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SurveNIR **PAPERTREAT**

Organised in the frame of the European Community, 6th Framework Energy, Environment and Sustainable Development Programme, contracts no. SSPI-006594 (SurveNIR) and SSPI-006584 (PaperTreat).

PROGRAMME

MONDAY, JULY 7TH

SESSION 1		Chairperson: Gerrit de Bruin
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9:20	M. Strlič et al.	<i>SurveNIR Project - a Dedicated Instrument for Collection Surveys</i>
9:30	J. Kolar et al.	<i>PaperTreat Project - Preserving our Paper-Based Collections</i>
9:40	J. Havermans et al.	<i>Cost Action D42 - Enviart: Its Relation to Paper Conservation Research</i>
10:00	T. Łojewski et al.	<i>"Acidic Paper" - Polish Government Programme 2000 - 2008, a Summary</i>
10:20	J. Hanus et al.	<i>The Kniha Project in Slovakia</i>
10:40		Coffee Break
SESSION 2		Chairperson: Barry Knight
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11:30	H. Neevel	<i>Development of a Portable Micro-destructive Light-Sensitivity Testing Instrument</i>
11:50	L. Campanella et al.	<i>Photosensor Application for Studies of the Effect of Ink on Aging of Paper</i>
12:10	M. Bicchieri et al.	<i>Structural Characterisation of Logwood and Redwood Inks</i>
12:30	B. Havlinová et al.	<i>Influence of Deacidification with MMC on Stability of Iron Gall Inks</i>
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15:30	J. Thomas et al.	<i>Evaluation of Anoxic Environments for the Display and Storage of Works of Art on Paper</i>
15:50	A. Balažic et al.	<i>Size Exclusion Chromatography of Cellulose</i>
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17:00	A.-L. Dupont et al.	<i>Simultaneous Deacidification and Reinforcement of Paper by Treatment with Aminoalkylalkoxysilanes</i>
17:20	B. Vinther Hansen et al.	<i>The Lifetime of Acid Paper in The Collection of the Royal Library</i>
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13:40	R. Padoan et al.	<i>Applicability of Quantitative Hyperspectral Imaging to Historical Documents</i>
14:00	U. Henniges et al.	<i>Non-Destructive Determination of Cellulose Functional Groups and Molecular Weight in Pulp Sheets and Historic Papers by NIR-PLS-R</i>
14:20	C. A. Maxwell et al.	<i>X-Ray Diffraction Analysis of Paper Samples - Investigation of the Effects of Water, Deacidification Treatments and Artificial Ageing on Cellulose Crystallinity</i>
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15:30	K. Vizárová et al.	<i>Strengthening and Deacidification of Acidic Groundwood Paper with the Ternary System Chitosane - Methyl-Hydroxyethyl-Cellulose - Cationic Starch in $Mg(HCO_3)_2$ Aqueous Solution</i>
15:50	J. Malešič et al.	<i>Assessment of the Effect of Various Bleaching Agents on Foxing Stains</i>
16:10	D. Krstić et al.	<i>Effects of Previous Treatments on the Drawing "The Holy Family Under the Oak" from the Croatian National and University Library</i>
16:30	Y. Keheyan et al.	<i>Analysis of Historical Papers Using SEM/EDX</i>
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V. Bukovský et al.	<i>Paper Strength and Acidity of Model Collections</i>
I. V. Burtseva et al.	<i>Quantative and Qualitative Changes of Deacidification Solution and their Influence on the Neschen "C-900" process</i>
L. Campanella et al.	<i>Study of Artificially Aged Extra-Strong Paper: Comparison of Trends Obtained from Kinetic Processing of Thermal Analytical Curves</i>
L. Cséfalvayová et al.	<i>Determination of Gelatine in Historic Rag Papers Based on NIR/Chemometrics</i>
J. Hanus et al.	<i>Non - Destructive Survey of Bratislava Antiphonaries Collection - Bratislava Antiphonary II</i>
J. Havermans et al.	<i>Old Mass Deacidification Processes. Where they good?</i>
B. Havlinová et al.	<i>Stability of Arylmethane Dyes on Papers Deacidified by the Booksaver Process</i>
A. Možir et al.	<i>New Antioxidants For Treatment of Transition Metal Containing Inks and Pigments</i>
D. Pucko Mencigar et al.	<i>Determination of Rosin Acids in Paper</i>
R. Radvan et al.	<i>Use of Laser and Optical Diagnostic Techniques on Paper: The 'Pomelnic' from Sucevița Monastery, Romania</i>
T. Sawoszczuk et al.	<i>Application of the Near-Infrared Moisture Meter for Contactless Measurements of Paper and Parchment</i>
M. Strlič et al.	<i>The Papyrus Project: Chemiluminometry for Studies of Material Oxidation</i>
V. S. Šelih et al.	<i>Quantitative Approach to Laser Ablation - ICP-MS Analysis of Iron Gall Ink on Paper</i>
T. Trafela et al.	<i>Determination of Mechanical Properties of Commercial Pulp Samples Using IR Spectroscopy</i>

ORAL PRESENTATIONS

SURVENIR PROJECT - A DEDICATED INSTRUMENT FOR COLLECTION SURVEYS

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1. Introduction

Collection surveys are necessary in order to reveal the condition of a collection, the general conservation needs and in order to plan preservation activities. For such a task, a simple instrument is necessary, which allows us to survey a collection in a non-destructive, non-invasive and chemical-free manner.

In the context of the SurveNIR project, co-funded by the European Commission 6th Framework Programme (2005 - 2008), a consortium of research institutions and end-users built a dedicated NIR spectroscopic instrument, which enables the user to determine a variety of chemical and mechanical properties of paper, including naturally aged paper. The approach has been validated in several European collections in the British Library (London), Victoria and Albert Museum (London), National Archives (The Hague), National Archives (Stockholm), National Museum of

Denmark (Copenhagen), National and University Library (Ljubljana), and State Archives of Dubrovnik.

Traditionally, the condition of a paper-based object or a whole collection is assessed visually, and simple physical and chemical tests are performed, such as the folding test¹ or determination of the pH of paper using pH-indicator pens. During the folding test a paper corner is actually torn away, and the pens leave some of the dye used as a pH indicator on the object. Neither of the two tests can be described as non- or micro-destructive. Even determination of paper pH using a flat surface electrode, which is probably the most often used methodology in paper conservation workshops, is destructive as an area of paper has to be wetted in order that the measurement can take place at all. In addition, traditional surveying methods are also highly subjective.²

Based on the chemical and spectroscopic analysis of more than 1,500 historical samples from AD 1650 onward, we developed a method which enables us to characterize historical paper in terms of gelatine content, mechanical properties, lignin content, pH, degree of polymerization of cellulose and other properties.^{3,4} A lightweight and portable instrument has been developed and designed in cooperation with conservators and curators (Figure 1).⁴ The approach provides museums, libraries and archives with a non-destructive chemical-free low-cost surveying tool that gives more in-depth information than the traditional methods and is at the same time also user-friendly and does not require extensive technical knowledge on the part of the surveyor.⁵



Figure 1: The SurveNIR instrument for non-destructive evaluation of paper chemical and mechanical properties for collection surveying, based on chemometric evaluation of NIR spectra.

Additionally, software has been developed which allows the surveyor to work in three different modes:

- Single item assessment: for condition assessment of an individual item, where chemical and physical data are needed for several locations on the same object,
- Random collection survey: for surveys of large collections, where a subset of a collection is first pre-selected and on the basis of condition assessment of the subset, the condition of the whole collection is deduced (with a pre-calculated confidence interval and a level of significance),
- Total collection survey: for smaller collections, where all objects in a collection can be surveyed.

The software provides chemometric (partial least squares - PLS) methods both for single sheets (graphical or archival documents) as well as for books. In addition to providing the chemical and physical data on the paper, the software also enables the user to build a survey questionnaire based on a set of descriptive criteria, which can be freely defined, e.g. binding condition, evidence of mechanical damage etc., however, these need to be evaluated visually.

2. Acknowledgement

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3. References

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PAPERTREAT PROJECT - PRESERVING OUR PAPER-BASED COLLECTIONS

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1. Introduction

In the 19th century, changes in production technology gave rise to a decrease in paper quality, which resulted in a massive decay of library and archival holdings. In order to increase the useful lifetime of the vast quantities of original materials, paper collections may be deacidified and/or stored in appropriate conditions. Although preservation strategies are well known and have been used for decades, their effect on real-time ageing has not yet been evaluated. Together with the evaluation of side effects and cost estimates, these data are essential for the development of a suitable preservation strategy.

The main aims of the PaperTreat project, co-funded by the European Commission 6th Framework Programme (2005 - 2008), were to estimate the extension of the useful life of paper, as achieved by traditional and novel treatments

as well as by storage at low temperatures, to identify the side effects of the treatments and to provide cost estimates for each treatment, thus enabling the development of the most cost-effective preservation programmes.

The main achievements of the project are the following:²

- A new methodology for the determination of the condition of paper was developed. The technique (size exclusion chromatography) for the first time allows us to reproducibly determine the condition of paper which contains a significant amount of wood-derived lignin. A few fibres suffice for the analysis, which renders the methodology suitable for characterisation of historical materials. This represents a significant advantage over the traditionally used methods, where mechanical properties are determined, which require an ample amount of sample and are burdened with a high uncertainty of measurement.¹
- The technique was used to survey the condition of the collection of Narodna in univerzitetna knjižnica (National and University Library, Slovenia). Together with micro-pH and fibre furnish analysis, an overview of the types of the papers used and the condition of paper, manufactured between 1850 and 2000 was obtained.
- Based on the results of the survey, two model papers, representative of papers made in the 19th and 20th centuries, were produced. A model paper containing a variety of inks was produced as well. These model papers will enable quality control of deacidification processes and significantly simplify the evaluation of future new or modified processes.
- A database of immediate side effects together with a damage atlas was developed. This will help in the selection of materials for treatments, as well as simplifying the evaluation of side effects by the end-user institutions.
- The volatile organic compounds (remaining solvents and reaction products) emitted by treated books were identified and quantified in order to determine the rate of emission under storage conditions. The health and safety regulations were consulted in order to estimate their effect on health.
- The effect of a variety of deacidification methods on the stability of paper at room temperature and under cool and cold storage (15 °C and 5 °C) was determined.² In addition, pollution ageing and light-induced degradation of treated papers were studied. The new ASTM standard on closed-vessel ageing of paper was critically evaluated.³ This will enable evidence-based paper preservation management in libraries and archives.

- Administrative procedures, such as contracts and insurance, as well as costs of various treatments were evaluated and compared.

Results of the PaperTreat project will enable development of the most cost-effective preservation strategies for the decaying collections and thus ensure safekeeping and long term access to the endangered written cultural heritage.

2. Acknowledgement

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3. References

1. A. Balažic, J. Kolar, M. Strlič, E. Žagar, *Size Exclusion Chromatography of Cellulose*, Durability of Paper and Writing 2 Book of Abstracts, Ljubljana, July 7-9, 2008.
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COST ACTION D42 - ENVIART: ITS RELATION TO PAPER CONSERVATION RESEARCH

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1. Introduction

COST stands for Cooperation in Science and Technology and is the longest running network funding organisation in Europe. Within the COST network, Action D42 is dedicated to the role of the indoor environment on the behaviour of the materials present in archives, libraries and museums. Under storage, use and or exhibition. The indoor environment is characterised by many factors contributing to deterioration of cultural artefacts. Networking in this field is therefore very important, in order to exchange knowledge, to cooperate and not to duplicate research. This paper gives an overview of COST Action D42 in networking and research, including its role in paper conservation science.

The accessibility of movable heritage depends not only on its direct conservation but also on preventive conservation actions as the quality of the indoor environment is decisive for the preservation of a collection. Sensitive materials, displayed in an aggressive environment may suffer from chemical attack of pollutants, leading to irreversible damage within only a few weeks of inappropriate exposure. The interpretation of results on the impact of pollutants on the degradation of the artefacts (in combination with other environmental parameters, such as humidity and temperature) and consequently, any appropriate measure to prevent damage requires a close collaboration between multidisciplinary key players: chemists concerned with environmental effects and material degradation, conservators, conservation scientists, art historians, curators, environmental engineers, show case manufacturers, and even politicians and decision makers concerned with international standards.¹

2. COST D42 - ENVIART

The aim of COST D42 is to explore chemical interactions between cultural artefacts and typical indoor environmental conditions through field studies and laboratory experiments and transfer the results into preventive conservation practice. Within this action, three working groups have been established. WG 1 on Preservation (with task group 1 “degradation and stabilization” and task group 2 “Prevention”), WG 2: Analysis (with task group 1

“materials” and task group 2 “environment”) and WG 3: Guidelines (with task group 1 “methods” and task group 2 “storage and health”). Members of the Management committee of COST D42 can be found at:

www.cost.esf.org/index.php?id=188&action_number=D4.

2.1. WG 1 - Degradation and Stabilisation

Within the working group 1, applications of sensitive techniques such as AFM, HPLC and synchrotron FTIR and XRD are discussed in order to improve our understanding of the chemical changes occurring to e.g. proteinaceous materials in different environments. Based on the knowledge of deterioration processes, and influences of environment on the material, strategies can be set for preventive actions. Furthermore, strategies are discussed for the active prevention of our cultural properties. Correlations have been made between the microscopic and physical properties of such materials, dramatically improving our early assessment of damage and allowing an artefacts vulnerability to catastrophic environmental changes to be assessed. Questions arose, such as ‘what will happen if Dead Sea Scrolls, which have been encapsulated into Stabiltex fabric for 10 years, are reopened’.³ Ageing experiments are fundamental in this area of interest of COST D42 and the results are heavily influenced by the methodology.²

2.2. WG 2 - Analyses

Analyses play a fundamental role within D42. Destructive and non-destructive ones, and application of newly developed tools. Based on the three principal meetings, in Ohrid (FYR Macedonia, June 6), Padova (Italy, October 4th) and in Copenhagen (Denmark, November 24), the topics could roughly be divided to analysis of artefacts and analysis of the environment. Considering the lively activity within this WG, we foresee that areas of research of increasing importance are the use of spectroscopic methods in combination with chemometrics, the use of chromatographic methods for both environmental analysis and polymeric materials (natural and synthetic), and environmental monitoring.³⁻⁵

2.3. WG 3 - Guidelines

The input of WG1 and WG2 forms the motor behind the work of WG3. There is also a strong synergism between D42 WG3 with the European standardisation body CEN, TC346 WG4.^{6,7} Recently, this resulted in the first discussion of a harmonised application of simple industrial devices measuring the relative humidity. Here, standardised sensors are applied, however, the housing design made the sensors not adequately responsive. Items, such as: “new specification for light and lighting for exhibitions of art and artworks”; “harmonisation of indoor environmental conditions”; “scientific differences between current methods for artificial pollution”; “RH in cultural heritage and interaction of moisture with historic materials”; and “the role of a historical climate” are frequently discussed.

