

# Papierzerfall - chemische Veränderungen erkennen und stoppen

## Deterioration of paper – identifying the changes and stopping the degradation

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### Zusammenfassung

Papier ist eines der beständigsten organischen Materialien zum Aufbewahren und Transportieren von Informationen. Dennoch gestaltet sich die chemische Analyse von Cellulose und Papier immer noch als schwierig, obwohl es bereits viele Untersuchungsmethoden zur Beschreibung von diversen Papiereigenschaften gibt. Vor allem die Tatsache, dass Cellulose ein natürliches Polymer ist, und dass Papier immer ein komplexes Verbundmaterial aus Cellulose, Hemicellulosen, Füllstoffen und Leimung darstellt, macht eine direkte und schnelle Analyse sehr schwierig. Um Aussagen zum Zustand der Cellulose treffen zu können, sind sensitive Methoden erforderlich, die in der Lage sind, bereits geringe Veränderungen des Polymerisationsgrades und des Oxidationszustandes zu erfassen, da diese die Festigkeit und die Farbstabilität des Papier maßgeblich beeinflussen.

In diesem Beitrag werden zunächst die allgemeinen Alterungsprozesse von Papier durch Umwelteinflüsse (z.B. Temperatur, Feuchtigkeit und Schadgase) vorgestellt, welche zu einer Veränderung der molekularen Struktur der Cellulose führen. Im Anschluss daran werden einige der aktuellen mikroinvasiven oder zerstörungsfreien Methoden vorgestellt. Ihre Anwendung erfolgt hinsichtlich der Zustandsbestimmung des Papiers und zur Beurteilung restauratorischer Fragestellungen.

### Abstract

Paper is one of the most durable organic materials used for storage and transfer of information. The chemical analysis of cellulose and paper still represents a scientific challenge, although numerous advanced analytical techniques are placed at the chemists' disposal. The polymeric character of the material and the presence of accompanying substances, such as hemicelluloses, fillers and sizing agents to name but a few, render a quick and straightforward analysis difficult. Nevertheless, an accurate characterization of the cellulosic material is needed as already minute alterations of degree of polymerization or state of oxidation may cause considerable macroscopic effects, such as strength loss or brightness reversion, and may substantially influence the material's behavior.

In the first part, the present paper summarizes possible chemical changes of the cellulose matrix in response to humidity, temperature, and mechanical stress as the major triggering factors encountered upon aging of cellulose-containing objects. The second part covers state-of-the-art analytical techniques to detect and monitor changes in the cellulose structure, also in the trace concentration range.

## INTRODUCTION

According to its chemical formula, cellulose is a well-defined molecule with three different types of hydroxyl groups per monomeric repeating unit and just one carbonyl (hemiacetale) at the reducing end of each polymer chain. However, real-world cellulose samples have undergone a number of processing steps on the way from wood via pulp processing and bleaching to the final cellulosic product, and may suffer from further aging accelerated by adverse environmental conditions. All these effects cause the introduction of additional oxidized functionalities, such as carbonyls (C=O) and carboxyls (COOH). Such groups, even though present in very low concentrations only ( $\mu\text{mol} / \text{g}$  range), are the cause of many adverse and undesired macroscopic phenomena. Carbonyl groups are held responsible for yellowing or decreased brightness stability of bleached lignin-free papers. They are involved in thermal and light-induced aging, and they cause stability problems under alkaline conditions as well. When it comes to paper permanence, not just carbonyls add to losses in strength and brightness, but also carboxyl groups are involved. Those functionalities are a crucial factor in retention of chemicals and water or in influencing surface charges. Their levels are increased during paper aging, acidification, and corrosion by ancient inks or color pigments. This short compilation already shows that small changes within the celluloses' carbonyl and carboxyl contents may result in large and numerous changes of macroscopic properties.

To measure the extent of oxidative damage to cellulose, some classical methods for the determination of carbonyl and carboxyl groups are available. However, these methods suffer from several shortcomings, such as high limits of determination and detection combined with rather large amounts of material needed. In addition, those methods provide only sum parameters, yielding an overall content. Generally, this results in less accurate data; smaller differences between samples remain invisible. In order to address these analytical challenges our approach aimed at two goals: to find a more sensitive and precise method, and to determine the functional groups not just as a sum parameter, but as a profile, i.e. in relation to the molecular weight of the cellulose.

