

- Visual aspect[2,6,11]
  - Spots may be localised or spread all over the sheet of paper, intensity may be very differentand the question whether the foxing stain shape has a regular/irregular structure may or may not be relevant in respect to the identification of the foxing type.
  - The observation under binocular lenses show a surface phenomenon or an embedded phenomenon which is different in terms of treatment.
  - In some cases, fungal hyphae are still visible even a long period of time after the fungal growth stopped.
  - Patterns of foxing stains have been observed on several consecutive pages of books[12] leading to the interpretation of either diffusion of chemicals or fungal infestation during themaking of papers.
- Fluorescence. Gallo and collaborators[2] proved the fluorescence of the centre of some foxing spots observed under 254 nm or 365 nm UV light. Some spots fluoresce quite well and other do not. The question still arise whether this fluorescence reveals different steps of the same phenomenon (the production of brown end products) or different phenomena.
- Destructive analysis. Some observations of foxing stains area with a Scanning Electron Microscope have been made by Michaels and Boyd[13]. The authors clearly evidenced the presence of conidial spores and fungal hyphae. Our personnel observations confirm the latter results. Nonetheless,this method is destructive and does not bring any information concerning the type of fungi orbacteria involved. Still, bacterial and fungal regeneration on agar plates is the only available method to identify the microbial strains responsible for paper deterioration.

NON-INVASIVE METHODS

The development of non invasive tools for the characterisation of foxing stains will help to define objective keys for a taxonomy and will help to investigate archives and graphic art collections in order to assess the priority for intervention. In the present work we report theuse of FTIR and fluorescence as non invasive tools for the characterisation of foxing stains in respect to their physical chemistry.

MATERIAL AND METHODS

Papers

154 samples of foxed papers from the XVIIth to XXth century were kindly given by the French Bibliothèque Nationale, the Graphic Art Department of Louvre museum, the archives of Charente Maritime, and others from private collections. These papers were analysed (fibres, size, fillers, lignin content, copper number, cold extract and surface pH) using the corresponding TAPPI standards. This paper collection is not representative of all types of papers since these papers were obviously chosen for the presence of foxing. There are mainly three categories:

- textile fibres with gelatine size, absence of lignin (97 out of 154)
- bleached softwood fibres, rosin size, presence of lignin (26 out of 154)
- others (31 out of 154)

Fluorescence

Perkin Elmer™ LS 50, equipped with LS 500 (X,Y shuttles with optical fibres).
Excitation slit = emission slit = 5 nm.
Resolution = 2 nm.
Optical fibres are mounted on a X,Y shuttle and points were taken each 0.5 mm (approximately 5 Dots Per Inch).
Excitation and emission wavelength maxima were determined statically on a fluorescent spot, by successive approximation until maximum is reached.

FTIR

Perkin Elmer™, Paragon 1000 in Transmission, Reflection and DRIFT (Diffuse Reflectance Infra Red Fourrier Transformed).
Reflection: papers are directly laid on a ZnSe crystal (1 cm x 5 cm).
In Transmission spectroscopy, results are poor due to the paper thickness.
DRIFT mode : direct analysis of papers of 2 cm^2.
Detection: 4000–450 cm^{-1}.
Resolution: 2 cm^{-1}.
Working conditions: air.
Accumulation number: 512 (T-DRIFT)/1000 (ATR).

Samples were extensively dried out overnight in a desiccator with P_2O_5, spectra were recorded and then samples were allow to full Deuterium exchange

(overnight) and eventually spectra were recorded again. This procedure ensures that if water is present, deuterated samples will display a typical peak at 2500 cm^{-1} and remove others due to the presence of water.

The smoothing, second derivative, curve fitting and peak integration were performed using GRAMS/386 (Galactic Co.). All the spectra were smoothed with the Savitsky Golay function (second degree polynomial, with 11 convolution points) and baseline corrected. The curve fitting and peak area integration were performed with the interactive mode of the software. We assigned the peak type to Graussians. Iterations were conducted until convergence was reached, with a Chi Square less than 3.

RESULTS

Four typical foxing spots are displayed in Fig. 1, displaying different sizes, shapes and intensities.

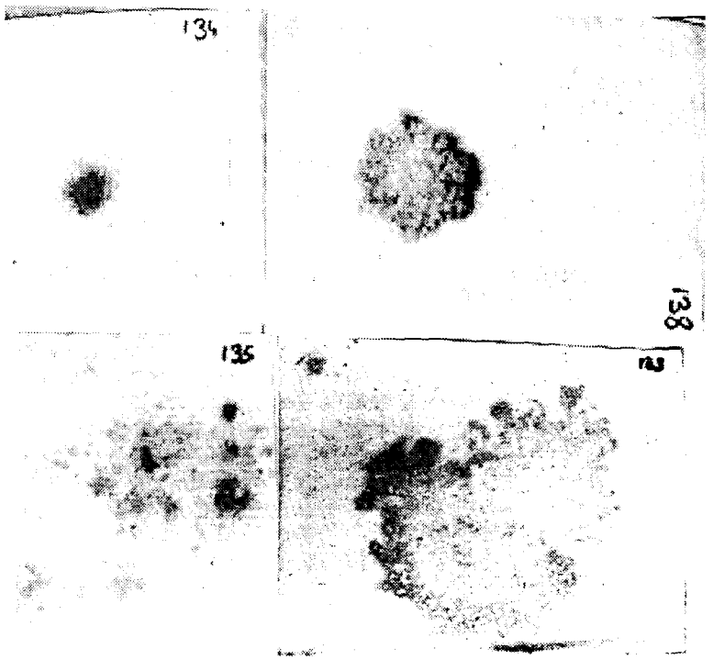


Fig. 1: Typical foxing stains (magnification 1:1)

The image analysis (colour, edge, and shape) of the foxed area is complex and eventually provides a minimal key for a taxonomy. Foxing stains may be circular or irregular and the centre may be either deeply coloured or less coloured that the edge. In fact a simple experiment of a water soluble pigment would behave the same depending on the level of hydration of the paper. Indeed an artificial spot will tend to be irregular and the edge deeply coloured under high water content (diffusion) whereas the spot tends to remain circular in a dry environment. So it is likely that the appearance of foxing spots may be a bad key for a taxonomy.

This is the reason why we have been seeking for other non-destructive methods providing more chemical information. We report here the information provided by the use of FTIR and Fluorescence for the characterisation of foxing spots.

Fluorescence

Surface fluorescence consists in the analysis of the emitted light out of a surface which is isolated with a defined wavelength (excitation).

The spectrometer provides a cold source of light through optical fibres with an 8° angle. The emitted light goes through other optical fibres and are then analysed. The level of energy is controlled by the size of the slit (excitation and emission). Obviously the energy may be raised up by enlarging the slit but then the precision is lowered. We found an acceptable compromise of the ratio signal/noise with the papers previously described with a slit of 5 nm. This equipment is mounted on a surface analysis which is as less invasive as possible since the scan speed is not less than 1 cm/sec.

Such an apparatus allows a qualitative analysis of the maxima of excitation/emission wavelength and a semi-quantitative analysis (in arbitrary units: A.U.) of a surface which is useful to locate the spots which are invisible under day light observation on the one hand and, on the other hand, to monitor the ageing of these fluorescent spots.

Qualitative analysis

The maxima of excitation and emission wavelengths are determined by successive approximations, i.e. the first maximum of fluorescence intensity of an excitation spectrum is taken as a basis for the next emission spectrum and repeated until the couple of maxima is reached.