Based on the scientific discussions, advice was given for the development of new CEN documents e.g. "N129 on recommendations for showcases"; and "N127 on guidelines of environmental conditions".

2.4. Short Term Scientific Missions

STSM is an instrument which can be applied for exchanging researchers from one institution to another institution in order to e.g. learn new techniques or to solve certain scientific questions. There are some restrictions. The home and the host institutions must be from a so called COST member state, the duration should be at least 5 days and there is a maximum grant per mission. For this purpose COST D42 has STSM four calls per year, which are evaluated. A STSM proposal must address the aims of the action D42. More information can be found at the COST general website and at www.enviart.org.

3. References

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“ACIDIC PAPER” - POLISH GOVERNMENT PROGRAMME 2000 - 2008, A SUMMARY

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1. Introduction

The long-term Government Programme “Acidic Paper. Mass-scale preservation of endangered Polish library and archival collections” has been launched nearly nine years ago and this year is the last year of the project. The program is financed mainly by the Ministry of Culture and National Heritage, with support coming from the Ministry of Science and Higher Education (investments at the Jagiellonian University and several research and educational sub-projects) and Ministry of Economy (sub-project focused on the introduction of the acidic-free technology for paper production). The main objective of the Programme are the 19th and 20th century collections printed on poor quality acidic paper and stored at the main repositories in Poland - National Library (Warsaw) and Jagiellonian Library (Krakow) - as well as National Archives.

There are three main objectives which have been outlined within this programme:

1. A complete and competent definition of hazards. The defining process includes also a selection of library and archival collection items based on their degree of endangerment attributable to Poland's geographical and administrative classification.
2. Undertaking firm preventive measures limiting, and in some cases completely excluding, an inflow of acidic materials into library and archival collections.
3. Creating, in Poland, a network of mass deacidification and strengthening installations for the impermanent 19th and 20th century paper which would work in conjunction with large scale microfilming equipment for endangered collections.

An important outcome of a project is also setting up a new research groups which devoted their activities to the problem of paper stability and degradation.

2. Research Projects

Within the framework of the Acidic Paper Programme three research projects have been completed:

1. Survey on the preservation status of the 19th and 20th century collections in Polish libraries and archives (National Library, Warsaw).

2. Comparative study of paper and books deacidified by different methods - microbiological aspects (The Centre for Paper and Leather Conservation, Nicolas Copernicus University, Toruń).

3. Influence of technological parameters on the stability of alkaline papers (Pulp and Paper Research Institute, Łódź).

The most important conclusions for the whole Programme came from the project carried-out by the National Library - using methodology developed at the Stanford University¹ the conditions of Polish collection were evaluated, taking into account their physical and chemical (pH, fibre composition, lignin content) characteristics. The obtained results² allowed for the estimation of the extent of destruction caused by the acidic paper - 17.4% of tested books belongs to the category 3 (very poor condition), 31.3% to the category 2 (intervention needed) and 51.3 to the category 1 (overall good condition). 90% of tested books were printed on acidic paper, with the median pH value equal to 4.1 units. The total number of acidic books in the major Polish collections was estimated to 43 - 45 millions.

In the separate study³ on the condition of Polish collections over 24.000 of books from six libraries were tested with the pH-pen (produced in-house and distributed in a large number to educate and promote the awareness of the acidic paper problem). The survey confirmed findings of the National Library team on the low pH of books and newspapers in Polish repositories and showed that the era of acidic-paper finished around 1996. In the period 1994 - 1998 the percentage of acidic acquisitions in Polish libraries has dropped from 86.6% to 0.73%.

3. Major Investments

The most important aim of the project was to build infrastructure for mass-scale deacidification in Poland. The experiences of other countries (USA, Canada, Germany) have shown that major libraries and archives could organize large mass-scale deacidification projects committing themselves to the service of a private companies which provides the know-how and the technology. Poland decided to take a different route. At first, thanks to the developments made by the Neschen AG in the year 2003 the Bueckeberg method became available in the form of a relatively small machine - Neschen C900. This method of deacidification allows for the treatment of single-sheets only (the method is water based) but with a high efficiency - one operator in an 8-hours shift is able to treat up to 1500 pages. In the year 2003 one of the first machines C900 produced by the Neschen AG was installed in Krakow. In the year 2005, in a second tender announced by the Jagiellonian Library, the Bookkeeper technology was purchased from the Preservation Technology L.P. (USA). The National Library (Warsaw) and the State Archives followed the Krakow example and in the years 2006 - 2007, the second, bigger Bookkeeper installation was purchased (National Library) as well as six C900 machines (National Library and central and regional

branches of the State Archives). Apart from deacidification apparatuses at five branches of the State Archives new microfilming and digitalisation units were organised and equipped.

At the last year of the Acidic Paper Programme the total capacity of the two Bookkeeper installations working in Poland could be estimated to 85 tons per year (Paper Clinic Krakow - 35, Warsaw - 50).

Both deacidification centres installed vertical and horizontal reactors, which allowed for deacidification of bound volumes as well as single sheets or over-sized volumes (i.e. bound newspapers).



Figure 1: The Bookkeeper installation at the Paper Clinic, Jagiellonian University, Krakow.

The investments financed by the Programme were not limited only to deacidification and microfilming equipment and the facilities where the new centres were located. At the Faculty of Chemistry of the Jagiellonian University a new laboratory unit was organized and equipped with modern analytical tools to carry-out research in the field of paper degradation (Laboratory on the Permanence and Degradation of Paper - <http://www.chemia.uj.edu.pl/~kp>). The Laboratory is currently engaged in several national and international research projects dealing with the paper deacidification (EU 6th FP: "PaperTreat") and protection of movable cultural heritage (COST Action D42: EnviArt - Chemical Interactions between Cultural Artefacts and Indoor Environment).

4. Education

An important part of the Polish Acidic Paper Programme was to build and develop various tools for exchange of information as well as education on different levels. The problem of degrading paper-based collections was presented to the general audience through publications in every-day newspapers, popular science magazines, open access lectures during book-fairs and science days. A poster exhibition travels through major cities in Poland, also a multimedia CD and two books on the acidic-paper problem were published. The programme partners has set up web-pages which present the technology applied for the mass

conservation and collects information on the chemistry of the problem, data on the collections conditions, inform on other techniques of mass-scale deacidification:

- State Archives - www.archiwa.gov.pl/?CIDA=549.
- National Library - www.bn.org.pl/inne/wpr/kwasny.html.
- Jagiellonian library - <http://www.bj.uj.edu.pl/KP>.

A two-semester post-graduate study was initiated in 2008 at the Faculty of Chemistry, Jagiellonian University aimed at conservators and researchers working in the field of cultural heritage - Instrumental analysis for the conservation of heritage objects.

The first year of the studies was financed by the Ministry of Science and Higher Education through the Acidic Paper Programme.



Figure 2: The tent with an exposition devoted to paper degradation. Festival of Science, Krakow, May 16th, 2008.

5. Summary

The Long-term Government Programme 'Acidic Paper' resulted in Poland in a major change in the field of mass-scale conservation at the key national institutions. Spending approximately €20 millions Poland has organized a network of centres with well educated personnel and furnished with modern equipment for mass-scale deacidification and microfilming. The coming year will be a difficult test for the newly established centres and their host institutions which will demonstrate how well we are prepared for the operation without the support of the Programme...

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THE KNIHA PROJECT IN SLOVAKIA

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1. Introduction

The Kniha^{SK} project is aimed at supporting education, research and industry in the field of Conservation Science, Technology and Industry (CSTI) in Slovakia. There are an adequate number of highly-qualified human resources which is the basic requirement for CSTI development in the country. The project is a consequence of the programme statement of the Slovak Government, and has been elaborated by the Consortium of the Slovak University of Technology, Slovak National Library, Slovak National Archive, Slovak Academy of Sciences and the private sector. The project Kniha^{SK} should lead to establishment and development of a modern conservation industry in the field of preservation of millions of books and documents in Slovakia in the first decades of the 21st century. According to the project scheme, it will be oriented also to the field of protection of other information carriers - wood, textile, inorganic and metal materials, as well as preservation of other historical artefacts and monuments.

2. Results

The most substantial results of the Project Kniha^{SK} were accomplished:

1. Consortium Kniha^{SK} is presently the owner and a co-owner of know-how, of 33 patents, licences and trademarks. The solutions of the project problems were published in 257 publications¹⁻⁷ of which 77 in current contents and peer-reviewed journals and 16 in scientific monographs and book publications.
2. The number and interest of high school and university students in chemistry and preservation technology of cultural heritage has increased, including the interest of higher university education, research and modern technologies of analysis and preservation; 2 PhD - dissertation theses were successfully defended, 76 diploma, bachelor and student science theses elaborated.

3. The shared space of world-wide and new own knowledge, intranet communication system and virtual work space for researchers of the project, which can be found at <http://kniha.chtf.stuba.sk/dav>, as well as the shared potential of instruments and devices available for education and research of protection of cultural heritage was enlarged and improved. The information on the shared potential of instruments and equipments is now available for the Consortium Kniha^{SK} members as multimedia DVD catalogue; the new internet portal informing about aims and continuous results of the project Kniha^{SK} was created and can be found at <http://www.knihask.eu>.

5. A system of sorting books was improved. Guidelines for description of the state of documents in stores of libraries and archives in SR were prepared. Conditions for evaluation of the state and for sorting of the other (non-paper) traditional material carriers of information and objects of cultural heritage were established as well.

One of the goals of the Kniha^{SK} project lies in the elaboration of a multi-criteria system of evaluation of the efficiency and quality of deacidification processes and related equipment, and in selection of technologies intended for further development in Slovakia in the nearest period.

The evaluation system of the Consortium Kniha^{SK} takes into account the needs of Slovakia in the field of promoting own university education, research, technological development and culture. Up to now, the evaluation has been applied to test mainly wood-containing types of paper, the type most sensitive to ageing and important paper type for the Slovakian collections.

3. Evaluation Criteria

The following criteria stem from a multi-criteria evaluation systems of Kniha^{SK} and Library of Congress.⁸

3.1. Innovation Potential

The selected technology platforms must possess good innovating potential for the continuing university research and technological development (RTD), higher education in Slovakia or in cooperation, and continuing employment rise of highly-qualified human resources in the RTD and innovative new industries in the Slovak Republic and in collaborative RTD with EU partners. This implies for the CSTI area, the protection of cultural and natural heritage, renewable resources as well as new industries areas.

3.2. Efficacy in Term of Increased Mechanical Permanence and Lifetime Prolongation

This criterion, proposed by the Library of Congress (LoC, USA, 1994), reads as follows: "efficacy of deacidification process on tested paper, which is expressed as the rate at which paper loses strength upon accelerated ageing (e.g. at 90 °C / 50 RH for up to 30 days), it shall be decreased by at least a factor of 3.0, when the logarithm of the folding endurance is plotted against time in days. The permanence of

the treated paper shall be increased by a factor of 300%, the books should keep their utility properties 3 - times longer”.

3.3. pH and Alkaline Reserve, their Stability

3.4. Price of Technology and Deacidification

3.5. Risk Assessment:

- Damage of documents.
- Explosion hazard.
- Fire hazard.
- Health hazard.
- Environmental hazard.
- Chemical hazard.

4. Results of Comparative Evaluation

The first part of the comparative evaluation has been completed based on wood-containing test paper and test books evaluation. The objective testing and evaluation of stabilised paper, documents and conservation technologies, along with the development and improvements of new non-destructive, micro-chemical, micro-sampling and quasi-non-destructive methods and validation of the testing methods is the continuing activity of the Consortium Kniha^{SK} in the Slovak Republic.

4.1. Innovation Potential.

Based on the multi-criteria evaluation system, in particular on the criterion of “innovation potential”, the best option for continuous research, development and university education in Slovakia is the HMDO (ZFB/Nitrochemie) and air (Libertec/SoBu) platforms. Stemming from the inherently free nature of the university research, no platforms, companies or cooperation activities requiring or trying to retard or forbid to publish the research results and/or to exploit them in university educational activities, can be accepted.

4.2. The Efficacy

The efficacy in term of increased stability of mechanical properties and life-time prolongation requirement as adopted by the Kniha^{SK} consortium and the project proposed by the LoC, Washington, has been best met by the processes implemented the HMDO (Nitrochemie, Wimmis; Battelle, Eschborn; ZFB, Leipzig) and air (SoBu, Fürth) platforms.

The wood-containing test paper composed of 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, with surface pH = 5.6 was subjected to testing; model test books were prepared from the paper and treated at the Battelle, Eschborn; ZFB, Leipzig; Nitrochemie, Wimmis; UPC, Barcelona; Preservation Academy, Leipzig (PAL); SOBU, Fürth. Sheets of wood-containing paper were sent to Neschen, Bückeberg; and Preservation Technologies (PTI), Heerhugowaard.

The ageing was carried out with samples encapsulated in a PET-Al-PE foil bags at 96 ± 2 °C with an exception of Bookkeeper process (PTI, Heerhugowaard) using dry ageing process of loose sheets of the test paper at 105 °C. Mechanical, optical and chemical properties were measured, published in internal research reports of the Consortium. The results obtained at the testing laboratory IPST, Atlanta for the Bookkeeper deacidification process,⁸ were accepted as provided.

A part of the results presenting the mechanical folding endurance permanence evaluation is shown in Figure 1. The order of deacidification processes quality was made based on Consortium Kniha^{SK}, Bratislava, and LoC, Washington methods. The requirement: the coefficient of lifetime prolongation $S_{t,\omega}$ must reach the value of 3 as a minimum.

Requirements concerning pH and alkaline reserve were met at all evaluated processes, but some of them, e.g. PAL-CSC process failed at both the pH stability and the alkaline reserve stability during accelerated ageing in closed vessels.