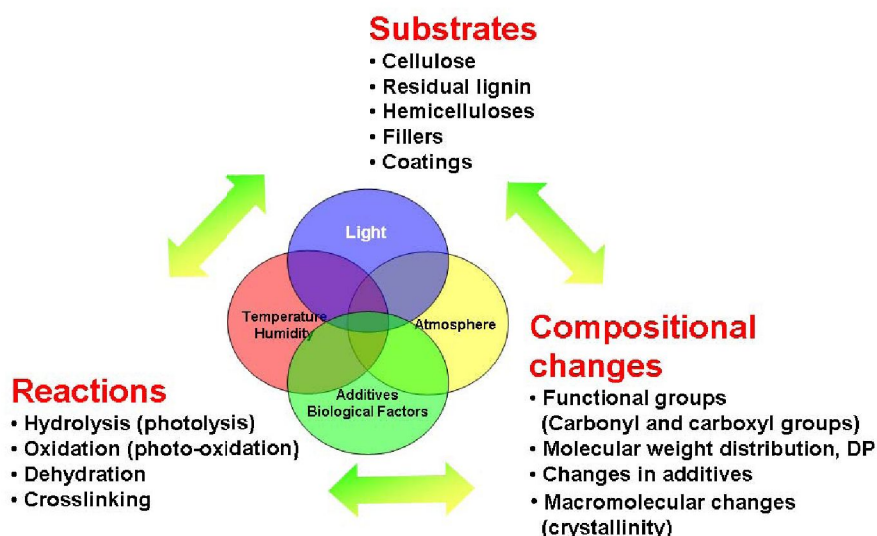


Fig. 1: Relationship between reactions, substrates and compositional changes in papers.

## ANALYTICAL TECHNIQUES

Figure 2 provides a brief overview on the modern analytical tools in order to address chemical changes occurring at the cellulose molecule. Non-invasive methods are superior compared to micro-invasive techniques with regard to sample demand. However, they quite often lack detailed information.

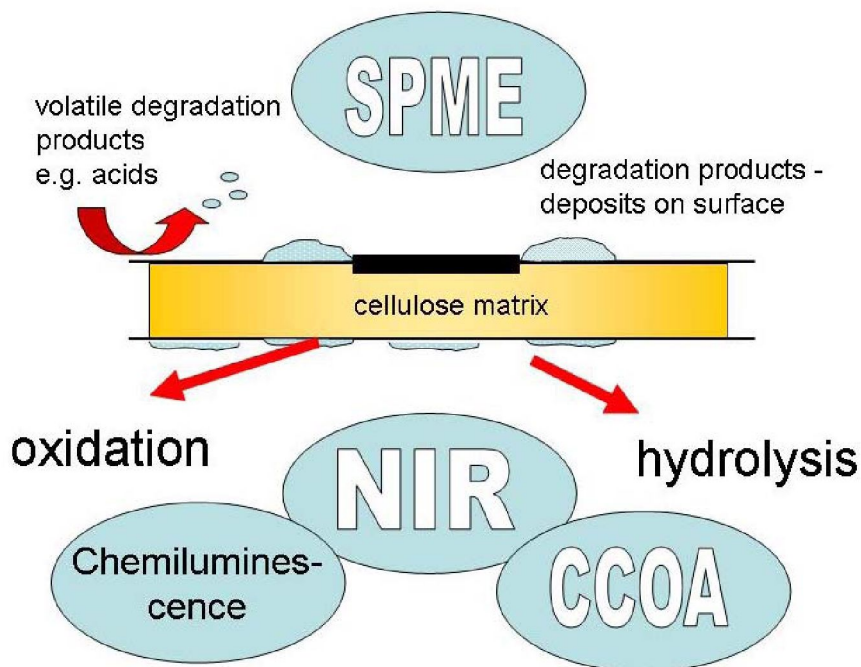


Figure 2: Examples of microinvasive and non-destructive techniques available for cellulose and paper analysis.

### *Solid Phase Micro Extraction (SPME)<sup>i,ii,iii,iv</sup>*

SPME allows the analysis of volatile compounds released from the paper or present at the paper surface. The volatile compounds are taken up by fibers coated with a liquid (polymer) and/or a solid (sorbent), either by absorption in the case of liquid coatings or by adsorption in the case of solid coatings<sup>v</sup>. The fiber is subsequently introduced into a gas chromatograph unit where the compounds are thermally desorbed, chromatographically separated and analysed. Up to 100 different compounds may evolve from an old book, for example. Advantages of the SPME method are the high sensitivity and the semi-quantitative nature of the measurement. Drawbacks consist in the difficulty to work in open systems (best on book stacks).