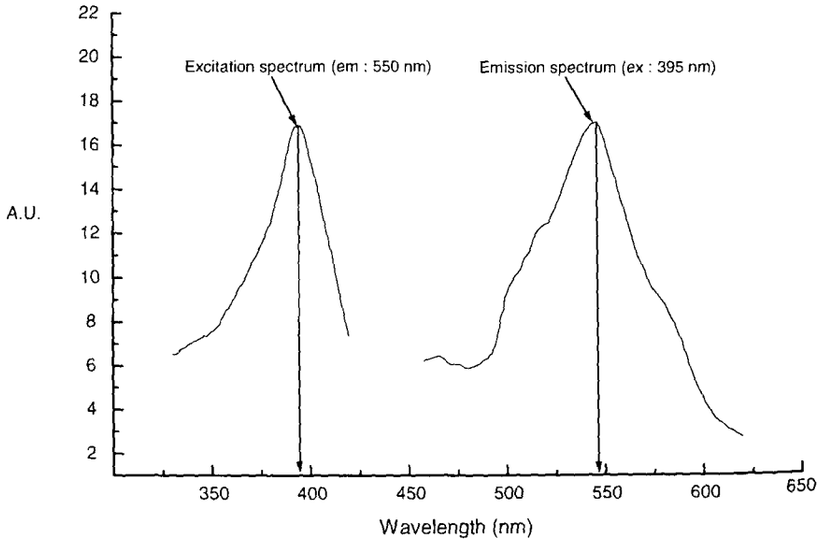


Fig. 2: Excitation/emission spectra of the optical brightener in papers

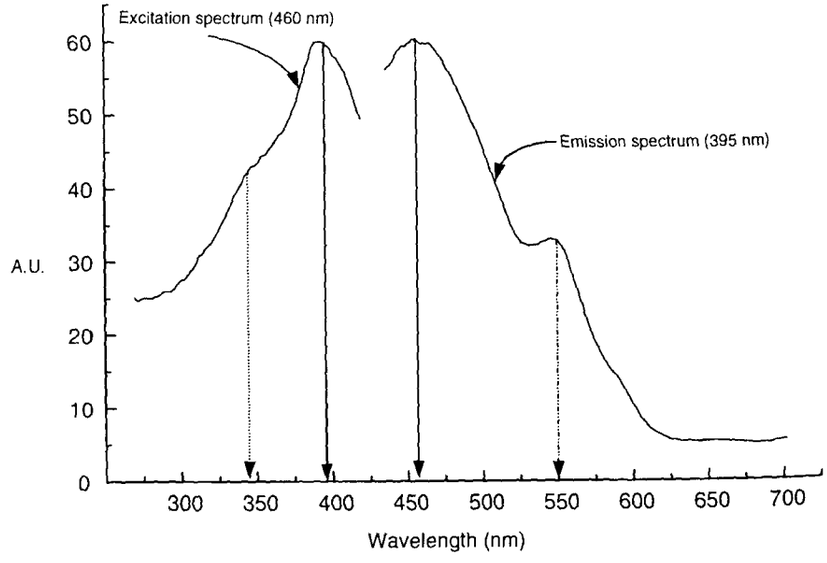


Fig. 3: Typical spectra of foxing spots

Table 1: Excitation/emission maxima of fluorescence of foxing spots.

Sample number	total	excitation max. (nm)	emission max. (nm)
4, 34, 42, 65, 69, 81, 137	7	365	420
12, 17, 19, 26, 29, 54, 58, 64, 101, 102, 113, 117,	15	365	430
6, 38, 46, 72, 78, 88, 94, 114, 124, 133	10	365	440
10, 22, 24, 35, 48, 59, 61, 70, 71, 73, 82, 86, 95, 106,	21	395	460

With the papers used for this analysis, an optical brightener may be present but hopefully thespectra do not overlap. Fig. 2 shows the weak fluorescence of papers made of textilefibres, with gelatine size. The maximum of excitation is 395 nm and the maximum of emission is 550 nm.

Fig. 3 displays a maximum of the excitation wavelengths at 395 nm with a shoulder at 340 nm, an emission maximum at 460 nm with a shoulder at 550 nm. We interpret these curves as follows: the shoulder at 340 nm could be due to the gelatine size and the one at 550 nm to the optical brightener. The fluorescent molecules involved in foxing stains have relatively pure spectra which tend to prove that the molecule or the fluorogenic group of this molecule ha a defined chemical structure.

Among the 154 samples analysed, we have observed only slight differences between the spectra. The latter suggests a great similarity of the fluorescent molecules and probably the slight difference in the spectra may be explained by the different side chemical residues branched on this fluorogenicstructure. In the Table 1 we report the summary of the different couples of maxima observed.

Semi-quantitative analysis

As soon as the excitation/emission maxima are measured it is possible to analyse the overall surface ofa paper. The variation of intensity allows to determine the edge of the fluorescent spot. For instance, in the lower part of Fig. 4 we have represented the day light observation of a piece of a paper and in the part below the same surface with the intensity of fluorescence in grey levels. The area where the black ink is present correspond to the lowestfluorescence intensity (less than 20 A.U.). The background fluorescence of this paper is about 25 A.U. and the spots display maxima as much as 55 A.U.

Fig. 5 gives a map of the same area as in Fig. 4 with an additional edge extraction simply filtered as twice the background signal. The correlation between yel-

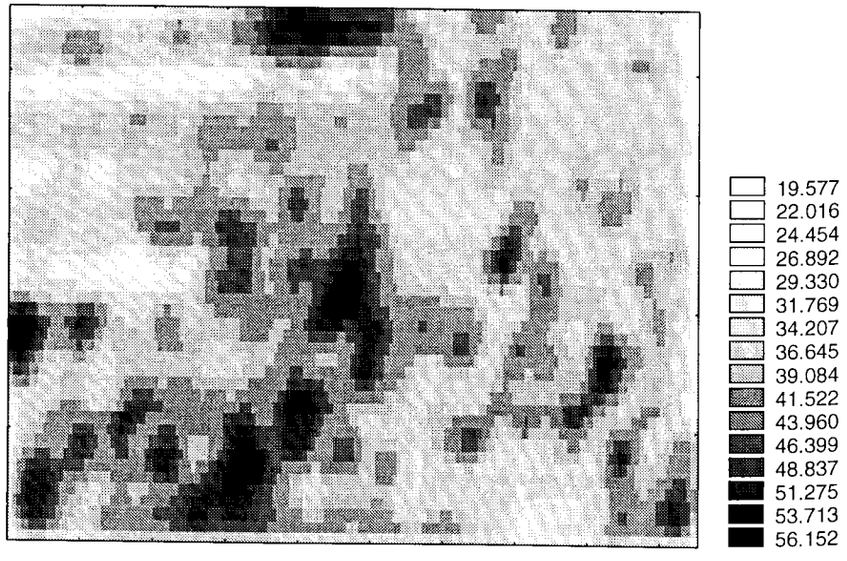
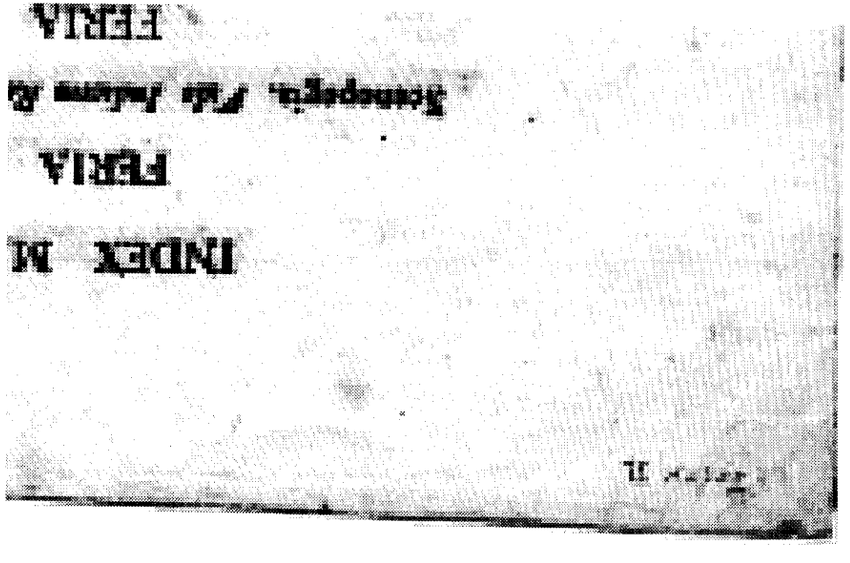