Based on the criterion of price, air based technology is the most cost-efficient.

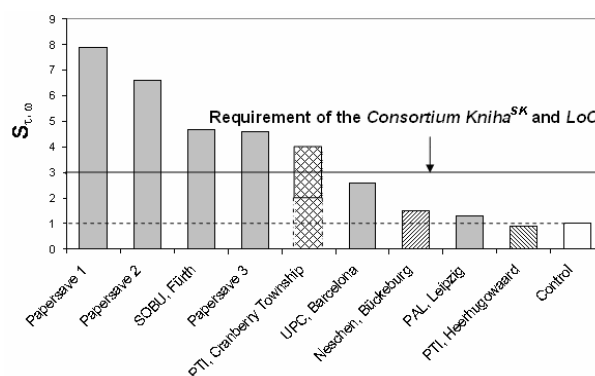


Figure 1: Comparative evaluation of deacidification efficacy based on the 1st criterion of the Consortium and Testing Lab Kniha^{SK}, Bel Novamann International, Bratislava and the Library of Congress, Washington.⁸

$S_{t,\omega}$ - coefficient of ageing time change; the index $S_{t,\omega}$ is related to a non-modified, non-deacidified control sample having $S_{t,\omega} = 1$.

- Processes evaluated in the Consortium Kniha^{SK} Testing Lab, the test books of A5 format (wood-containing paper, 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, surface pH = 5.6), ageing conditions: accelerated ageing in closed bags from composite foil (PET-Al-PE), 98 ± 2 °C, 15 days.⁹⁻¹¹
- Ditto, the test sheets of A5 format, accelerated ageing, 105 °C.¹²
- Process evaluated in the Consortium Kniha^{SK} Testing Lab, the test sheets of A5 format (wood-containing paper, 55% of mechanical bleached groundwood, 20% of bleached kraft pulp, 15% scrap fibres and 10% clay, surface pH = 5.6), ageing conditions: accelerated ageing in closed bags (PET-Al-PE), 98 ± 2 °C, 15 days.¹⁰
- ☒ Process evaluated at the IPST, Atlanta and at the LoC,⁸ various kinds of test sheets (pH = 5.7 - 9.42), accelerated ageing at 90 °C and 50% RH during 30 days.

Control - untreated paper of the same type as the treated/ deacidified one.

4.3. Risk Assessment.

It is known that the older water-based deacidification processes Neschen, Bückeberg, or Vienna process cause the most severe deformation, buckling, cockling of paper and

mainly the deformations of book cover, either evaluated subjectively, or using objective laser methods, and therefore they are not suitable for book deacidification. On the other hand water enables the deepest diffusion of water-soluble deacidifying agents into the cell walls and molecular structure of lignocellulosics. The deformation in other processes is either negligible or small.

Considering the criterion fire and explosion hazard, the safest options are the air platforms (SoBu / Libertec/ Bückeberg), followed by techniques employing freons and halogenated hydrocarbons (UPC Barcelona; PAL, Leipzig; Bookkeeper, PTI, Cranberry Township and Heerhugowaard) and ending with the most dangerous techniques with regard to fire and explosion hazard, HMDO (ZFB, Leipzig; Nitrochemie, Wimmis; Battelle, Eschborn) due to the large volumes of the liquid HMDO per 1 kg of processed documents, with high flammability and the flash point 1 °C.

The processes exploiting water and air are characterised by low health and chemical risks or none.

These air and water based technologies are also the most ecological with the lowest environmental risk. Higher environmental risk is attributed to procedures supporting the increase of production, and utilisation of freons or other halogenated hydrocarbons (as compared by the Global Potential Warming (GPW) indicator), or organic solvents.

Based on the unbiased multi-criteria evaluation, HMDO and air based stabilizing technologies are at the time being the most suitable procedures, both having currently their specific advantages and drawbacks, as well as sound potential for the future development, creating good conditions for the further development of the university education and RTD in the country in the conservation science and technology area.

5. Acknowledgement

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NEW ANTIOXIDANTS FOR TREATMENT OF TRANSITION METAL CONTAINING INKS

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1. Introduction

Corrosive iron ions and acids in iron gall inks lead to enhanced degradation of paper. Due to the extent of damage, the topic has been in the focus of several recent studies. It is generally accepted that the most effective aqueous stabilisation method developed to date is the so called "Calcium phytate" method. It involves treatment with an aqueous solution of an antioxidant calcium ammonium phytate, followed by the deacidification with calcium bicarbonate. Recently, use of magnesium phytate solution was proposed.¹ Contrary to "Calcium phytate" method, ammonia solution is not needed in its preparation, thus minimising health risks. Also, as magnesium phytate is fully dissolved at the conditions of use, risks of formation of the surface deposits are minimised. In addition to aqueous treatments, the EC co-funded project InkCor proposed the use of bromide antioxidants for non-aqueous stabilisation of iron gall inks.²⁻⁴ Within this study, the stabilising effect of aqueous treatments with calcium and magnesium phytate and non-aqueous treatments involving several new imidazolium antioxidants was evaluated.

2. Experimental

Iron gall ink was produced by dissolving 31.4 g of gum Arabic, 98.4 g tannin and 8.34 g FeSO₄·7H₂O in 100 mL of deionised water. It was applied to model paper made from historical rag fibres using a plotter (Roland DXY 990, pen 0.7 mm, pen speed 1 cm s⁻¹). Samples were then pre-aged in a climatic chamber (Vötsch Climatic Chamber Type VC 0020) at 80 °C and 65% RH for 4 h. After pre-ageing, the samples were treated using a solution containing

0.05 mol L⁻¹ (C₂H₅O)₂Mg (code MgEtO) and 0.03 mol L⁻¹ of antioxidant in ethanol. The following antioxidants were used: tetrabutylammonium bromide (TBABr), 1-benzyl-3-butylammonium bromide (BBABr), 1-ethyl-3-methylimidazolium bromide (EMIMBr), 1-butyl-3-methylimidazolium bromide (BMIMBr), 1-butyl-2,3-dimethyl-imidazolium bromide (BDMIMBr) and 1-hexyl-3-methylimidazolium bromide (HMIMBr) and 1-hexyl-3-methylimidazolium chloride (HMIMCl). After the treatment, samples were aged at 80 °C and 65% RH. Viscosity was determined according to ISO 5351/1.

3. Results

Rate constant were determined from viscometric data using the Ekenstam equation.⁵ The results are summarised in Table 1.

Table 1: Degradation rate constants at 80 °C of untreated paper containing iron gall ink (Untreated) and the ones stabilised using prototype non-aqueous treatments or aqueous calcium or magnesium phytate treatments.

treatment	<i>k</i> (mol mol ⁻¹ h ⁻¹)
Untreated	1.01E-05 ± 8.83E-07
MgEtO	7.05E-06 ± 5.36E-07
TBABr	4.54E-06 ± 6.74E-07
BBABr	4.45E-06 ± 4.36E-07
EMIMBr	1.84E-06 ± 2.25E-07
BMIMBr	2.98E-06 ± 4.96E-07
BDMIMBr	1.68E-06 ± 3.81E-07
HMIMBr	2.64E-06 ± 4.58E-07
HMIMCl	3.30E-06 ± 3.67E-07
Ca phytate	2.65E-06 ± 1.71E-07
Mg phytate	2.49E-06 ± 2.38E-07

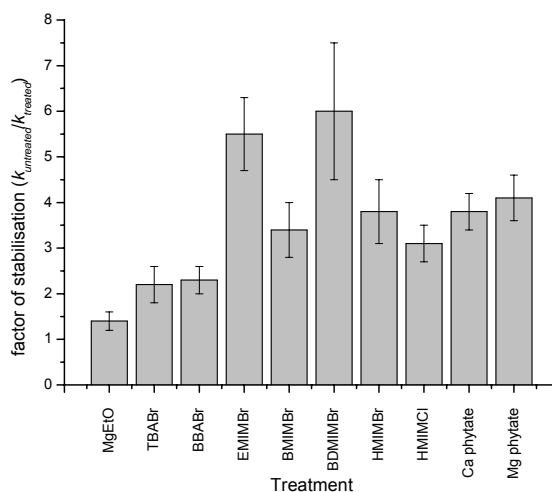


Figure 1: Degradation rate constants of untreated paper containing iron gall ink (Untreated) and the ones stabilised using prototype non-aqueous treatments or aqueous calcium or magnesium phytate treatments. The papers were aged for 168 h at 80 °C and the 65% relative humidity. Non-aqueous treatment solutions contained either alkali (MgEtO), or a combination of an alkali and antioxidants tetrabutylammonium bromide (TBABr), 1-benzyl-3-butylammonium bromide (BBABr), 1-ethyl-3-methylimidazolium bromide (EMIMBr), 1-butyl-3-methylimidazolium bromide (BMIMBr), 1-butyl-2,3-dimethyl-imidazolium bromide (BDMIMBr) and 1-hexyl-3-methylimidazolium bromide (HMIMBr) or 1-hexyl-3-methylimidazolium chloride (HMIMCl).

The extent of stabilisation, as achieved by each treatment may be expressed as a factor of stabilisation, obtained by dividing $k_{\text{untreated}}$ with k_{treated} (Figure 1). Results show that the most effective stabilisation (ca. 6-fold) is achieved using 1-ethyl-3-methylimidazolium bromide (EMIMBr) and 1-butyl-2,3-dimethyl-imidazolium bromide (BDMIMBr). The two treatments were superior to the ones using tetrabutylammonium bromide (TBABr) or 1-benzyl-3-butylammonium bromide (BBABr), which were so far among the most effective non-aqueous bromide inhibitors of ink corrosion.³ The two imidazolium bromides EMIMBr and BDMIMBr were also superior to the aqueous treatments using calcium or magnesium phytate.

During ageing, colour of the ink gradually changes (Figure 2). The most prominent changes are observed in b^* component of CIE $L^*a^*b^*$ colour space, which is a result of the ink's shift in colour from blue to brown. Due to more extensive degradation, the effect is the biggest in the case of untreated sample. The two most effective treatments, EMIMBr and BDMIMBr, did not result in significant alteration of the other two colour coordinates, namely L^* , denoting brightness and a^* , denoting red/green component.

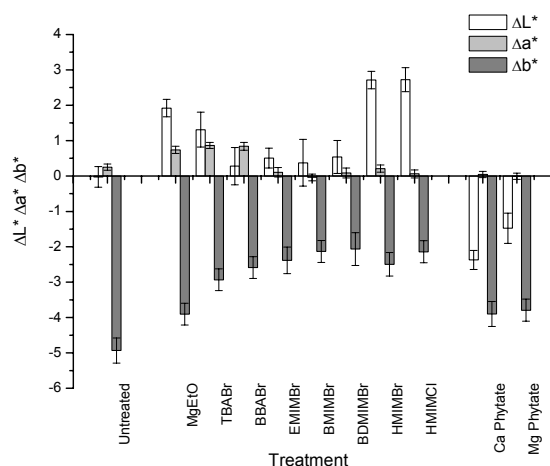


Figure 2: Colour changes ($X_{\text{before ageing}} - X_{\text{after ageing}}$) of ink during accelerated ageing (80 °C, 65% RH, 168 h), expressed as difference of L^* , a^* and b^* colour coordinates of the CIE $L^*a^*b^*$ colour space.

4. Conclusions

Two new antioxidants, 1-ethyl-3-methylimidazolium bromide (EMIMBr) and 1-butyl-2,3-dimethyl-imidazolium bromide (BDMIMBr), in combination with alkali magnesium ethoxide in ethanol, effectively stabilized iron gall ink containing model paper. The effect of stabilisation was superior to the previously studies antioxidants, either bromides or phytates. No adverse effects on colour of the ink were observed, which makes the two antioxidants potential attractive alternatives to the currently used aqueous phytate treatments. However, more studies are needed before they may be considered safe for use on historical documents.

5. Acknowledgement

The authors gratefully acknowledge the support of the Nationaal Archief, The Netherlands. Further financial support has been obtained from the Ministry of Higher Education, Science and Technology of Slovenia, Programme No. P1-0153. Conservators at Hoogduin Papier conservation lab in Delft, The Netherlands are thanked for valuable discussions regarding calcium phytate treatment.

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DEVELOPMENT OF A PORTABLE MICRO-DESTRUCTIVE LIGHT- SENSITIVITY TESTING INSTRUMENT

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Traditionally, museums organise special exhibitions to show the “treasures” in their collections. In recent years, an aggressive policy to exhibit key objects is more and more adopted by libraries and archives. By exhibiting certain types of artefacts, light damage will occur. Lighting policies favour the use of a low light level of 50 lux for exhibiting sensitive artefacts, e.g. tapestries or drawings and a higher level of 150 lux for less sensitive artefacts, e.g. paintings. Until now, lighting standards are based on general indications about the light fastness (LF) of the materials involved and the public perception. Light fastness testing is usually carried out on references, made with new materials. This does not reflect the real situation, where products of thermal and light ageing will influence LF. Whitmore’s “microfadeometer”, introduced in 1999, opens up the possibility of determining LF directly on the artefact by exposing a tiny area (< 0.5 mm) to a very high light intensity (~ 5 Mlux), obtained from a xenon light source, and measuring the spectral changes this exposure inflicts as a function of time. Different versions of this instrument have been built by several institutions and LF-testing is carried out. At ICN, a laboratory set-up has also been built and results of LF-tests on artefacts with synthetic dye inks, as well as chrome-logwood and iron gall inks will be presented. Furthermore, the intention to construct a portable micro-fadeometer, which can be taken to the collections, will be presented.

Funding has been requested within the framework of cooperation between the Royal Library, the National Archives and ICN, for developing new methodologies to preserve library and archival collections. In early 2009, ICN will organise an international expert meeting to exchange findings and set up cooperation between the different institutions.