### *Near Infrared Spectroscopy (NIR)<sup>vi,vii</sup>*

NIR is a very universal technique which is widely applied in diverse areas. As the spectra do not have well defined peaks that reflect certain structures of the investigated substrate as it is the case in conventional IR spectra, the NIR method needs sophisticated correlation which does not depend on an individual wavenumber (univariate calibration), but on several ones (multivariate calibration). The calibration of the method, i.e. the correlation with analytically accessible parameters, is based on wet-chemical analysis. From the same set of samples used for this chemical analysis, near-infrared spectra are recorded and statistically analysed by a computation software to obtain a calibration for the desired properties. When this correlation has been successfully established, new samples can be investigated without the need for chemical analysis, just by retrieving data from near-infrared spectra based on the calibration. Thus, once the calibration has been established the method is very fast, easy, and straightforward. The sensitivity, however, relies on the quality of the underlying wet-chemical technique and the subsequently established calibration model. The NIR technique can also be used to monitor the quality and effect of conservation treatments.

### *Chemiluminescence*<sup>viii,ix</sup>

The application of chemiluminescence for non-destructive analysis was suggested to assess various characteristics of paper. The term chemiluminescence denotes light emission originating from the relaxation of electrons which populated excited states in an elementary process of a chemical reaction and upon returning to their non-excited ground-state emit radiation. In general, chemiluminometry is considered to be a complementary method to study the role of oxidized functionalities and radicals during oxidative polymer degradation. Especially the formation of radicals can easily be followed by chemiluminometry. A correlation between the decrease of DP and an integrated chemiluminescence signal at different temperatures under nitrogen atmosphere and isothermal heating was shown. Some studies have also focussed on the applicability for cellulose analysis in the context of non-oxidation reactions. However, chemiluminescence is a rather complex process and the emitted light can neither be attributed to an individual chemical species nor to a defined chemical process. Chemiluminescence depends upon polymer characteristics, such as previous oxidation, temperature, water, and additives to the studied polymer, e.g. paper additives when analyzing cellulose, which may mislead interpretation.

### *The CCOA/FDAM Methods*<sup>x,xii</sup>

Both analysis techniques use group-selective fluorescence labeling of oxidized functionalities followed by gel permeation chromatography (GPC) to derive the oxidation state of celluloses on a molecular level. The data obtained allow a clear statement on oxidative or hydrolytic degradation pattern in the sample investigated and provide information on changes in the molecular weight distribution in addition. Therefore, not only the extent of oxidation is monitored but also a very sensitive measurement of the condition of cellulose molecules in terms of their degree of polymerization and distribution statistics is performed. As a destructive test method, it cannot be applied to all sample objects of interest, but it is suitable to analyze test samples (dummies) that are stored together with the object of interest. The sensitivity of the CCOA and FDAM protocols is high with respect to both, molecular weight and functional groups. The sample requirement is in the range of 5 mg.

## **CONSERVATION TREATMENTS**

Two examples will be given to illustrate conservation treatments and their effect on the stability of paper. The first example will cover the deacidification of books produced in the period between 1860 and 1980. In this period, a significant decline in paper producing quality occurred when the rising demand of raw material was met by an increased bulk production. More and more chemicals such as potassium aluminium sulphate (alum), and bleaching agents based on chlorine compounds had been used. Materials of inferior quality were thereby provided for paper production even before the introduction of low-quality ground wood pulp. Alum rosin sizing that was added to the pulp slurry provides a permanent source of acidity. Thus, the predominant aging pathway of cellulose and therefore of paper is hydrolytic chain scission. This is closely related to lowered pH values causing increased brittleness of the paper. Usually those papers from the last two centuries contain significant amounts of lignin as well, which can be oxidized more easily. Besides these inherent factors of paper degradation, storing conditions also influence the aging behaviour. All these degradation reactions are reflected by changes in molecular weight, molecular weight distribution and cellulose functionalities.

During the investigation of old, well preserved books it was found that their medium was mostly only slightly acidic or even alkaline. The reason for this was the content of some magnesium and calcium ions in historic papers that established moderate pH conditions. It was therefore concluded that an active input of alkaline substances should improve paper permanence and the idea of paper deacidification was born.