Fig. 4: Mapping the fluorescence of foxing spots. Above: Fluorescence intensity (arbitrary units) at 395/460 nm. Below: Day light picture of the same area



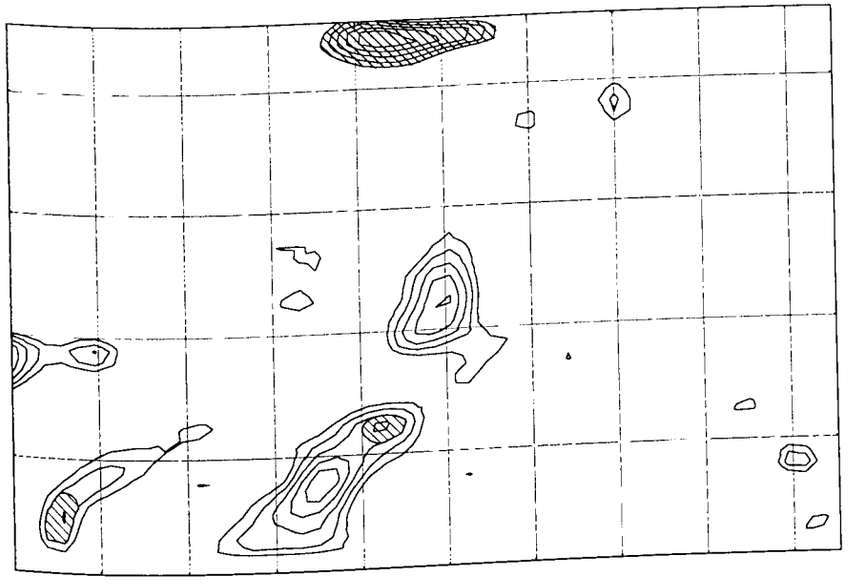
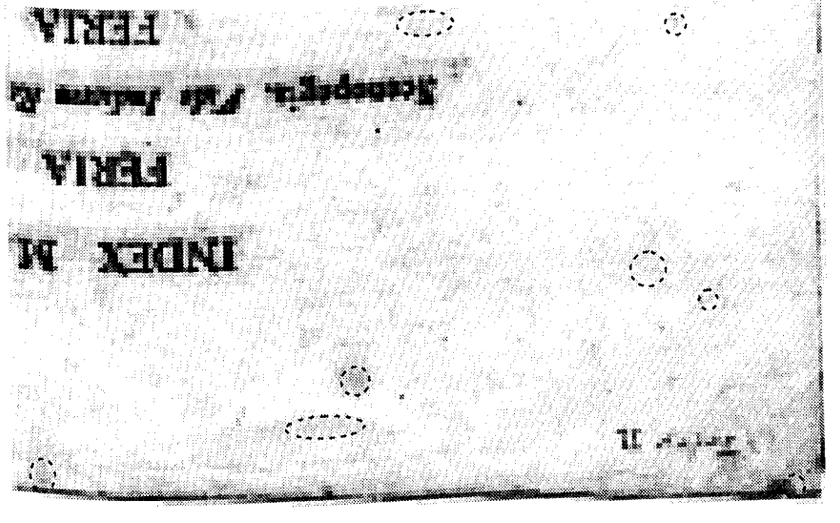


Fig. 5: Edge extraction of foxing spots (fluorescent only: clear area; brown and fluorescent: hashed area; brown only: black area)



low/brown area and fluorescent area is made easy this way. It reveals the presence of: fluorescent only, yellow-brown only and both fluorescent and yellow-brown area. This method will make possible the monitoring of fluorescence evolution under ageing conditions.

The quantal ratio is hard to determine since it depends on different qualities of paper (reflectance, type of fibres, sizing agent, fillers and optical brightener), humidity, etc. Nevertheless we have observed a large range of the intensity of fluorescence of the different samples: from 40 A.U. to 300 A.U. as in Fig. 6. This analysis remains semi-quantitative in the way that one may follow the evolution of fluorescence versus time only in the same experimental conditions.

As a conclusion, surface fluorescence of foxing spots displays a qualitative similarity which can be interpreted as a homology of chemical structure. This is a fully non-invasive analysis since the speed of acquisition is high and light goes through optical fibres which lowers the risks of temperature increase. This method allows semi-quantitative measurements and as such may be used to follow the evolution of fluorescence versus time during ageing. In terms of foxing investigation, the keys for a taxonomy are less interesting due to the similarity of fluorescence spectra. Nevertheless, since one may find either fluorescent only/brown only and both types of spots, the question arises whether fluorescent compounds represent a special type of foxing or precursors of the chromogenic brown compounds. If the latter proposition would be true, fluorescence would become the major investigation mean in order to monitor the risk for a collection to display disgraceful brown foxing spots with ageing.

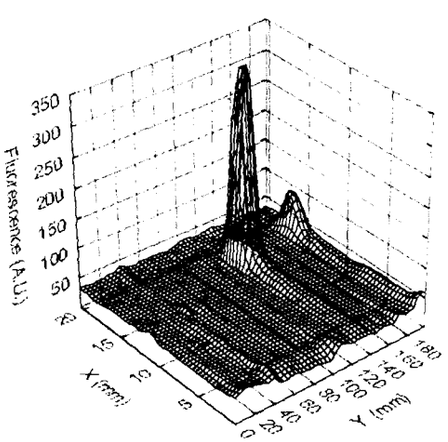


Fig. 6: Fluorescence 395/460 nm of sample number 81

FTIR

FTIR has been used for the investigation of paper materials for a long time[14,15,16]. Its use for monitoring paper ageing has not been fully successful[17], but it seems that the presence of collagen in the size may be evidenced by the presence of amide bonds in the region 1600±20 cm^{-1} [18]. In this work, we have used FTIR as a tool for identifying the type of chemicals found in either fluorescent or brown stains, taking as reference the same paper material in clear area. Papers have been tested either under transmission (T), reflection (ATR) or DRIFT (a combination of reflection and transmission).

Most of the papers are too thick to be directly analysed in transmission. Nonetheless, very thin papers or tracing papers may be analysed this way. A small amount of stained fibres included in a KBr pellet analysed versus non stained fibres would provide good quality spectra but still, the procedure is destructive.

ATR is a fully non destructive mode since it is based on the reflection of a crystal (we have used a ZnSe crystal) directly applied on the paper. The quality of the spectra are greatly influenced by the level of pressure applied on the paper. Indeed, since most of the papershave poor reflectance properties, the higher the pressure applied the better will be the reflectanceand as a consequence, the better the spectra. However, once more the procedure makes it not totally non invasive.

DRIFT spectroscopy combines reflectance and transmission. In this case, papers do not undergo any treatment, but in our conditions only small samples may be analysed (2 cm^2). The development of this method directly applied on papers would be of great interest in the future. Since DRIFT spectroscopy seems the most promising, we chose to report its use for foxingstain analysis.