PHOTOSENSOR APPLICATION FOR STUDIES OF THE EFFECT OF INK ON AGING OF PAPER

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1. Introduction

The quality of both ink and paper affects the lifetime of a document. The ink must be of a quality high enough to be stable and durable and it should not affect a document negatively. It has to be resistant to abrasion, to light, to heat, to water, to various chemical agents, and it must not damage paper. Experimental investigations in different laboratories have been performed according to the international standard ISO 11798 "Information and documentation - Permanence and durability of writing, printing and copying on paper - Requirements and test methods", that establishes requirements and test methods to evaluate durability of ink used on paper documents that have to be preserved for the future.¹ Considering that the composition of the ink is usually the following: pigment (black or coloured, organic or inorganic) and binding agents (gelatine, gum Arabic, oil, glycerine), the aim of this research is to set up and apply a titanium dioxide based photosensor^{2,3} to study the effect of ink on contemporary paper samples artificially aged using a weathering tester. The ability of paper to preserve its characteristics for a long time, without showing deterioration signs is evaluated using the index of environmental persistence.

2. Results and Discussion

A photosensor based on titanium dioxide has been used to examine paper samples. The samples have been extracted from a sheet printed using a typographic process, in parts where the ink was absent (Figure 1) and in parts where the ink was present (Figure 2).

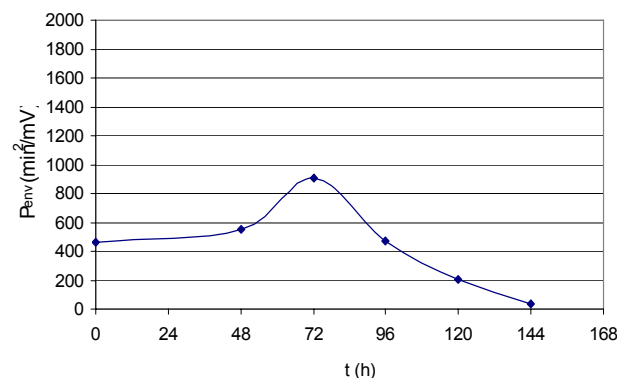


Figure 1: Environmental persistence versus time of artificial ageing of paper samples without ink.

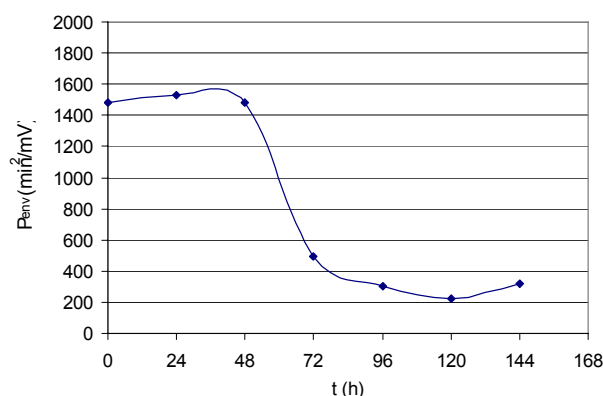


Figure 2: Environmental persistence versus time of artificial ageing of paper samples with ink.

The results indicate that a decrease of the environmental persistence is observed:

- In the case of printed paper samples after only 72 h of ageing, then durability of paper continuously decreases.
- In the inked paper samples after 48 h until a stationary state.

Therefore, the presence of ink has a marked influence on the degradation of paper, i.e. cellulose. Contemporary inks are made of inorganic pigments, oil matrix and other components such as siccatives, anti-fouling components etc. They also are subject to degradation, and can thus modify paper characteristics.

3. Conclusions

In conclusion, printing inks as used today, seem to decrease the environmental persistence already during the first hours of artificial ageing at a greater extent than in the case of not printed paper.

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STRUCTURAL CHARACTERISATION OF LOGWOOD AND REDWOOD INKS

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1. Introduction

Haematein, widely known for its medical use as a marker dye, is the primary component in recipes for inks obtained from *Haematoxylum campechianum*, commonly known as Campeachy wood, or logwood: this tree species belongs to the same family as other redwoods, like Palo Brasil (*Haematoxylum brasiletto*), and Pernambuco (*Caesalpinia echinata*). The latter are used in combination to produce brazil wood dye, a red purple dye that contains brazilein as the principle colouring substance, and haematein in a smaller amount. Hot extraction of logwood in water and exposition to air causes the haematoxylin contained in the wood to oxidise into haematein (Figure 1).

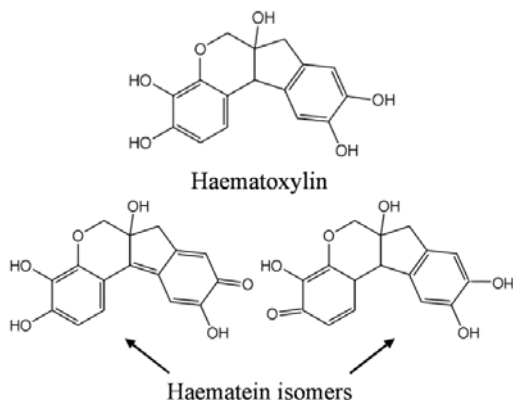


Figure 1: Structure of haematoxylin and haematein: the latter has two isomeric structures.

This oxidation product, and therefore the ink, is very stable and has been widely used in western countries since the 16th century. However, since the rate of oxidation is quite low, the solution darkening was enhanced by means of addition of metal salts. Some of them act as mordants and lead to formation of a stable lake. On the other hand, other salts just colour the solution and occasionally form precipitates,¹ which can induce degradation of paper due to the presence of metals. In this work, Fourier Transform Infrared spectroscopy for characterisation of haematoxylin, haematein and derived inks is presented.

2. Materials and Methods

Standard haematoxylin powder from Sigma Aldrich was used in this experiment. Haematoxylin was oxidised by heating and bubbling oxygen in a saturated water solution of the standard sample for 4 weeks. Standard haematein (Vandoni) was used to check whether the oxidation was complete. Logwood extract was prepared according to an ancient recipe^{2,3} by dispersion of 10 g of logwood chips (Zecchi S.p.A.) in 100 ml of deionised water. The dispersion was then covered and heated at boiling temperature for 60 min. After cooling, the resultant decoction was decanted for a day, filtered and left under oxygen flow for a month.

Redwood extract (Vandoni) and brasil lake made of redwood precipitated with alum (courtesy of ICPL museum) were also characterized.

FTIR transmission measurements were performed with a Nexus Nicolet interferometer, equipped with a KBr beam splitter and DTGS KBr detector. The system was operated in dry air, with a resolution of 4 cm⁻¹. The samples were dispersed in KBr pellets. In the case of written documents, a few inked fibres were sampled with a micro-scalpel. Measurements were performed in the 4000 - 400 cm⁻¹ range, averaging 200 acquisitions on each sample.

The same instrument was used also for ATR-FTIR measurements by means of a ZnSe cell and a liquid-nitrogen-cooled MCT/A detector. These measurements were performed in the 4000 - 650 cm⁻¹ range with a resolution of 8 cm⁻¹, averaging 400 acquisitions on each sample. Transmittance and reflectance spectra were converted into optical densities and peak centres and amplitudes were computed as overlapped Lorentzian curves.

3. Results and Discussion

The major modification expected to take place during haematein preparation is oxidation, which implies the formation of a carbonyl group and variations in the -OH, C=C and ring modes.

However, in the spectra in Figure 2, the main effect that we can observe is that, along with oxidation, the spectrum seems to become less resolved. This is interpreted in terms of the isomeric nature of haematein, as a superposition of the modes between the two isomers. As far as the oxidation process is concerned, this is verified through the shift to about 1610 cm⁻¹ of the ring C=C stretching peaks, and the appearance of a shoulder at about 1695 cm⁻¹, due to carbonyl formation.⁴

When comparing the extracts with the inks, it can be seen that the logwood preparation performed according to the ancient recipe leads to a product whose spectrum is fully comparable with the haematein one (Figure 3). When adding metal salts to logwood or redwood, on the other hand, the salts spectra become dominant over organic features, as we could observe by comparison of the brasil lake

spectrum (redwood + alum) to the redwood one and of the logwood and $K_2Cr_2O_7$ to the logwood one.

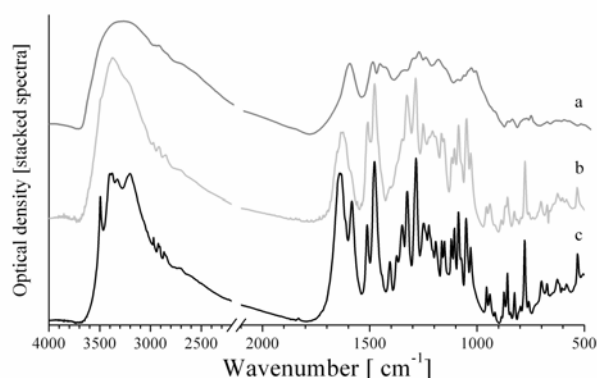


Figure 2: FTIR transmittance of a) haematein; b) half-oxidized (treated for 2 weeks) haematoxylin; c) haematoxylin.

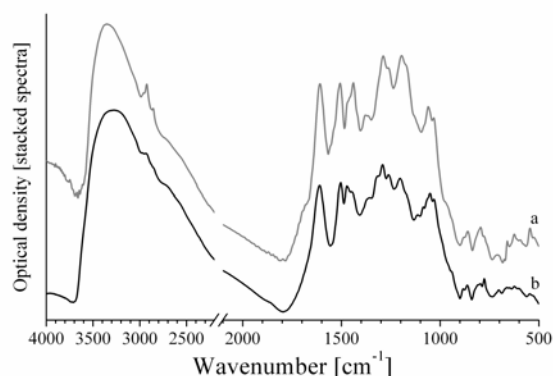


Figure 3: FTIR transmittance of a) logwood extract ink; b) haematein.

Figure 4 shows that shift and deformation of the ATR spectra, with respect to transmittance spectra, are minimal and the fingerprint region is definitively recognizable, providing an effective and non-destructive diagnostic tool. The correct identification of inks is a major issue in conservation, since wrong attribution could lead to inappropriate, even damaging, restoration.

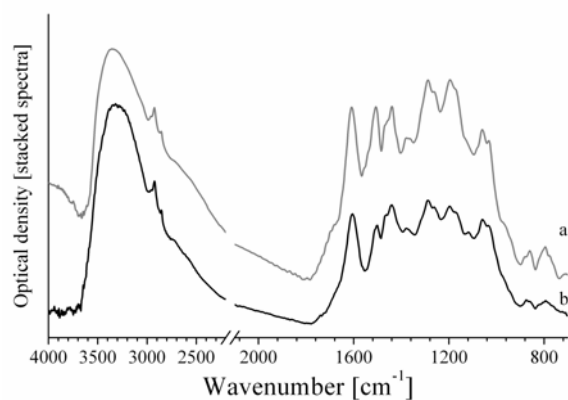


Figure 4: a) FTIR transmittance of logwood extract in KBr; b) ATR-FTIR spectra of logwood writing on paper. The intensity of the ATR spectra was corrected assuming an index of refraction $n = 1.55$ for paper.

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INFLUENCE OF DEACIDIFICATION WITH MMMC ON STABILITY OF IRON GALL INKS

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1. Introduction

This work deals with the application of neutralization reagent MMMC (Methoxy Magnesium Methyl Carbonate) as well as antioxidant BHT (2,6-di-*tert*-butyl-4-methylphenol) on documents containing iron-gall inks and its influence on document properties after stabilization.

MMMC is an organo-metallic compound which is used as a deacidification agent in Wei T'O non-aqueous process of book deacidification. It is possible to place magnesium in this form into paper structure using non-aqueous system from fluid gas.¹ MMMC belongs to compounds suitable for deacidification of heavily damaged objects. MMMC does not dissolve iron-gall inks from the substrate hence ink fixation is not needed prior to its application. BHT belongs to the group of synthetic antioxidants produced commercially, and it is also present as a natural substance in plants, e.g. in rosemary. BHT is a white powder that is used in the food industry, pharmacology, and also medicine for its anti-carcinogenic effect and it is also used in the rubber industry. BHT belongs to the group of sterically hindered phenols and it had been recently introduced as a paper stabilization agent. Its effect as "chain-breaking" antioxidant is a consequence of deactivation of alkylperoxyl radicals.^{2,3}

2. Experimental

The experiments were performed using Whatman No.1 (Cat. No. 10001917) filter paper (pure cellulose without additives). A set of paper squares (8 x 12 cm) was immersed in a 1% gelatine solution and 5% solution of aluminium sulphate for 5 min.

The iron-gall ink was composed of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, tannic acid and gum Arabic, resulting in a molar ratio of iron and tannin acid 5.5 : 1.

The samples were placed into a climatic chamber for 3 h at 50 °C, and then immersed in a 6% solution of methoxy magnesium methyl carbonate.

The antioxidant BHT was prepared in two concentrations (0.1% and 0.01% solution in ethanol), and samples were immersed in these solutions for 10 s.

One part of the samples was artificially aged in an OMT OVEN for 1 day to 24 days at 80 °C and 50% RH.

The second part of the samples was aged in the chamber APT Line Series FED for 1 day to 24 days at 105 °C.

The changes in chemical structure of iron gall ink and iron gall ink with the deacidification reagent MMMC during artificial ageing were characterized using FTIR spectroscopy. FTIR spectra were recorded using the spectrophotometer Digilab Excalibur Series using the transmission method (KBr pellets). pH value of the cold extract of paper was determined by ISO 6588 (50 0381), pH-meter JENWAY model 370, with accuracy 0.01. Coordinates of colour space were measured using the spectrophotometer SpectroDens A504009 Premium (Techkon) (D50, 2° standard observer).

3. Results and Discussion

3.1. Chemical Properties

pH value of samples increased from 2.88 to 7.48 after deacidification using the 6% solution of MMMC. We can see that pH decreased during accelerated ageing in the presence of BHT, too (Figure 1). From two concentrations of BHT, using the 0.1% solution, a slightly higher value is achieved.

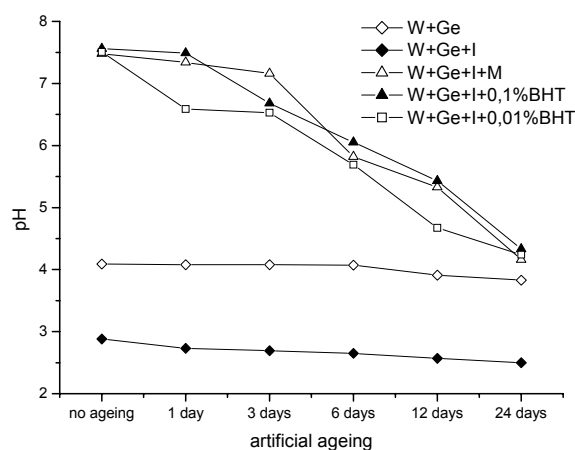


Figure 1: Changes of pH during artificial ageing at 80 °C and 50% RH (W+Ge-Whatman paper modified with gelatine and sulphate, I-application of iron gall ink, M-treatment with neutralization reagent MMMC, BHT-treatment with BHT antioxidant).