With regard of the huge quantities of acidified books, large-scale mass treatments for the deacidification of whole library and archive stocks have been invented and successfully introduced into the market. With few exceptions, mass deacidification is performed on the basis of magnesium

containing components. Many of the systems use non-aqueous solvent systems in order to be able to treat whole books without damaging the bindings through the swelling action of water.

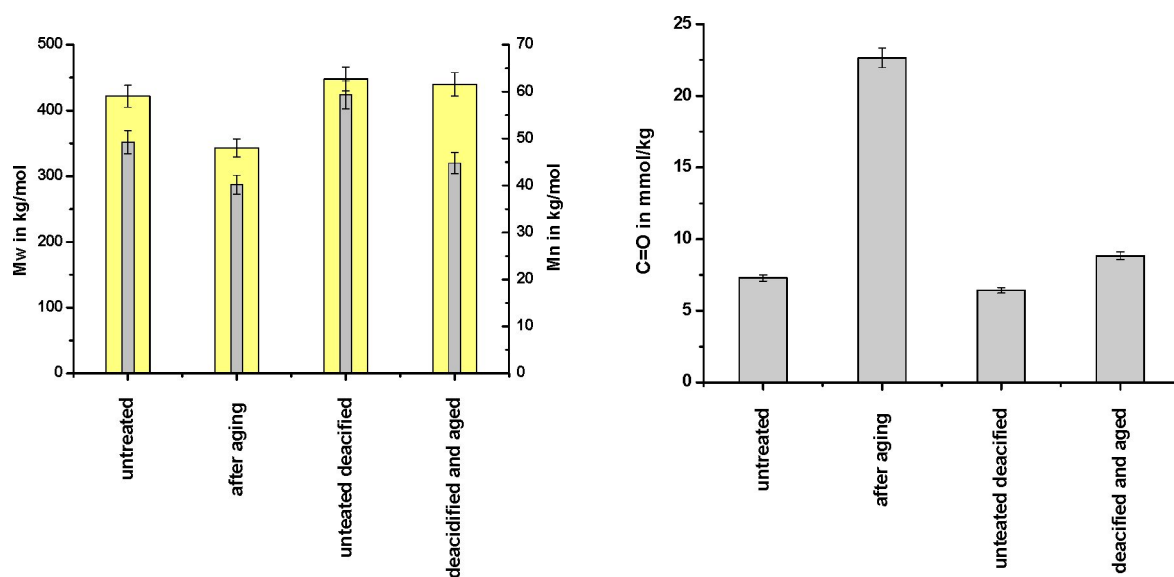


Figure 3: Development of deacidified versus untreated paper in the course of accelerated aging. Left: Weight average and number average molecular weight indicating chain scission due to acid hydrolysis. Right: Carbonyl group content indicating oxidation of the cellulose.

Usually, tests for quality control include on the one hand visual control for unwanted effects on the optical appearance of the treated material. On the other hand pH, amount and distribution of alkaline reserve are determined to document the success of deacidification. Colour measurements and several mechanical tests are performed on mock-up material due to their high sample demand. In our studies, the impact of deacidification on the molecular structure of cellulose was evaluated. In figure 3 the beneficial influence of a deacidification treatment in the course of accelerated aging is demonstrated. Both parameters under investigation - the Mw describing the average length of the cellulose molecule and the carbonyl group content describing the oxidation occurring on the molecule - benefit significantly from the treatment and retain their initial values while untreated and aged papers show a less positive development.

#### *Treatment of papers showing iron gall ink corrosion with calcium phytate*

This study focused on preventive means to stop the iron gall ink-induced deterioration of cellulose and to prevent further damage, keeping in mind that a suitable conservation treatment has to hinder both hydrolytic and oxidative processes at the same time. A combination of the complexing agent calcium phytate and the deacidifying agent calcium hydrogen carbonate in aqueous solution proved to give optimum results. To gain insight into long term stability, an aging step was performed after treatment and different ink modifications were tested. Recording of molecular weight distributions and carbonyl groups over time (CCOA) unambiguously verified for the first time the preventive effect of this treatment on a molecular basis, which was not only seen for the ink-covered areas, but extended also for areas remote from the ink lines.