A typical IR spectrum of a paper made of textile fibres, gelatine sized is displayed in Fig. 7. There are many bands which seem overlapped and the contribution of gelatine in the spectrum is difficult to deduce. In Table 2 we report the different interpretations of the peaks found in this kind of paper[17,18,19,20,21,22,23]. If one would analyse a foxing stain on papers, all the previous peaks will interfere, overlapping some very informativepeaks. Hence the spectra of foxing stains have to be recorded versus a reference of the same paper in a clear area (without fluorescence 365–395 nm, without dark area at 254 nm and without coloured spots).

Another typical IR spectrum of a paper made of chemical pulp from softwood containing lignin is displayed in Fig. 8. Table 3 reports the interpretation of the peaks found in a lignin containing paper[14,17,19,24]. The typical lignin bands are 1600 and 1510 cm^{-1} (aromatic ring vibrations) and 1470–1460 cm^{-1} (C-H deformation vibration and aromatic ring vibrations). With this kind of paper, the direct analysis of foxing stains is even harder to interpret since we expect carbonyl band which are partially overlapped by lignin.

Table 2 : Peak table and interpretation of cellulose (bold) and gelatine (italic)

Wave number (cm^{-1})	i	Interpretation
3335	***s***	***O-H stretching vibration; RO⇔H : broad band 3770-3000 cm^{-1}***
3500-3300	*m*	*N-H stretching vibration, broad band*
3500-3200	*s*	*CON-HR monosubstituted amide*
2900	**s**	**C_6-H stretching vibration *(C-H, C-H_2), broad band 2990-2790 cm^{-1}***
1690-1650	*s*	*amide I band C=O stretching vibration*
1680-1580	*s*	*N-H bend in plane*
1640	m	O-H stretching vibration, water in cellulose
1570-1450	*m*	*C-N-H bending vibration*
1430	***m***	***C-H_2 bending vibration, internal deformation (scissoring)***
1370	***m***	***CO-H bending vibration***
1320	***m***	***C-H_2 bending vibration, external deformation (wagging)***
1250-1020	*m*	*C-N stretching vibration*
1200	***s***	***C-OH bending vibration***
1160	***s***	***C-O stretching vibration (C_1⇔O⇔C_5)***
1110	**s**	**C-O-C symmetric stretching vibration**
1060	**s**	**C-O-C asymmetric stretching vibration**
1035	***s***	***O-H bending vibration (primary alcohol)***
895	**m**	**skeletal vibration - anomeric cellulose**
710	**m**	**CH_2 rocking, cellulose type I**
665	**m**	**C-OH bending vibration, out of plane (bond)**

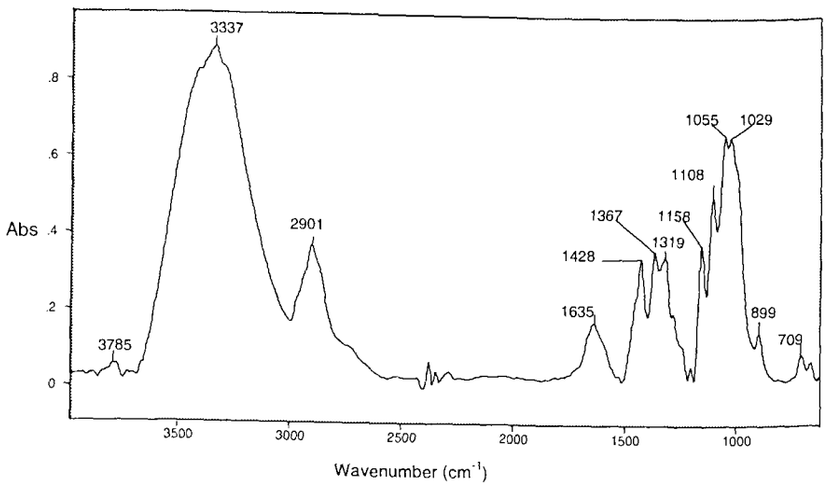


Fig. 7: Typical IR spectrum of pure linen, gelatine sized paper

Table 3: Peak table and interpretation of the IR spectrum of lignin

Wave number (cm^{-1})	Interpretation
3455	O-H stretching vibration
2995	C-H stretching vibration; aromatic C-H
2940	C-H, C $\lessgtr$ H_2 stretching vibration, broad band
2845	C-H stretching vibration (CH_3)
1740-1725	C-O stretching vibration
1665	C-O stretching vibration (aromatic conjugated)
1640	O-H stretching vibration, water in cellulose
1600-1595	C=C aromatic skeleton vibration
1510-1505	C=C aromatic skeleton vibration
1465-1460	C-H_2 bending vibration, internal deformation (scissoring)
1420	C=C aromatic skeleton vibration
1365-1360	CH_3 symmetric bending vibration
1330-1325	aromatic ring vibration (syringyl unit)
1270-1265	aromatic ring vibration (guaiacyl unit)
1225-1220	aromatic ring vibration (syringyl unit)
1140-1085	C-H bending vibration, aromatic
1035	lignin skeleton vibration
860-820	1,3,4,5 substitution pattern, aromatic

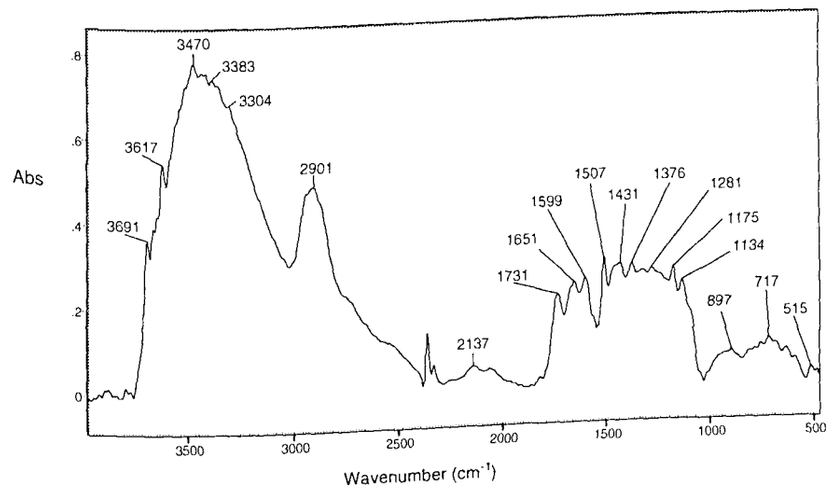


Fig. 8: Typical spectrum of a paper made of chemical pulp with presence of lignin.