3.2. FTIR Measurements

The comparison of FTIR spectra of non-aged ink and non-aged neutralized ink measured in pellets is presented in Figure 2. Ink neutralization with a 6% solution of MMMC caused peak decrease at 1093 cm^{-1} which is characteristic for C-O bond. Another difference caused by ink neutralization was formation of a new peak at 1429 cm^{-1} which represents the vibration of magnesium carbonate.

Magnesium carbonate forms an alkaline reserve in deacidified paper which is important from the viewpoint of paper substrate stabilization, thus the peak characteristic for magnesium carbonate during ageing was observed. Figure 3 demonstrates the decrease of peak relating to vibration of

magnesium carbonate (1429 cm^{-1}) after 3 days of ageing. After 12 days of ageing, the peak at 1429 cm^{-1} disappears and we assume that the alkaline reserve has been consumed.

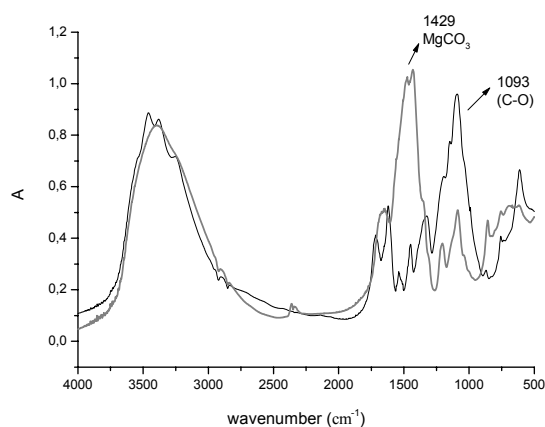


Figure 2: Transmission FTIR spectra of iron gall ink (black line) and iron gall ink with MMMC (grey line).

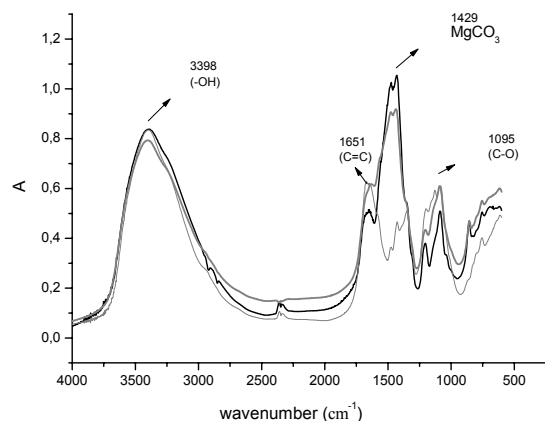


Figure 3: Transmission FTIR spectra of iron gall ink with MMMC. Black line: no ageing, grey line: aged 3 days, light grey line: aged 12 days.

3.3. Optical Properties

After the deacidification of ink samples using MMMC (with and without BHT), the total colour difference increased compared with the untreated sample (from 5 to 13 after the first day of ageing). This value was stabilised during ageing, although ΔE^*_{ab} of untreated sample increased very rapidly and achieved the value of ca. 23 (Figure 4).

The changes of ΔE^*_{ab} were caused mainly by increase of value of chromatic coordinate b^* from -8.36 to 13.56 for acid samples and only from -4.99 to -2.57 for the treated samples. The neutralization and application of BHT contributed noticeably to colour stabilisation of iron gall inks on paper.

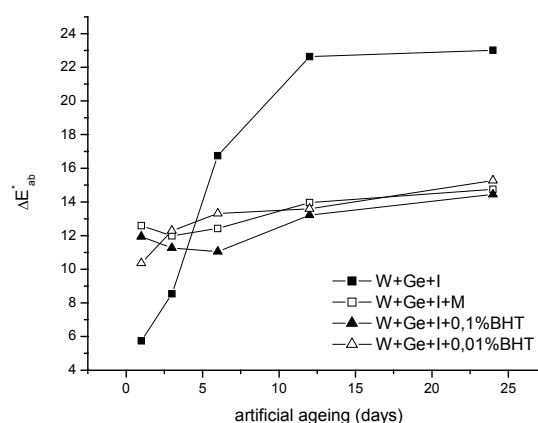


Figure 4: Changes of ΔE^*_{ab} during artificial ageing at $80\text{ }^{\circ}\text{C}$ and 50% RH. (W+Ge-Whatman paper modified with gelatine and sulphate, I-application of iron gall ink, M-treatment with neutralization reagent MMMC, BHT-treatment with BHT antioxidant).

4. Conclusion

The obtained experimental results showed that deacidification of inked samples with a 6% solution of methoxy magnesium methyl carbonate (MMMC) caused a considerable improvement of optical and chemical properties for non-aged and aged inked samples. The FTIR measurements confirmed the formation of alkaline reserve in neutralized ink.

These results support the conclusion that treatment of objects with MMMC has a stabilising effect. However, the alkaline reserve after 12 days of artificial ageing was exhausted. An addition of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT) to neutralized samples improved the studied properties of non-aged paper samples, however, no stabilization effect of the antioxidant during artificial ageing was found.

5. Acknowledgements

This work has been supported by Ministry of Education of Slovak Republic - project Kniha.SK, Slovak Grant Agency VEGA under the contract No 1/0800/08 and project MVTS COST D42/08.

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THE ROLE OF VOLATILE ORGANIC COMPOUNDS IN PAPER DEGRADATION

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1. Introduction

A number of factors are known to influence the degradation of historical paper, among which the environment undoubtedly plays a crucial role, along with paper composition. During paper degradation, a variety of low molecular weight products are formed, several of which are volatile and thus have an increased mobility not only within the material, but also within a collection. In Figure 1, we summarise the numerous exogenous and endogenous factors influencing cellulose degradation - among which volatile degradation products (VOCs) can be both emitted but also absorbed by paper.

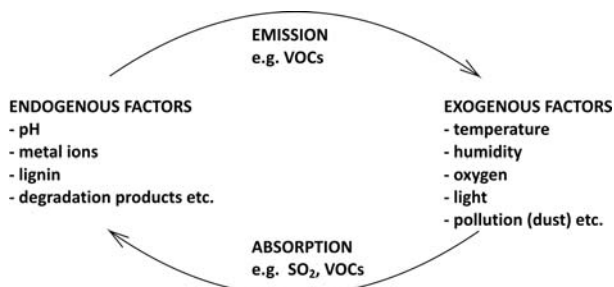


Figure 1: Endogenous and exogenous factors affecting paper degradation.

Lately, the interest in determination of VOCs emitted from paper has increased, however, there are only limited studies available on the information which can be extracted from VOCs and on their effect on cellulose degradation.

2. Experimental

For sampling, SPME fibres (Supelco, Bellefonte) with DVB/CAR/PDMS stationary phase, thickness 50/30 μ m were used. Before each sampling, the fibre was pre-conditioned at 230 °C for 30 min. For static headspace sampling-SPME sample preparation procedure, approximately 100 mg of paper was placed in a closed

20-mL vial and thermostated for 18 h at 80 °C and then cooled down to 40 °C in 5 min. During actual sampling, the pre-conditioned SPME fibre was then placed in the vial for 1 h at 40 °C. A Hewlett-Packard 5890 series II gas chromatograph, coupled to a Hewlett-Packard 6890 quadrupole mass spectrometer (Palo Alto) was used. A 60-m VOCOL column, I.D. 0.25 mm and stationary phase thickness 1.5 μ m was used (Supelco, Bellefonte). Further details are given in ref. 1.

3. Results and Discussion

Volatile organic compounds (VOCs) formed during paper degradation are numerous and varied,^{2,3} and their identity and quantity depends on paper composition.¹ Data shown in Figure 2 demonstrate that the quantity of furfural, a volatile degradation product of cellulose, is indicative of paper acidity. Thus, VOCs may be regarded as a source of information on paper quality.

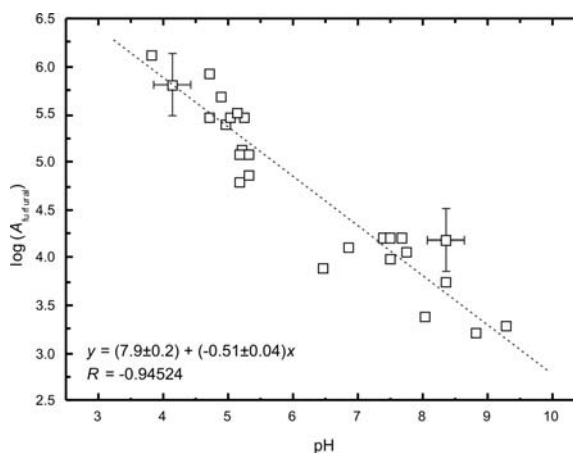


Figure 2: Dependence between furfural emission and pH of real paper samples.¹

On the other hand, many simple organic acids, aldehydes and even aromatic compounds, which have been shown to form during degradation, may also initiate or accelerate degradation of cellulose. The usual and often used technique for analysis of VOCs in paper makes use of solid-phase micro-extraction (SPME) coupled to GC-MS,^{1,2} although other ways of sampling have also been employed, e.g. cryo-trapping² and thermal desorption.

Studies of the impact of several identified VOCs on degradation of paper can easily be performed in closed vessels at elevated temperatures. We evaluated the impact of the following: furfural, iso-butylbenzol, 1,4-diethylbenzen, acetic acid, formic acid, toluene, hexanal, 2-pentylfuran, formaldehyde and vanillin, on papers of three different qualities. Apart from volatile acids, a statistically significant negative effect of all compounds with a carbonyl group in the structure was noticed.

The effect of removal of VOCs using VOC scavengers or absorbent media can also be studied in closed vessels at

elevated temperature. Similarly, the effect of oxygen removal can also be evaluated.

In our study, we included several commercially available products and compared their effect on degradation of cellulose in a closed vessel at an elevated temperature.

The complex role of volatile degradation products in mixed paper collections should not be underestimated. Our research shows that the effect of cross-infection due to emission and re-absorption of these compounds may be significant and strategies for removal of VOCs from storage facilities should be given due consideration.

4. Acknowledgements

The authors gratefully acknowledge financial support of the Ministry of Higher Education, Science and Technology, Republic of Slovenia, Programme no. P1-0153, and project PaperVOC, partly funded by The National Archives, The Netherlands.

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THE IDENTICAL BOOKS PROJECT - A SURVEY OF CONDITION OF PAPER ACROSS 6 UK LIBRARIES

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1. Abstract

The UK has established six legal deposit libraries which are entitled to receive a copy of every printed publication published in the UK. The aim of the research is to identify the differences between books resulting from different storage regimes, in order to compare the results of natural ageing (both past and future) with artificial ageing experiments. These pages are being assessed by a battery of criteria, both qualitative visual appraisal and quantitative instrumental analysis (colour, pH, furnish, molecular weight, near-IR, volatile organic compounds emissions).

2. Introduction

The Andrew W. Mellon Foundation awarded a grant in December 2005 to study the deterioration of paper and books in libraries and archives. The British Library (BL) leads the project partnership with other UK Legal Deposit Libraries (LDLs) - Bodleian Library (OULS), Cambridge University Library (CUL), National Library of Scotland (NLS), National Library of Wales (NLW) and Trinity College Dublin (TCD) - and two national archives - The National Archives, National Archives of Scotland. The project runs from October 2006 to March 2009. When the project started, the scope of work and methodologies were reassessed in the light of recent advances in paper science, enabling clarification of the questions to be addressed. The aim is to use current state of the art methods to determine the condition of the books and paper in these institutions, and to cascade these ideas and techniques to conservators and curators in the UK. The work was divided into six interwoven strands.

3. Strands

- Choosing Identical Books: Types of books, choosing books by libraries, long-term use of identified books
- Measurements by libraries: Methodology, sampling of books,
- Condition assessment: Current state of the art,
- VOCs: Current knowledge, methodology, scoping VOCs produced by books, comparison with condition data,
- Environmental modelling: Construction of model, methodology, comparison with condition data,

- Capacity building: Training conservators (training trainers), building a community of research aware conservators, building external partnerships.

4. Choosing Identical Books

This study builds upon a number of previous studies comparing the condition of books stored in different places.¹⁻³ Publications were chosen from the 20th century and from different categories of items, ranging from maps and newspapers to government publications and music. The long list of "Identical Books", IBs, was initially identified from the library catalogues and by specialist curators in the libraries. Over 450 items were identified as common in all the LDLs. They were then retrieved and evaluated by the conservators in each of the libraries. This revealed items that were missing, were variant editions etc. Comparisons were made by capturing bibliographic information and photographs from the item.

5. Measurements by Libraries

Conservators at each of the libraries were trained in the use of the survey tools (the UK National Preservation Office Preservation Assessment Survey)⁴ and colour measurement using a Konica Minolta spectrophotometer CM-2600d. A single, identical, page from each item was chosen for assessment. A template for each page was prepared to ensure that the sampling positions avoided potential distortion of measurements by ink etc. and were consistent between libraries. Two positions were measured for colour, one near the top outside corner of the item and one near the middle of the page.

The measured yellowness, b* (from the Lab colour space) from reflection spectra, was used to compare the books (Figure 1). Preliminary results demonstrate that, in general, the edge of the book is yellower than the middle (Figure 2) and that the books from London are more yellow than those from other libraries (Table 1).

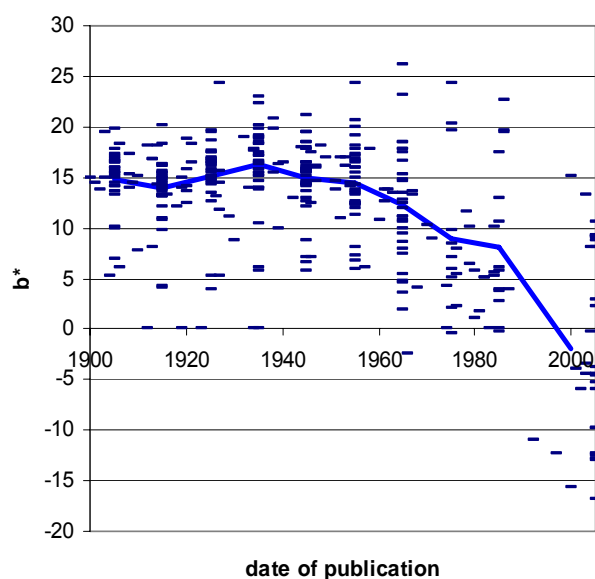


Figure 1: Colour measurement of BL IBs: values of b^* at top corner of item. Line shows the average value per decade.