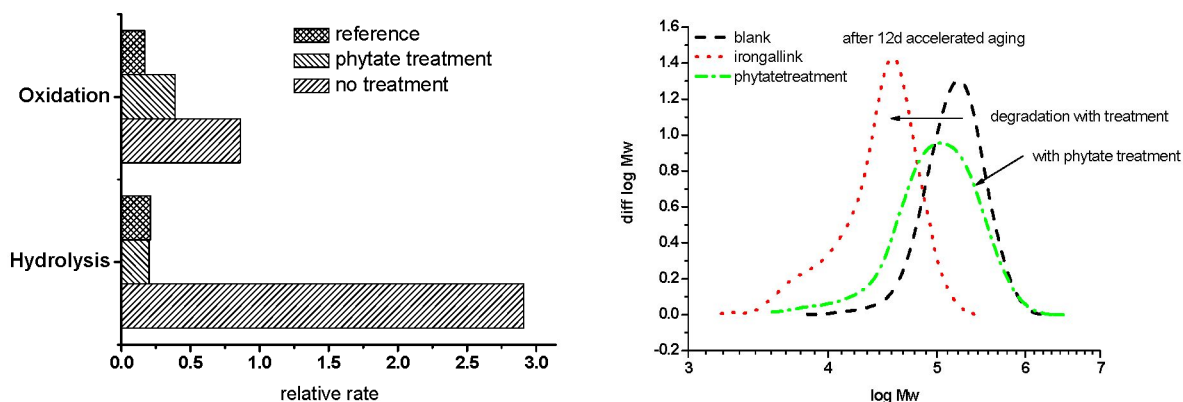


Figure 4: Comparison of phytate-treated and untreated paper in the course of accelerated aging. Left: Relative rate of oxidation and hydrolysis, showing hydrolysis to be completely suppressed by the phytate treatment and oxidation to be slowed down considerably. Right: Molecular weight distribution, revealing a stabilization of the cellulose condition after phytate treatment.

## SUMMARY AND OUTLOOK

Some paper-analytical methods are able to reflect reactions in general, but without reporting specific chemical processes or species (SPME, chemiluminescence). Others are based on well-defined chemistry, but still lack sensitivity (NIR) or are not entirely non-invasive (CCOA/FDAM). The development of improved methodology goes hand in hand with increasing awareness of the chemical changes occurring during use, exhibition and loan traffic of paper objects.

Based on studies on the molecular level according to the CCOA/FDAM fluorescence labelling methodology, the beneficial effect and the sustainable action of a mass deacidification treatment was demonstrated. Similarly, the beneficial effect of a calcium phytate treatment on gall-ink damaged samples was shown and the long-term effect of such treatment has been demonstrated.

<sup>i</sup> Banik et al. *Proceedings of the 27th Research Conference of IARIGAI*, 2001, GRAZ

<sup>ii</sup> Döring, T., Dissertation, Universität Stuttgart, 2007

<sup>iii</sup> A. Lattuati-Derieux, S. Bonnassies-Termes, B. Lavédrine. Identification of volatile organic compounds emitted by a naturally aged book using solid-phase microextraction/gas chromatography/mass spectrometry *J. Chromatogr. A*, 2004, 1026, 8.

<sup>iv</sup> Buchbauer, G, Jirovetz, M, Wasicky, M and Nikiforov, A On the odour of old books, *J Pulp Paper Sci.* 1995, 21, 398.

<sup>v</sup> [http://www.sigmaaldrich.com/Brands/Supelco\\_Home/Spotlights/SPME\\_central.html](http://www.sigmaaldrich.com/Brands/Supelco_Home/Spotlights/SPME_central.html)

<sup>vi</sup> [www.ptspaper.de](http://www.ptspaper.de)

<sup>vii</sup> Strlic M., et al. SurveNIR project, Proceedings 9th EWLP, Vienna, 2006

<sup>viii</sup> <http://www.science4heritage.org/papyrus/index.html>

<sup>ix</sup> M. Strlic, J. Kolar (eds.) *Ageing and stabilisation of paper*, National and University Library, Ljubljana, 2005.

<sup>x</sup> A. Potthast, J. Röhring, T. Rosenau, A. Borgards, H. Sixta, P. Kosma, A novel method for the determination of carbonyl groups in cellulose by fluorescence labeling. Part III. Monitoring oxidative processes. *Biomacromolecules*, 2003, 4, 743.

<sup>xi</sup> R. Bohrn, A. Potthast, S. Schiehser, T. Rosenau, H. Sixta, and P. Kosma, The FDAM Method: Determination of Carboxyl Profiles in Cellulosic Materials by Combining Group-Selective Fluorescence Labeling with GPC. *Biomacromolecules*, 2006, 7, 1743.