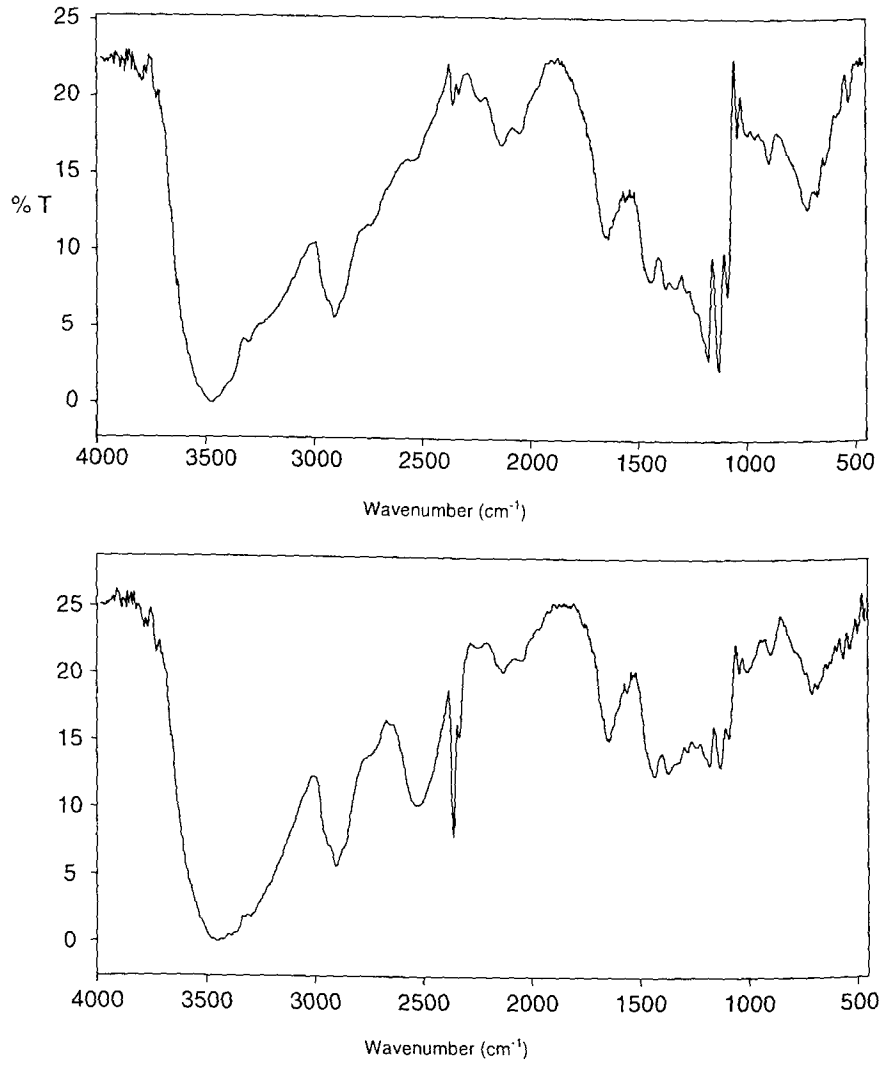


Fig. 9: DRIFT spectrum of a XIXth century, textile fibres and gelatine sized, dry sample (upper part) and after deuterium exchange (lower part)

In order to verify if the peak observed at 1650 cm^{-1} can be attributed to water, we have determined the water content (TAPPI 412-1990) of the paper used in Fig. 9 (XIXth century, gelatine size, textile fibres). This paper contains 4% of tightly bond water, and, in addition, at 45% RH, one have to had almost 6% which means an overall content of 10%. Even if we record IR spectra of stained papers versus a reference in a non stained area, it is likely that the peak at 1650 cm^{-1}

might be due to the presence of water. We have checked this hypothesis by full deuterium exchange with water: the paper is held in a desiccator under vacuum with deuterium oxide. We expect the peak of water do disappear and a new peak at 2500 cm^{-1} to appear. Fig. 9 clearly shows the peak at 2500 cm^{-1} but, still, the ratio of thepeaks: 1650 cm^{-1}/1189 cm^{-1} remains the same. This can be due to the presence of tightly bond water to cellulose or to the presence of other chemicals which are normally overlapped in this range by the water band.

In the following, we have used DRIFT spectroscopy after Deuterium oxide exchange offoxing stain area versus clear area. Since IR spectra are complex (many bands overlap) we report here the use of the curve fitting of the sum of Gaussian peaks which provides the peak identification and the surface of the peak. Obviously, there are an infinite number of solutions. In order to avoid such problems, we followed the following rules:

- A good fit is one for which convergence has been reached and the Chi square is less than 3.
- Among several solutions, the better fitting curve is the one which passes the first rule and which has the least number of peaks.

CATEGORIES

We must bear in mind that a mixture of chemicals is very likely to be found in foxing stain area. As a consequence, the following is not dedicated to the identification but rather more toprovide information on the possible chemical groups found in the stains and hence to providekeys for a taxonomy of the different stains found on paper. Among the 154 samples we may split the spectra recorded into three main categories*.

Category 1

The first category is defined by the very important peak at 1720 cm^{-1}, corresponding to the presence of carbonyls or ketones (C=O). We have subdivided this category into three subgroups:

- Category 1.1: Brown and fluorescent stains. In this category, no or very few OH are present which is very surprising if the stains are due to the modification of cellulose unless these molecules are from the family of dehydro-reductones as in Maillard reactions. The important band at 3047 cm^{-1} suggest the presence of unsaturated compounds which is confirmed by the peak at 640 cm^{-1}

(and possibly 1662 cm^{-1}) or conjugated aromatic compounds (1578 cm^{-1}). In any case, it seems that the unsaturated bonds are involved in conjugated systems which could explain the fluorescence found in these stains. Ketones at 1720 cm^{-1} are not conjugated but the peak at 1662 cm^{-1}, could be due to conjugated ketones. Since the peaks at 3041/1576/1508 and 800–700 cm^{-1} are present, it supports the hypothesis of aromatic compounds, with ketone groups and maybe O or N heterocycles or conjugated systems C=C/C=N/V=O. The peaks at 1200–1010 cm^{-1} could be due to sugars. It is very hard to assert if the sugars are linked to the aromatic or heterocycle compounds or just oxidised (ketones) alone and aromatic compounds alone.

- Category 1.2: Brown and fluorescent stains. This group is almost similar to the category 1.1. but here, bonded OH or NH (3419–3380 cm^{-1}) are present. The presence of aromatic compounds is inferred by the presence of a peak at 568 cm^{-1}. In this case the peak at 1662 cm^{-1} almost disappeared. The weak peak at 1636 cm^{-1} which could be amide, imine or again a residue of water.
- Category 1.3: Brown and fluorescent stains. The peak at 1720 cm^{-1} is identical to 1.1 and 1.2. The band at 3600–3400 cm^{-1} is identical to 1.2, but the band at 2934 and 2848 cm^{-1} shows that in this case, there are no aromatic compounds but more aliphatic compounds. Since there are no aromatic compounds and that the peak at 1657/1615/1584 are still present, we may wonder if they are due to imine R-C=N–. The latter and the presence of the peaks at 1186 and 1087 cm^{-1} (sugars) may support the hypothesis of Maillard reactions between reducing sugars and amino-acids leading to the formation of iminosugars of derived iminoreductones. In the previous groups (1.1 and 1.2) it is possible that conjugated C=C/C=N/C=O, aromatic compounds and imines may be present at the same time. Since many bonds may absorb at the same wavelength, we may only raise hypotheses. The extraction and the purification of the chromogenic or fluorogenic compounds could help to chemically identify the different compounds in the stains.

Category 2

Brown and fluorescent stains. In this group, OH or NH are present (3600–3400 cm^{-1}); aromatic (3154 cm^{-1}/800–700 cm^{-1}) or unsaturated compounds (3154 cm^{-1}/690–635 cm^{-1}) are present as well as saturated ones (2939–2905 cm^{-1}). The unusual weak peak at 1848 cm^{-1} could be interpreted as either the overtone of the peak at 919 cm^{-1} (alkene), or lactones or even ammonium salts. The simultaneous presence of a strong peak at 3300 cm^{-1} and 1637 cm^{-1} could reveal the presence of imine (RR'C=NH) or iminocarbonate (3377/1637/1331/ 1183 cm^{-1}). Amide I is often found at 1616 cm^{-1}. This group displays complex spectra leading to many possible interpretations. This is in favour of a complex mixture, but the interpretation is helped by the fluorescent property of this group. As a conclusion, even if a mixture of many chemicals is the most relevant hypothesis, aromatic and/or heterocycles and unsaturated C=C/C=O/C=N are likely to be found.