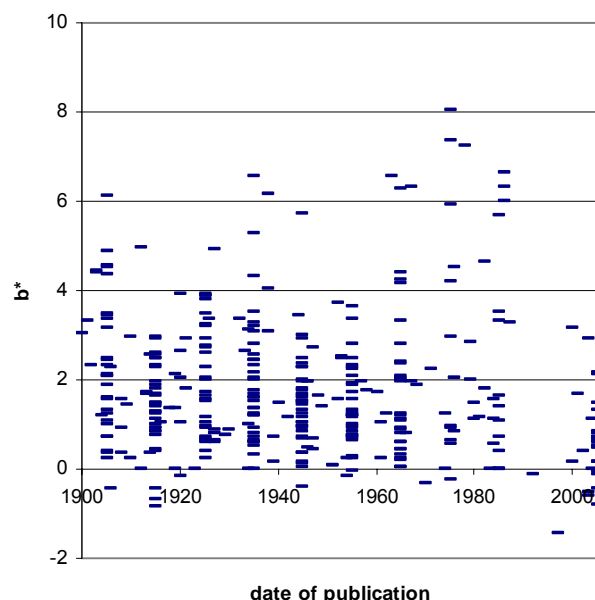


Figure 2: Colour measurement of BL IBs: difference between values of b^* at edge and in middle of chosen pages.

Table 2: Average values of b^* of the IBs in the Legal Deposit Libraries, measured at the top corner and in the middle.

Library	b^* top corner (average)	b^* middle (average)
BL	12.42	10.62
CUL	11.40	10.30
NLS	12.19	10.78
NLW	12.62	11.60
OULS	11.79	10.36
TCD	12.03	10.41

When paper composition of the IBs has been analysed, we shall compare similar papers over time. Qualitatively, the data from all the libraries show that yellowness increases over a 50 year period then reaches a plateau.

The increased yellowness at the page edge of these books is probably the result of greater exposure to the atmosphere. In books published since ca. 1995, UV fluorescence is observed in the spectra, due to optical brighteners (Figure 1). However, Figure 2 shows that these additives do not change the progress of the yellowing, they merely offset the yellowness measurement at both the edge and middle. With this limited period of ageing, it appears that the additives have not degraded significantly, as the rate of yellowing is roughly the same as that of books without brighteners.

The books from NLW are on average slightly more yellow than any other LDL. As NLW is in one of the cleanest areas of the UK, it appears that yellowness is not related to pollution levels, one of our initial hypotheses. Correlation with other physical characteristics will be sought as data become available, and hopefully causes for differences in colour will become clearer.

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EVALUATION OF ANOXIC ENVIRONMENTS FOR THE DISPLAY AND STORAGE OF WORKS OF ART ON PAPER

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a historically informed reconstruction of a watercolour paper to produce reproductions of some of Turner's watercolours.

These are currently being subjected to accelerated degradation experiments, as a test of an anoxic display system for the actual objects.

Over the past decade controlled atmosphere environments have received increased attention within the cultural sector. Anoxia has been used in multiple applications from de infestation to long-term storage and display of various classes of objects. However, to date, there has not been published a detailed study of the effects of anoxia on various classes of cultural objects. Rather anoxia has been perceived as being safe a priori. This may not be the case for certain materials.

The Anoxic Framing Project at Tate is evaluating the efficacy, efficiency, and risks of anoxia with respect to both storage and display of works of art on paper.

Work concentrates on the monitoring of produced volatile organic compounds (VOCs) and colorimetric behaviour of artists' watercolour materials within various anoxic environments under accelerated aging conditions.

Headspace-Gas Chromatography/Mass Spectrometry (HS-GC/MS) is used to identify and quantify volatile degradation products from the object/mounting system. By quantifying target analytes in parallel anoxic and oxygen-containing systems, it is possible to draw conclusions about the relative rate of chemical degradation of the object in the system.

In conjunction with the headspace studies, fugitive colorants (in either room atmosphere or anoxia) are identified with a high throughput screening micro-fadeometer. Pigments that have been identified as being fugitive are subjected to further studies, including wavelength dependence of fading and reciprocity testing using a second micro-fadeometer.

From this work Tate will be able to identify classes of objects and specific artist's materials that are not suitable or otherwise for display and storage in anoxia. It will also be possible to make more definite statements about the permanence and relative stability of different classes of works of art on paper.

Present research is focusing on late 18th through mid-19th century watercolours with a particular focus on the works of J. M. W. Turner, of which Tate holds more than 30,000 works on paper. Additionally Tate holds a large collection of Turner's studio pigments.

These have been used to create historically informed reproductions of Turner's paints; which have been used with

SIZE EXCLUSION CHROMATOGRAPHY OF CELLULOSE

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1. Introduction

The uniqueness and inherent value of cellulose-based cultural heritage limits the use of analytical techniques to non-destructive or micro-destructive ones.

Mechanical properties have been the focus of paper stability studies for more than a century and many different standards cover their determination. However, due to the inhomogeneity of paper and the many factors which affect the results of mechanical tests, repeatability is low and numerous measurements are needed to obtain a reasonably reliable result. Consequently, a large surface area, often as much as an A4 page, is needed per determination.

It has been demonstrated that the loss of paper strength and embrittlement during accelerated ageing are mainly the results of a decrease of fibre strength, which is due to the depolymerisation of its main structural component, cellulose.¹ The condition of paper may thus be determined using viscometry, where an average number of monomer units in cellulose molecules (degree of polymerisation, DP) is obtained, or size exclusion chromatography, where weight average (M_w) and number average (M_n) molar masses are determined. The destructive character and requirement for a large amount of sample render viscometric determination of cellulose DP and mechanical properties equally unsuitable for the characterization of historical documents. It was recently demonstrated that only a few fibres are needed for size exclusion chromatography (SEC), if cellulose is derivatised using phenyl isocyanate.² In our previous work, the applicability of the method for routine characterisation of paper from books was demonstrated. The weight average molar mass of a carbanilated sample, obtained using a hollow needle (Figure 1) correlated well with DP for a number of papers made from bleached chemical pulps.³ Furthermore, a correlation between weight average molar mass and zero span tensile strength was observed for papers made from

bleached chemical pulp as well as ones that contained higher amounts of lignin.⁴ The methodology thus offers the possibility of evaluating the condition of paper, even if containing groundwood, from a few fibres only.

The aim of the present study is to develop the methodology which would enable determination of the rate of degradation of cellulose using SEC. This would allow us to study the kinetics of degradation of papers containing groundwood.

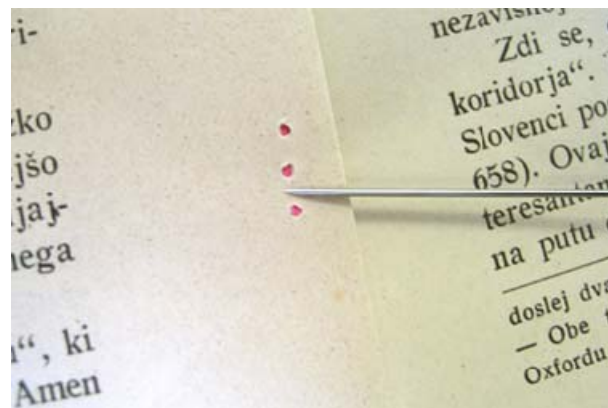


Figure 1: Sampling of paper using a hollow needle.

2. Experimental

To prepare cellulose tricarbonyl (CTC), ca. 0.2 mg of the material was isolated using a hollow needle, after which 100 μ L pyridine and 10 μ L phenyl isocyanate were added and the reaction was terminated with the addition of 10 μ L methanol. Prior to injection into the chromatographic system, the solutions were diluted to 0.0167 g L⁻¹ (with respect to cellulose) with THF.

Absolute molar mass averages and molar mass distribution of samples were determined by size exclusion chromatography coupled to a multi-angle light scattering photometer (SEC MALS). Measurements were performed at 25 °C using an Agilent Technologies pump series 1200 coupled to a Dawn HELEOS laser photometer with a GaAs laser (656 nm) and to an Optilab rEX interferometric refractometer operating at the same wavelength as the Dawn HELEOS photometer (both instruments are from Wyatt Technology Corp., USA). Separations were carried out using a 5 μ m linear AM GPC Gel column (300 mm length and 7.5 mm i.d., American Polymer Standards Corporation) with a pre-column in a solution of 0.05 M CF₃COONa in THF. The nominal flow rate of the eluent was 1.0 mLmin⁻¹. The mass of the samples injected onto the column was typically (1 - 1.4) $\times 10^{-4}$ g. Data acquisition and evaluation were carried out using Astra 5.3 software (Wyatt Technology Corp.).

Relative average molar masses, based on the universal calibration approach, were determined using a Hewlett-Packard series 1100 chromatographic system. The column thermostat was set to 35 °C and a UV detector was used.

PS standards were determined at 210 nm and CTC at 235 nm. The injected volume was 50 μL .

The columns used were a 5 cm Guard GPC MixedBed and two GPC MixedBedLinear, both by Jordi F.L.P. The eluent THF was pumped into the system at a rate of 1 mL min^{-1} . The chromatographic data were processed with HP G2182AA data analysis software. The polystyrene standards (PS, Polymer Standards Service) were prepared as mixed standards in three separate solutions containing in total 0.1 g L^{-1} of standards in THF.

The first standard solution contained PS of the following peak molecular weights (Mp): 1,090,000 g mol^{-1} , 130,000 g mol^{-1} , 17,800 g mol^{-1} and 1,620 g mol^{-1} , the second contained 2,570,000 g mol^{-1} , 246,000 g mol^{-1} , 34,800 g mol^{-1} and 3,420 g mol^{-1} and the third 579,000 g mol^{-1} , 67,000 g mol^{-1} and 8,400 g mol^{-1} . All chromatographic results are expressed as weight-average molar mass of CTC (MW) relative to polystyrene standards.

Viscosity was determined according to ISO 5351/1.

3. Results

In our previous studies, average molar masses of carbanilated cellulose were calculated from data obtained by SEC using a calibration with polystyrene. Average molar masses obtained in this way are relative, not true values, since SEC separates according to the hydrodynamic volume and not according to molar mass. To overcome this limitation, we have decided to compare the weight average molar masses (M_w) obtained this way with the ones obtained using SEC with a light scattering detector, which allows determination of absolute average molar masses. A reasonably good correlation between the two methods was observed (Figure 2). In the subsequent studies, we used the obtained calibration equation to calculate the absolute weight average molar masses from the relative ones.

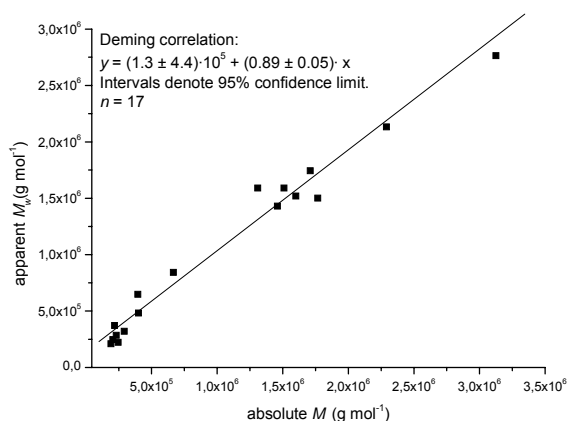


Figure 2: Correlation between relative weight average molar masses, determined using universal calibration approach, with absolute weight average molar masses obtained using MALS detector.

Unfortunately, calibration to absolute values is not possible in the case of number average molar masses, the

determination of which depend also on non-size exclusion separation mechanisms in SEC (e.g. adsorption on column packing). In addition, M_n values determined by SEC-MALS are usually overestimated since a MALS detector is not particularly sensitive towards low molar mass species. Consequently, M_w values were used to calculate the degradation rate constants.

In order to determine the rate of cellulose degradation at a given temperature, the Ekenstam equation is used,⁵ where t is time and k is the rate constant in $\text{mol}_{\text{bonds}} \text{mol}_{\text{monomers}}^{-1} \text{s}^{-1}$:

$$\frac{1}{\text{DP}_t} - \frac{1}{\text{DP}_0} = k \cdot t.$$

In our case, the weight average degree of polymerization (DP_w) of samples was obtained by dividing the average molar masses by molar mass of the carbanilated glucosidic monomeric unit (537 g mol^{-1}). The results presented in Figure 3 demonstrate that rates of degradation of cellulose in groundwood containing paper may be calculated using the approach.

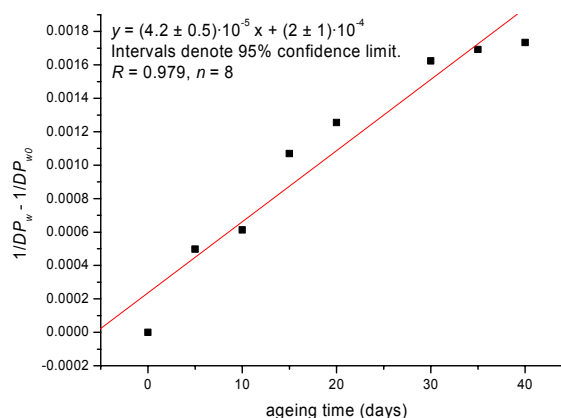


Figure 3: Rate of degradation of cellulose in groundwood containing paper during accelerated ageing at 90 °C and 65% RH.

4. Conclusion

The methodology presented here allows us to study the kinetics of degradation of cellulose in papers containing groundwood, which represent a considerable amount of the 19th and the 20th century book and archival collections. In addition, the approach may be used whenever the amounts of available sample are extremely limited, as is the case for ink lines on papers.

5. Acknowledgement

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The work is the sole responsibility of the authors and does not represent the opinion of the Community. The Community is not responsible for any use that might be made of the data appearing herein.