Category 3

In the third group, the main peak is found around 1670–1680 cm^{-1} and typical ketone bands (1700–1730 cm^{-1}) are weak. Hence these compounds are conjugated ketones, alkenes or aromatic compounds. We have subdivided this category into two subgroups:

- Category 3.1: Brown and fluorescent stains. Alcohols or amines are present (3600 cm^{-1}). Saturated C-H bonds (2987–2783 cm^{-1}) and unsaturated bonds are present (3154–3033 cm^{-1}/800–700 cm^{-1}). At 1679 cm^{-1}, conjugated C=C, C=O or C=N are very likely to be found. This may explain either the fluorescence or the colour of these products. Further more an unusual band around 2100 cm^{-1} is also present and this band cannot be an overtone of 1100 cm^{-1} (absent). Since C≡C or C≡N bonds are unlikely as natural products (and usually they display narrow strong peaks), these peaks (2234/2165/2135/2044) may be due to the presence of dienoids X=C=Y (with X=C/N and Y=C/N/O). These chemical groups would be responsible of the strong yellowish colour some foxing stains. The last band around 2100 cm^{-1} is not specific to this group. In the other group, some of the spectra display this band, independently of the other characteristics of the spectrum.
- Category 3.2: Brown and fluorescent stains. In this group, the characteristics are basically the same as 3.1. Alkenes (669 cm^{-1} and 3041 cm^{-1}) and aromatic compounds (786/1546/3041 cm^{-1}) are present. The main difference between the two subgroups relies on the sugar like spectrum of the latter (3.2) Indeed, the same typical peaks are found, which could support the hypothesis of aromatic derivatives of sugars.

Chemicals involved in foxing stains

The FTIR analysis of a mixture is difficult to interpret. Nonetheless the previous results show that in most of the cases sugar derived compounds are involved in the stains or in thefluorescence. Further more, aromatic or O/N heterocycles are

likely to be found in some stains, or imino sugars or dienoid compounds in some other stains. Only the extraction of the chromogenic and fluorescent chemicals out of the paper would allow the complete analysis ofthe stains. Preliminary results show that this is not as simple as it may seem, probably due to the polarity and to the length of the carbon chain.

The second important feature of the previous analyses relies on the apparent inconsistent dichotomy of fluorescent-yellow/brown stains. It seems that there is no strong evidence for the difference why we believe that fluorescent and yellow/brown compounds may not be deeply different. If their chemical structures are close, the question arises whether one is the precursor of the other?

Conclusion

Fluorescence is a full non invasive characterisation of foxing stains. Maxima of excitation andemission of fluorescence show that the molecules responsible for fluorescence belong to one family and the fine differences may be explained by the different substitutions of a same chemical skeleton. The surface fluorescence analysis is a semi-quantitative measurement which provide information on the evolution (area and intensity) of fluorescent foxing stains. If the fluorescent stains were precursors of the brown stains, surface fluorescence would be the best method to improve preventive conservation in graphic art conservation.

FTIR as a routine analysis is more difficult to set up. The presence of water tightly bond to cellulose absorb in a large band which overlap other fundamental information (1650 cm^{-1}). The most secure way to get rid of this band is to allow a full deuterium exchange. Then the difference between the spectrum of a stained area and a non stained area is normalised (stained area spectrum - (factor x non stained area spectrum)) in the way to neutralise the peak of 2500 cm^{-1} (D_2O). The same procedure can be followed without deuterium exchange but, in this case, the normalisation factor has to be automatically determined by the software (GRAMS 386) which uses an algorithm called "dewiggle". Nonetheless it seems that this is the only non invasive method which can provide useful chemical information on foxing stains. We have set up the back-bone of a taxonomy based on FTIR spectra, made of three main categories:

- Non conjugated ketones which may come from the degradation of cellulose
- Unsaturated compounds (=C, C=N, C=O)
- Conjugated systems of C=C and C=O or C=N linked to sugars.

The question arises whether foxing stains studied here in a limited set of paper samples belong to one superfamily or may be divided into categories. If foxing

stains would belong to the same superfamily, the different spectra would only be relevant of different states of the same process of staining. During the first steps, fluorogenic compounds appear, then chromogenic compounds appear in conjugated chromophores, and eventually, full colour is reached with free ketones.

The latter remains a hypothesis. Only the extraction, the purification and the analysis of the chemicals found in foxing stain area would provide the answer. Another approach would be to use the same analytic procedures applied to *in vitro* models of foxing. The two complementary research tasks are in progress.

Acknowledgement

This research has received financial supports form the French Ministry of Culture, DAP grant n° 053. We want to thank the French Bibliothèque Nationale for the kind gift of stained papers, the Archives of La Rochelle for the nice gift an old XVIIIth century paper and the graphic art Department of Louvre Museum (Mr A. Le Prat) for technical supports. This work has been realized in the University of La Rochelle, in close collaboration with members of the Association for Applied Research in Conservation (A.R.E.C.R.).

Summaries

Non Invasive Techniques for the Investigation of Foxing Stains on Graphic art Material

The yellow/brown stains of circular or irregular shape known as foxing spots have been fully described in conservation literature but still, this phenomenon do not find any scientific agreement since many hypotheses have been raised concerning their origin but we deplore a lack of chemical and experimental evidences. In this work we have used two non invasive techniques for the chemical identification of foxing stains in order to define objective keys for a taxonomy of these stains. Fluorescence gives poor chemical information but if fluorogeniccompounds would be the precursors of the brown end products, the quantitative measurement of fluorescence would be of major interest for preventive conservation. FTIR spectroscopy provides more chemical information and as such, FTIR is a very relevant tool for a taxonomy of foxing stains. Since many chemical bonds may overlap in the same region, the interpretation of FTIR spectra are discussed.

Techniques non-agressives pour l'investigation des taches de moisissure sur les feuilles comportant des graphiques

Les taches jaunes et brunes, rondes ou de formes irrégulières que l'on appelle taches de moisissure ont été souvent décrites dans les ouvrages de littérature spécialisée relatifs à la conservation

et à la restauration. Cependant nous n'avons toujours pas d'explication à leur sujet qui serait acceptée par le monde scientifique en général. Plusieurs hypothèses ont été émises concernant leur origine mais nous déplorons un manque d'évidence du point de vue chimique et des preuves expérimentelles. Dans notre étude nous avons utilisé deux techniques non-agressives pour l'identification chimique des taches de moisissure afin de définir objectivement les critères pour la taxonomie de ces taches. La fluorescence donne peu d'informations chimiques mais s'il s'avérait que les composés fluorescents étaient les précurseurs des substances brunes, alors les mesures quantitatives de fluorescence pourraient être d'un intérêt majeur à titre préventif pour la conservation. La FTIR spectroscopie fournit davantage d'informations du point de vue chimique et dans cette mesure est un instrument très approprié pour la taxonomie des taches de moisissure. Comme plusieurs combinaisons chimiques pourraient se superposer dans un seul et même domaine on discute l'interprétation des spectres FTIR.

Materialschonende Techniken zur Untersuchung von Stockflecken in graphischen Blättern

Die als Stockflecken bezeichneten, gelben und braunen, rund oder unregelmäßig geformten Flekken sind in der konservierungskundlichen Fachliteratur vielfach beschrieben worden. Es gibt jedoch für sie keine von der Wissenschaft allgemein akzeptierte Erklärung. Es wurden mehrere Hypothesen über ihre Ursache aufgestellt, denen es jedoch an chemischer Evidenz und an experimentellen Beweisen mangelt. In dieser Untersuchung wurden zwei nicht-materialzerstörende Techniken zur chemischen Beschreibung von Stockflecken angewandt, mit dem Ziel, einen objektiven Ansatz zu ihrer systematischen Beschreibung zu gewinnen. Fluoreszenz bietet wenig chemische Information, aber wenn die Proto-Substanzen für Flecken Fluoreszenz zeigen, könnten quantitative Fluoreszenzmessungen von Interesse für die vorbeugende Konservierung sein. FTIR-Spektroskopie bietet insgesamt mehr chemische Information und ist deshalb ein sehr gut geeignetes Hilfsmittel für die systematische Beschreibung von Stockflecken. Da sich mehrere chemische Gruppierungen in ein und demselben Bereich überlagern können, wird die Interpretation von FTIR-Spektren diskutiert.

NOTE

* Details of each category, i.e. the spectrum, its deconvolution and its peak table are available upon request from the editor of this journal.

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The Conservation of Papyri Documents Dated to the 4th Century BCE

by MICHAEL MAGGEN

Prologue

In November-December 1993, the Israel Antiquities Authority (IAA) conducted "Operation Scroll", for the purpose of gathering new archaeological information about the caves of the Judean Desert. Within the framework of this operation, an archaeological survey was undertaken in the Ketef Jericho caves (grid.ref.1912 1419) and excavations took place in two caves south of Wadi El-Magfar (Fig. 1), directed by H. Eshel (Bar Ilan University) and B. Zissu (IAA) and many archaeologists and volunteers.

Abi'or Cave

The caves of Ketef Jericho situated in a cliff west of Jericho, were first surveyed in the years 1978, 1979 by the Israel Cave Research Centre of the Society for the Protection of Nature. The most prominent caves form a large cave complex located south of Wadi El-Mafgar. In 1986, H. Eshel carried out excavation work in a cave positioned approximately 5 meters above this cave system. Here he unearthed the remains of thirty-eight refugees of the Bar Kokhba Revolt, where many of one family perished. In addition, six fragments on papyrus scrolls were found alongside the remains: one, in Aramaic, dated to the end of the fourth century BCE; two in Aramaic and three in Greek, approximately dated from the first or second century. These were apparently brought to the cave at the end of the Bar Kokhba Revolt.

During "Operation Scroll" 1993, the large cave complex was excavated in four areas referred to as areas: A, B, F and G. During work in area A, located on a terrace at the foot of the Abi'or Cave, a number of papyrus documents were discovered (Fig. 2), which had apparently fallen, from the Abi'or Cave above some time in the 14th century CE, in the tumult Moslem disturbances when

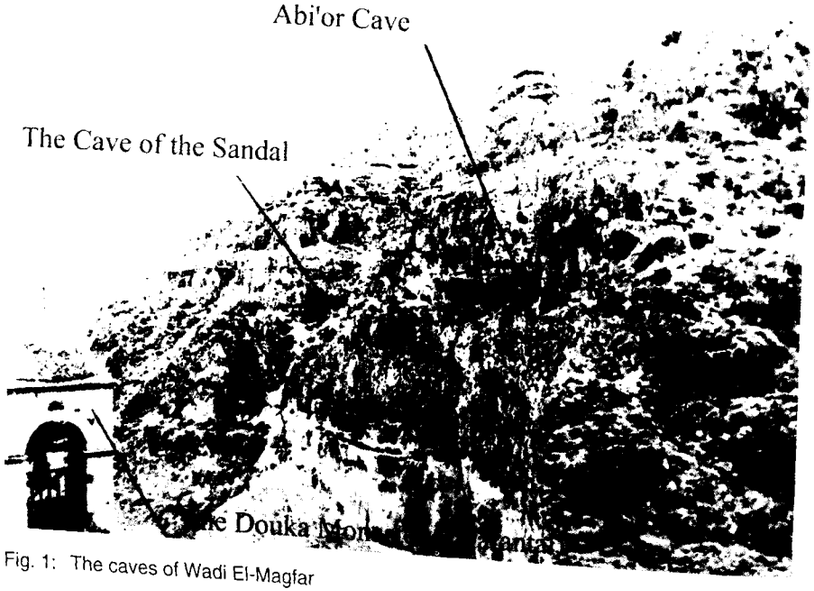

Fig. 1: The caves of Wadi El-Magfar

Fig. 2: Terrace at the foot of the Abi'or Cave, where the papyri were discovered.

monks forced to leave the (Douka) "Qarantal" Monastery found shelter in the caves south of Wadi El-Mafgar. A Mamluk bronze coin from the period was found with the documents. Stratification identification of the layers of fallen sand and particles surrounding the documents provided clues as to the history of the caves. A Silver *drachma* from the reign of Alexander the Great was also unearthed in this area.

Under the small Papyrus fragments items, brought to Abi'or Cave during the Bar Kokhba Revolt, were discovered the remnants of disintegrating mats, a roughly woven textile bag fastened with a rope, and fragments of fourteen different documents. Nine documents written in Aramaic and five in Greek, all pertaining to the sale and

purchase of immovable property. Some of the Aramaic documents fastened with a tiny papyrus thread, are promissory notes.

It is hoped that once the documents have been deciphered we will gain clearer understanding of the history of the Jericho region during the Bar Kokhba Revolt, and particularly, the tribulations of the family that sought refuge and perished in the cave.

Initial excavations were undertaken in three additional areas: B, G and F. A group of Chalcolithic finds including: pottery vessels such as storage jars and cooking pots, partially cremated adult and infant graves and a variety of organic objects, including wooden utensils for daily use were found.

THE CAVE OF THE SANDAL

The Cave of the Sandal, discovered during "Operation Scroll", is a natural, karstic cave, located about 300 m. south of the large cave complex discussed earlier. The excavation of this cave was conducted under difficult conditions. There was poor ventilation, the air was dusty and the approach to the cave was difficult, the team had to climb a vertical cliff and crawl through a narrow tunnel to get inside. The Cave of the Sandal was used as a burial ground during the Chalcolithic and the Early Bronze periods, and for refuge at the end of the Bar Kokhba Revolt. Numerous Chalcolithic and Early Bronze finds were unearthed, together with secondary human burials.

The skeletal remains of at least 12 individuals were found in the cave. The bones of seven humans, gathered in small heaps, were dated to the Chalcolithic and Early Bronze periods. We assume that the other five skeletons are the remains of the refugees of the Bar Kokhba Revolt.

Some of the Chalcolithic bones were wrapped in mats made of palm branches; others bore remains of red ochre pigment, Holemouth jars, decorated with broad red stripes, spouted red painted craters and a miniature jug were found, together with organic remains such as ropes, strings, textiles, and wooden arrowheads. Two axe blades and one club head made of pure copper were also found.

Above this layer of early artefacts, were the remains left by the Bar Kokhba refugees. The ceramic objects found are typical of the period: two oil lamps, cooking pots, storage jars and glass shreds. Parts of leather sandals, other worked leather strips, ropes, strings, remnants of reed mats and baskets were also found. Two tiny pieces of papyrus, written in Greek, were found next to the entrance of the "hall". The metal finds include, two gold rings and a gold earring, a silver spoon and a bronze needle. The coins are the most important find in the cave: 26 silver and bronze coins were found in three clusters[1].

INTRODUCTION

Artefacts found in two burial caves (Vizier and Hemaka) situated in the Sahara Desert and dated to the year 3000 BCE attest that this papyrus document is probably the most ancient ever found. Papyrus is mentioned in Pliny's famous book *Natural History*[2], in which he describes the methods by which the Ancient Egyptians used to prepare their papyrus sheets. The papyrus plant, (*Cyprerus Papyrus*) was found in abundance in the Nile Delta area and in marsh areas. The plant is characterised by a long reed stem about 2.5–4 m long, and a floral top. There were many uses for papyrus in Ancient Egypt, the plant was used for producing fuel and for building reinforcements as well as for making furniture and utensils.