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QUALITY CONTROL MEASURES IN MASS DEACIDIFICATION

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In the last decades, different mass deacidification methods were developed which are able to deacidify complete books.

The quality and sustainability are determined by the potential of the deacidification method and its stage of development. The risks from side effects can be reduced significantly through pre-sorting. The mass deacidification process can be monitored by considerable controls of quality criteria and therefore, if necessary, adapted. These quality controls are carried out following the DIN (German Institute for Standardization) recommendation for “Conservation in archives and libraries” and verifiable measuring methods are used. The DIN recommendation defines standards (defined testing material, limit values), provides analysing techniques (for example pH value in aqueous extracts) and displays standardized documentation (presentation of certificates).

The **papersave**[®] mass deacidification method of ZFB Zentrum für Bucherhaltung is a non-aqueous deacidification method. Books are soaked in a treatment solution which contains magnesium. This solution deacidifies the paper and leaves an alkaline reserve in the paper at the same time. Extensive pre-sorting measures (insertion of copying paper sheets) are carried out to avoid unwanted side effects like bleeding of stamp inks or colours in the cover.

Since 2005, the ZFB Zentrum für Bucherhaltung works according to DIN EN ISO 9001 (quality management system) and 14001 (environment management system).¹ In this regard, mass deacidification with its pre-sorting, analysis and documentation is carried out according to the German DIN recommendation “Conservation in archives and libraries”.²

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SIMULTANEOUS DEACIDIFICATION AND REINFORCEMENT OF PAPER BY TREATMENT WITH AMINOALKYLALKOXYSILANES

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Some acidic library and archival objects are so brittle that they cannot be handled without risking loss of material. The currently used deacidification processes do not impart improved mechanical properties to paper. Aminoalkylalkoxysilanes (AAAS) can efficiently achieve deacidification of paper and simultaneously deposit an alkaline reserve in the cellulosic network¹ while improving its mechanical resistance.² The treatment of cotton paper by immersion in a solution of ADMBTMS (4-amino-3,3-dimethylbutyltrimethoxysilane) in ethanol or in a silicon based solvent (9 - 10% w/w) and dried under vacuum was studied. The dry uptake of AAAS in the paper was about 5 - 6% (w/w). It was shown that in addition to deacidification and improvement of the stability of papers by providing an alkaline reserve, the treatment also significantly improved the mechanical resistance, measured by the folding endurance (FE) of papers. The results are in Table 1.

Essential for the appraisal of the deacidification process, the behaviour of the treated paper was investigated after accelerated ageing. For the aged samples, the folding endurance was significantly improved compared to before the ageing. It can be assumed that a chemical reaction between the AAAS and the cellulosic substrate is favoured by the ageing procedure. This shows that incorporation of ADMBTMS in the cellulosic web significantly improved the folding endurance, before as well as after ageing (Table 1).

The molar masses of cellulose of untreated paper and paper treated with ADMBTMS were determined using size-exclusion chromatography with multiangle light scattering detection (SEC/MALS). Table 2 gathers the values of average molar masses (M_r) obtained for cotton paper before and after ageing. The initial value of weight average molar mass M_w of 251 kg mol⁻¹ dropped to 208 kg mol⁻¹ due to acid hydrolysis during the ageing, a decrease of 17.5%. This result confirmed that the period of ageing was appropriate as it allowed the observation of measurable and significant changes in molar mass.

The incorporation of ADMBTMS in the fibres induced a 10% increase in M_w of cellulose in unaged paper. Surprisingly, the M_r values of cellulose for the ADMBTMS treated paper after ageing were slightly higher than before

ageing. The effectiveness of protection of paper from acid hydrolysis taking place during ageing was indeed found significant.

The properties of inhibition of fungal growth of papers treated with ADMBTMS were investigated as well. It was found that AAAS acted as a surface-active antifungal agent, significantly reducing the growth of *Aspergillus niger* and *Paecilomyces variotii*, two fungal species commonly found in storage areas of libraries and archives. The antifungal activity of the treated papers was evaluated using a protocol based on the paper disc method.³ This clearly demonstrated that besides deacidification and reinforcement, the treatment of paper documents with ADMBTMS (as well as with other AAAS, as shown in recent publications),^{4,5} imparts antifungal properties. This is a great asset for a new mass treatment, as current processes presently in use at an industrial scale for libraries and archives documents only offer a deacidification action. The developed treatment provides a complete protection to paper, increases its lifespan and represents a novel approach to cultural heritage preservation.

Table 1: Folding endurance (0.5 kg load) (FE) and alkaline reserve (AR) of cotton paper treated with ADMBTMS unaged and aged at 90 °C during 14 days in closed tube (ASTM D6819-02E02).

	Unaged		Aged	
	Untreated	ADBTMS	Untreated	ADBTMS
FE (no. of folds)	32	98	34	252
AR (meq. OH ⁻ /100 g)	-	30	-	27

Table 2: M_r averages of cellulose of paper unaged and aged at 80 °C / 65% RH during 28 days (ISO 5630-3:1996), untreated and treated with ADMBTMS (paper dissolved in dimethylacetamide with lithium chloride, analysis with SEC/MALS⁶).

	Avg M_n (kg mol ⁻¹)	Avg M_w (kg mol ⁻¹)
Untreated unaged	145	251
Untreated aged	104	208
ADBTMS unaged	138	280
ADBTMS aged	153	297

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THE LIFETIME OF ACID PAPER IN THE COLLECTION OF THE ROYAL LIBRARY

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1. Introduction

In 2004, a national commission was established in Denmark with the task to identify the amount of acidic paper in collections of national significance, from the period 1800 to 1985, and to recommend whether Denmark should consider mass deacidification or not.

Therefore, a survey was conducted in the collections of the Royal Library and the National Archive between 2005 and 2007. The measured parameters were pH (micro cold extraction according to ref. 1), colour (CIE Lab), brittleness (manual folds up to 20), lignin content and weight.

The survey in the Royal Library collections consisted of 394 randomly selected objects among the library's paper based collections of national significance. The library has 1.3 million objects in this category and each sample thus represents 3.370 objects (a book, a map or a manuscript). The survey revealed that 93% - or 1.243 tons - of the paper from this period is acidic. About 7% of the objects from the period investigated is already very brittle (three manual folds) and has thus passed the point of useful lifetime. This was an expected result, considering that other libraries around the world already made similar surveys with similar results.

2. Brittleness Related to pH and Age

The rate of deterioration of unstable organic materials depends on temperature and humidity. However, it also depends on pH of the object.

From our survey, we know pH, the age of our objects and the brittleness. When these data are combined in a diagram, it is possible to see the tendency that with higher age and acidity, the brittleness of paper increases. This tendency was not found for objects from 1800 to 1850, probably because the paper quality from this period is more variable, and the samples from the first period were therefore excluded. A correlation between pH and age for the very brittle objects (<3 manual folds) is shown in Figure 1.

The line demonstrates at what level of age/pH the objects will exceed their useful lifetime (3 manual folds). In the future, when a point passes the correlation line (as the objects get older) 3.370 library objects will be so degraded that they will no longer be usable. Based on the survey of the collection of National and University Library, Slovenia, partners of the EC co-funded PaperTreat project established rates of degradation of paper of various pH values at ambient

conditions and used these data to estimate remaining useful lifespan of the collection.² The correlation line based on PaperTreat preliminary results is added to our results in Figure 2. As seen the two lines have the same slope but differ in the pH. This indicates that our collection have a shorter lifetime than the papers examined by PaperTreat. This may be caused by different environmental conditions affecting the degradation rate or by a difference in the manual fold procedure.

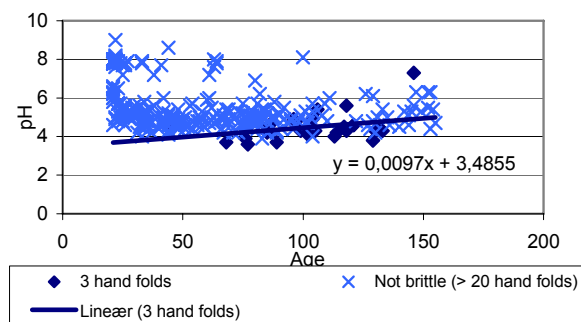


Figure 1: The relation between the age of objects, pH and brittleness (<3 manual folds) for documents from the period 1850 - 1985.

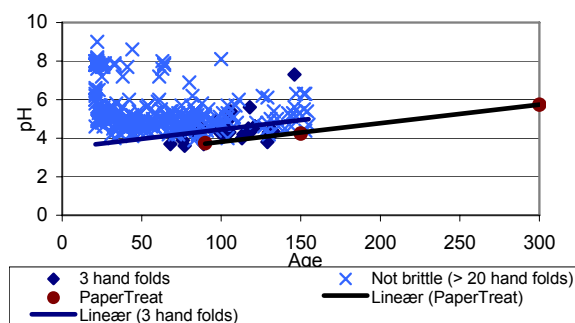


Figure 2: Comparison of object age, pH and brittleness (<3 manual folds) for paper from the period 1850 - 1985. The PaperTreat correlation is based on preliminary results.

3. Remaining Lifetime of The Collections of the Royal Library

The similarity of the correlations indicates that useful lifetime estimations based on our survey could be possible. Knowing the age and pH, the remaining lifetime was calculated using the correlation line equation from Figure 1.

When we know the remaining lifetime of our objects we can calculate when in the future the objects will pass the point when they will be too vulnerable for ordinary use, if the environmental conditions in our repositories remain the same in the future as they are today.

In Figure 3 we show how the share of objects in the library that pass the "3 manual folds" criterion increases until the year 2400. In 2400 all our acidic objects will have reached this advanced degradation state according to the calculations.

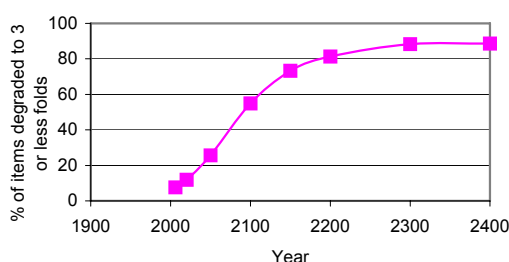


Figure 3: Share of objects of national significance in The Royal Library (in %) from 1850 - 1985, which reach the degradation state of 3 manual folds. Alkaline paper makes up 11.4% of the library collection from the period 1850 to 1985, which represents the difference to 100%.

The same calculations can be used to estimate how many objects the library will have to consider substituting each year in the future, if access is to be secured. The estimates are shown in Figure 4. The number of objects degrading to 3 manual folds each year steadily increases until 2050. During the period 2050 - 2100 we will see that the amount of objects passing the limit each year will be about three times as many as in these years. After 2100 the number of annually degraded objects will decrease.

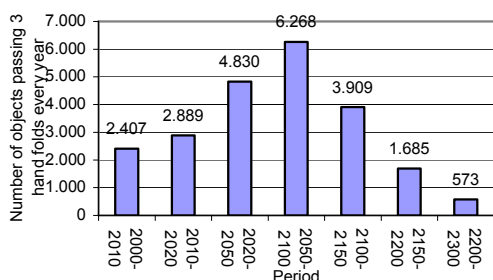


Figure 4: Number of objects from 1850 - 1985, which will reach the "3 manual folds" criterion every year if kept in the present environment.

4. Lifetime Estimations Related to Actions

To increase the lifetime of physical collections we can store them in cold, dry repositories and/or mass deacidify them.

According to the ASHRAE Handbook, 2007, the lifetime is prolonged by two times if the climate is changed from 20 °C / 50% RH to 18 °C / 40% RH. If the temperature is lowered to 12 °C with 45% RH the lifetime is multiplied by four. It is possible to multiply the lifetime by 20 if the temperature is lowered to 5 °C in combination with 30% RH.

Preliminary results from PaperTreat show, that mass deacidification (Book keeper) prolongs the lifetime by 3.5 times.

In Figure 5 the lifetime prolongation has been applied to our data to show a range of possible scenarios. The chosen scenarios represent (i) an un-regulated repository (like the situation is today for the majority of our collections), (ii) Godsbanen (a repository, where we plan to move part of our collection to; 16 °C / 45% RH), (iii) Njalsgade (where a part of our collection has been moved to; 12 °C / 45% RH) and finally (iv) cooling to 5 °C at 30% RH.

To make the scenarios as realistic as possible, the effect of actions is calculated as if mass deacidification or cooling to 5 °C was done in 2020, and the collections were moved to Njalsgade and Godsbanen in 2010.

Seen in a longer perspective there is a big difference in the effect of the different actions taken. As seen in Figure 5, where the share of object degraded to "3 manual folds" is projected to year 2200, then 82% of library objects will have reached this state in 2200 if they remain under the present environmental conditions. By moving the objects to Godsbanen the rate of degradation is halved and in 2200 about 57% of the objects will have passed the limit. By moving the collection to the Njalsgade repository (12 °C / 45% RH) the lifetime is multiplied by the factor of four and about 32% will be brittle in 2200. If we deacidify in 2020 about 40% of the collections will be brittle in 2200.

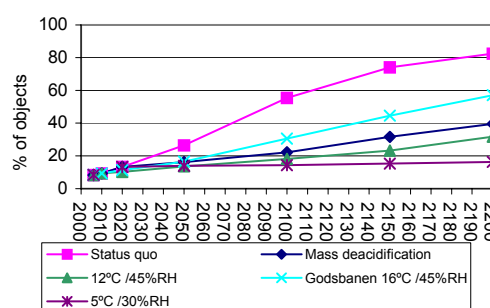


Figure 5: Lifetime estimations by different means calculated on the basis of age, pH and brittleness of the examined objects from The Royal Library collections from 1850 - 1985. The graph shows how big a share of objects will reach the degradation state "3 manual folds".

If the conditions 5 °C and 30% RH are chosen, as seen in the Figure, the degradation rate is decreased so much that the share of objects exceeding the 3 manual fold criterion will increase by 3% (from 13% to 16%) in the period 2020 to 2200. It is of course also possible to combine mass deacidification with cooling to for instance 16 °C / 45% RH and thereby increase the lifetime by seven (3.5 for mass deacidification multiplied by 2 for cooling).

By combining the lifetime estimations with costs for mass deacidification and/or cold storage at different temperatures, we now have a basis for the discussions on which strategy we will choose to preserve our collections for the future. In addition, we will get an idea of the consequences regarding the amount of degraded objects in relation to when the action is taken.