In order to prepare papyrus for writing the outer green bark had to be stripped off. The white fibrous layer underneath the bark contains about 54 %–60 % cellu-

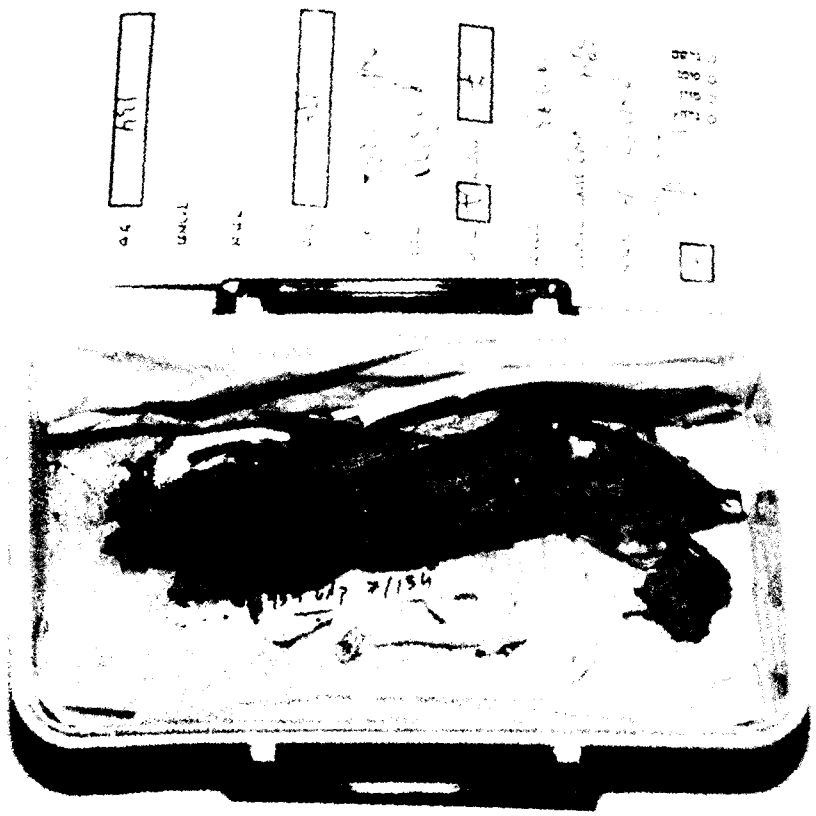

Fig. 3: How the scrolls were transported.

lose and 36 %–40 % lignin. The fibrous layer was spread lengthways into sections next to one another so that each section overlapped the preceding one until a sheet of 40–45 cm width was formed. A second layer was formed on top of the first this time with the direction of the fibres running perpendicular to the layer underneath. The damp papyrus layers were then pressed together in a wooden press or pounded with wooden mallets in order to squeeze out the excess water from the fresh papyrus layers. The tacky fluid adhered together to form integral unit. Starch adhesives were often added in order to obtain a stronger bond between the layers and to seal the porous papyrus fibres preventing over absorption of writing ink. Once the papyrus layers were dry they were glued edge to edge to form a scroll of the required length. Sometimes the direction of the fibres, followed a single direction other times attention was paid to the direction of the aligned sheets.

The most common ink that was first used on papyri in the long run of history was black carbon ink mixed with Gum Arabic, but later on iron gall ink was favoured because it presented better permanence qualities (strong black pigmentation and was not water sensitive) over carbon ink.

THE UNRAVELING OF THE PAPYRI

The papyri were brought to the Israel Museum conservation labs in Jerusalem just a few hours after they were unearthed. The experienced archaeologists, were fully aware of conservation needs and correct handling procedures which are mainly to maintain the original environment climates of the papyri and preventing minimal changes while transporting the delicate objects to the conservation lab. The papyri were transported in cotton padded boxes accompanied with meticulous documentation, including information on the location where the fragments were found and giving reference to earlier identified items of the same type (see Fig. 3). The papyri arrived still partially covered with earth and other foreign debris. Some of the documents were rolled and some partially open. The condition of the papyri varied from one sheet to the next – a small number were almost wholly intact, however, most were fragmented having been damaged by changing dry and humid conditions and by rodent attack.

The process of unravelling the papyrus had three main steps:

- humidification and relaxation of the papyrus
- unravelling the papyrus and spot drying it
- reinforcement and drying

Fig. 4: A scroll in the humifidication chamber

The papyrus scroll was put into a simplified humidification chamber (see Fig. 4). Humidification was provided by several layers of blotting paper soaked in water. The individual papyrus fragments were supported on a polyester web placed over the wet blotters. When the saturated relative humidity in the chamber effected the papyrus it was fully relaxed in about 20–35 minutes (see Fig. 5). The damp fragments were then removed from the humidity chamber and were carefully opened with tweezers and a micro spatula. In order to maintain the required flexibility of the papyrus it was necessary to humidify locally by spot wetting with an ultrasonic humidifier (see Fig. 6). Dry blotters weighted down with glass tile

Fig. 5: Unrolling the repeatedly wetted fragments.

Fig. 6: Unrolling the repeatedly wetted fragments.

were laid on the unravelled scroll, now measuring 5–7 cm long. During the unravelling process the foreign debris attached to the papyrus such as earth and other unidentified impurities were cleaned away. This was done by gentle brushing and vacuuming. The more stubborn encrustations were softened and removed with a small quantity of ethanol.

After the unravelling and straightening of the papyrus, the fragile areas that needed supporting were reinforced from the back with Japanese tissue paper and Methyl Cellulose of very low viscosity. The papyri were archival mounted by simple hinging into a window mat.

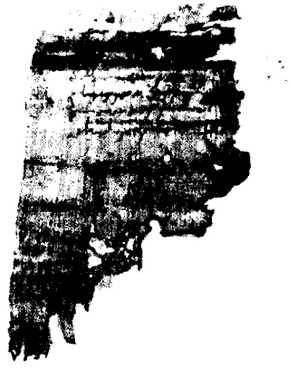

Fig. 7: An unrolled fragment.

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SUMMARIES

The Conservation of Papyri Documents Dated to the 4th Century BCE

In November-December 1993, the Israel Antiquities Authority conducted "Operation Scroll", for the purpose of gathering new archaeological information about the caves in the Judean Desert. During these excavations six fragmented papyrus scrolls were found alongside additional archaeological finds. The papyrus documents, dated to the 4th century BCE, were brought by the archaeologists to the Israel Museum conservation laboratories in Jerusalem where they underwent treatment in a humidification chamber in order to unravel them and to proceed with surface cleanings then reinforced fragile areas with Japanese tissue paper.

La conservation de documents en papyrus datant du 4ème Siècle avant Jésus-Christ.

En novembre/décembre 1993 l'Office Israélien de Protection des Monuments Antiques a entamé „l'opération des rouleaux de parchemin" dans le but de rassembler de nouvelles informations archéologiques sur les grottes du Désert de Judée. Pendant ces fouilles on a trouvé parmi d'autres objets archéologiques six rouleaux fragmentés de parchemin. Les archéologues ont apporté ces documents en papyrus, datant du 4ème Siècle avant Jésus-Christ, aux laboratoires de conservation du Musée d'Israel à Jérusalem, où on les a soumis à un traitememt dans une chambre d'humidification pour les dérouler, puis on a nettoyé leur surface et on a renforcé les endroits fragiles avec du papier japon.

Die Konservierung von Papyrus-Dokumenten aus dem 4. vorchristlichen Jahrhundert

November/Dezember 1993 rief das Israelische Denkmalsamt die „Aktion Rollen" ins Leben, deren Zweck es war, weitere archäologische Informationen über die Höhlen in der Wüste von Judäa zu sammeln. Während der Ausgrabungen wurden, zusammen mit anderen Objekten sechs fragmentarische Papyrusrollen gefunden. Die Archäologen brachten die aus dem 4. vorchristlichen Jahrhundert stammenden Stücke in die Konservierungswerkstätten des Israel Museums in Jerusalem, wo sie einer Behandlung in der Feuchtekammer ausgesetzt wurden, um sie zu entrollen, dann an der Oberfläche zu reinigen und brüchige Stellen mit Japanpapier zu verstärken.

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