The commission is now awaiting the results from the research done in PaperTreat before the final recommendations are decided upon.

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MASS DEACIDIFICATION OF NEWSPAPERS IN THE RUSSIAN STATE LIBRARY

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1. Introduction

The Russian State Library (RSL) - is one of the largest book depositories of the world with more than 43 million items. Beside modern books, magazines and newspapers, unique collections of ancient editions, manuscripts, maps, and photos are also stored in the collections. The well-known Gutenberg's bible, lifetime editions of Giordano Bruno and Nicolaus Kopernik, personal collections of the Russian emperors, hand-written archives of M. J. Lermontov, N. V. Gogolj, F. M. Dostoevsky, A. P. Chehov are also here.

A considerable part of the library funds are documents from the end of the 19th and the beginning of the 20th centuries printed on acidic paper, which are collapsing in front of the eyes of the collection keepers. In view of this, the library administration developed a program on preservation of printed book heritage, and the purchase in 2003 the machine "C-900" for mass deacidification of paper documents can be considered as a part of its realization.

2. Objects and Methods

The first step of the programme has become the mass deacidification of newspaper fund of RSL, the number of which is more than 1 million items. This collection consists of central and local newspapers of the 19th - 20th centuries. More than 370.000 newspapers issued in the period from 1870 to 1947 have already been treated, having the initial pH from 3.5 to 5.5. In these documents, the paper consists mainly of 60% groundwood and 40% cellulose.

The machine "C-900" uses the well-known "Buckeburg" method. It is built for deacidification of sheets in an aqueous medium. The deacidification liquid is a solution of magnesium bicarbonate, methylcellulose with addition of (rewin/mesitol) fixatives to protect water-unstable inks from migration. The initial pH of the solution, as delivered by the company, is 7.2.¹

The process consists of two stages: deacidification of paper in the bath and drying in the heating chamber. During the first stage wetting, impregnation and deacidification of the document is carried out and during the second stage phase separation occurs - water evaporates, magnesium bicarbonate converts into insoluble carbonate which is partly deposited on the surface of the document and partly penetrates into its volume. Methylcellulose, similarly to the carbonate, is deposited on the surface of the document,

forming a polymeric film, and partly penetrates into the volume, reinforcing the paper.

3. Results and Discussion

As a result of the treatment, pH of the documents increases to 8.0 - 9.0 and the alkaline reserve up to 2% of calcium carbonate is built, measured according to ISO 10716-2000.

During a working day (7 - 8 h) approximately 11 litres of a solution are spent. The machine treats 4 sheets of A4 format at a time. We treat 2 newspapers of A3 format (297 x 420 mm) or one newspaper of A2 format (420 x 594 mm). The documents remain in the bath for 3.5 min and in the drying chamber for 4 min. The parameters of process are: velocity of the conveyor belt (time of immersion) and temperature of the drying chamber are set by the operator via the microprocessor. The machine can be served by one operator who carries out the control of the whole process. To control the quality of the process we measure surface pH of the documents before and after deacidification. We measure one newspaper out of 80 items as it is impossible to measure each item. Newspapers are usually treated after microfilming and after deacidification they are transported to the storage.

3.1 Side-Effects and Deficiencies

However, this method, as well as any another has several deficiencies which have been revealed during application. The following side effects have been noticed:

- Lignin containing paper become more yellow after process.
- The fragile, damaged sheets must not be treated by machine. They should be treated manually.
- Photos and paper with zinc oxide must not be treated.
- The documents damaged by mould, before deacidification should be cleaned by 1% water solution of Metatin G.
- On some types of papers there traces from the grid of the conveyor belt can be noticed.
- It is necessary to control the deacidification liquid and its pH.
- Periodical cleaning of the machine covered by carbonate of magnesium should be done by a 2% solution of acetic acid in water every month.

There are also some construction deficiencies.

3.2 Technological Scheme

Having 3 years of experience we have created the following technological scheme:

3.2.1. All documents delivered to the centre should have certificates - act of inventory (names, numbers).

3.2.2. After reception and registration the documents are examined and selection using the following criteria is carried out:

- the documents should have pH less than 5.5, should not be significantly damaged, in order to be able to treat them safely. Heavily damaged newspapers have to be deacidified manually.
- Before deacidification, surface pH is measured.
- If the documents are going to be microfilmed, they should be deacidified only after microfilming and not before.

3.2.3. Following the treatment, the newspapers are pressed and the surface pH is measured.

3.2.4. The next step is the restoration of the newspapers which is carried out using the “Neschen” films, filmoplast P (short-fibre, transparent acid free paper with a non-yellowing, neutral adhesive, buffered with CaCO_3) or filmoplast R (transparent, long-fibre, Japanese, acid free paper, coated with an acrylic adhesive).

3.2.5. After restoration the papers are put into folders onto which notes are attached with the following information:

- Date of deacidification.
- Method of deacidification.
- pH before and after the treatment

3.2.6. Following the completion of the process, the materials are transported to the storage with a special certificate (act of transfer). The newspapers are packed into containers made of acid free cardboard. In such a way they are stored and not anymore delivered to readers. The originals are given out only in special cases under the supervision of the heads of the department.

3.2.7. The conditions of the treated documents are periodically checked by the members of the centre.

4. Conclusion

We consider that this process promotes preservation of the printed information heritage of the country.

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COMPARISON AND CORRESPONDENCE BETWEEN ARTIFICIAL AND NATURAL AGEING OF PAPER

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1. Introduction

Artificial ageing of paper allows us to estimate the behaviour of this important material if stimulated by perturbing agents; among these temperature, UV irradiation, humidity. These variations should be the same as those occurring naturally but in a faster manner in very short time span, so that the produced damage and the preservation actions can be measured and evaluated in a sustainable time. In this work, we try to compare artificial and natural ageing for their mutual correspondence also with regard to possible influences of ink, if present. Three types of paper were artificially aged and three from historical books sampled: white paper and printed paper, sampled from both the printed and unprinted parts. The analytical device used is an innovative photosensor,¹ with which we are able to measure the 'Environmental Persistence Index', determined as the ratio between the delay before photodegradation begins and the rate of the latter due to the combined action of UV light and catalysed by titanium dioxide.

2. Experimental

This study was performed on paper samples artificially aged for 144 h, using Weathering Tester (Model QUV - Panel LAB, operating conditions: UV radiation $\lambda = 310$ nm, 58% RH, 45 °C), and on naturally aged paper samples (from historical books).

3. Results and Discussion

The two processes were compared through the decrease of Environmental Persistence Index versus percent of ageing time and through the trend line showing a monotonous decrease of environmental persistence.

The trend of environmental persistence during artificial and natural ageing is shown in Figures 1 and 2.

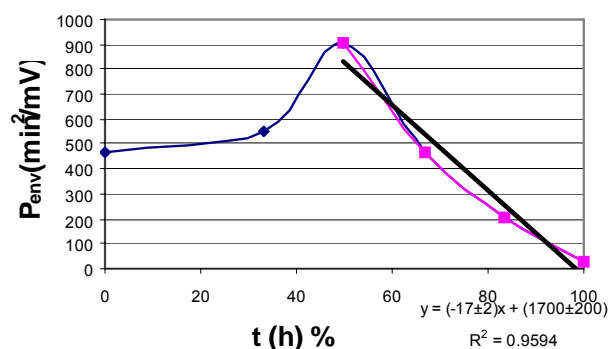


Figure 1: Environmental persistence versus % aging time for artificially aged papers.

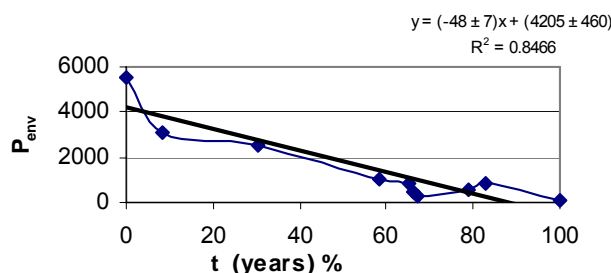


Figure 2: Environmental persistence versus % aging time for naturally aged papers.

By comparison of the slopes, it can be concluded that the rate of artificial ageing is three times higher than the rate of natural ageing.

4. Conclusions

In this work, artificial and natural ageing were compared, using the concept of Environmental Persistence Index.

At the same percentage ageing time the artificial and natural processes result in different decrease of environmental persistence: after 72 h of artificial ageing we have a decrease of 96.5%, while after 78 years of natural ageing (corresponding to the same percentage of the total ageing time) the decrease is 90.8%.

Therefore, it can be assumed that 1 h of artificial ageing at our conditions corresponds to about 2.5 years of natural ageing.

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APPLICABILITY OF QUANTITATIVE HYPERSPECTRAL IMAGING TO HISTORICAL DOCUMENTS

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1. Introduction

For some years, Het Nationaal Archief has been carrying out various projects focused on assessing and monitoring of degradation processes of archival materials and verifying their dependence on environmental conditions of storage and exhibition areas.

Various non-invasive analytical techniques, such as NIR and VIS spectrometry have been applied on test samples and original material preserved in storage rooms having different control systems for climate and pollution parameters. During this research it was possible to verify that most of the techniques lacked two properties that are crucial for such studies. Firstly, for a quantitative comparison it is necessary to make repeated measurements exactly on the same locations of the object. Secondly, it has to be possible to make measurements with a suitable spatial resolution over a sufficiently large object area, allowing a correct definition of the regions-of-interest of the analysis, especially in not homogeneous areas of the objects.

For these reasons the quantitative hyperspectral imaging technique (QHSI) has been taken into consideration to fulfil both these requirements and therefore to apply it for non-destructive condition and degradation monitoring.

2. Characteristics of the Technique

The term “hyperspectral imaging” (HSI) refers to the acquisition of a series of digital images at a large number of different well-defined wavelengths over a large spectral range. By applying proper calibration procedures, the value of each pixel of a digital image represents a precise measurement of the portion of energy reflected from the corresponding location on the target at a certain wavelength. The result of a hyperspectral imaging measurement is the so-called hyperspectral data cube, which contains a digital image for each recorded spectral band. In all images, a particular pixel coordinate corresponds to the same location on the recorded target. The values of all pixels with the same coordinate thus represent a complete reflectance spectrum at this location on the object.

The calibrated reflectance values in the hyperspectral datacube are independent from the specific instrument settings applied during measurement (camera exposure, light intensity etc.). In fact, as opposed to a mere qualitative

comparison of different spectral images, numeric data can be used to compare optical properties of the recorded target in a quantitative way. Multiple recordings of the same area of the object, taken at different times, can be compared almost at a pixel level. Another important feature is that data analysis can be performed without pre selection of the region of interest of the research.

3. Development of a Dedicated Instrument

Changes in spectral values of objects that are either exhibited or stored in controlled environments can be expected to be small even over time periods of several months or years. This had to be taken into account when a prototype quantitative hyperspectral imager for the analysis of historical documents was developed in a collaboration project between Het Nationaal Archief and Art Innovation BV. This instrument, called “SEPIA”, is based on two identical wavelength tuneable light sources, which illuminate the document from two sides under an angle of 45°, and a 4 megapixel monochrome CCD camera positioned above the document. Applying the spectral filtering in the light sources rather than in front of the camera sensor has a great advantage of keeping to a minimum the light intensity, to which the document is exposed during a measurement. During a recording the wavelengths of the two light sources are tuned synchronously via a PC software application in steps of typically 10 nm. In order to suppress the influence of any external light on the measurement, both the camera and the light sources are mounted inside a light-proof cabinet into which the document is placed for the measurement.

A reference recording is acquired for each measurement, using a Spectralon® (Labsphere Inc.) reflectance standard, covering the entire field-of-view of 125 mm × 125 mm. This enables a full calibration of the spectral images, so that the value of each pixel of a calibrated image represents the spectral reflectance value at the corresponding location on the document for a particular wavelength.

4. Preliminary Results

The described prototype instrument has been used to measure a number of original documents exposed or kept in Het Nationaal Archief. Preliminary analysis has shown very promising results about the study of aging processes and also a high potential of use of this technique in “forensic” investigations of palaeographic and diplomatic elements. Some of these results will be briefly presented in the following.

4.1. Paper Yellowing

Oxidation of paper components such as cellulose, hemicellulose, lignin, wood impurities, dyes, additives, and sizing agents results in the formation of coloured degradation products containing carbonyl (C=O) and carbon-carbon double bonds (C=C). These reactions generally occur in uncontrolled environmental conditions (at high and/or fluctuating temperature and relative humidity),

under the presence of pollutants (such as O_3 and NO_2) or following the irradiation by light. Both oxidative and photo-oxidative reactions contribute to the formation of new functional groups accelerating the yellowing process of paper. The human visual perception can detect small colour differences only if the colours to be compared are viewed simultaneously. The human eye is totally inadequate for a quantitative assessment of the progress of yellowing of a document, caused for example by exhibition or a conservation treatment. As opposed to human vision, hyperspectral imaging can quantify even small colour differences with high spatial resolution. For example, Figure 1 shows a colour-coded image of the paper yellow index calculated from a hyperspectral data cube. The two papers (left and right), which belong to the same archival unit, had been stored under different environmental conditions resulting in an inhomogeneous ageing process.

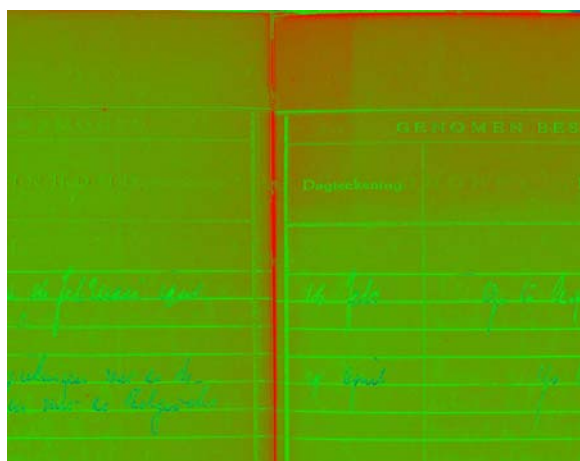


Figure 1: Colour coded image presenting differences in the yellowing of paper caused by two different storage environments (left page and right page have been kept for years in two different storage rooms). Red pixels, corresponding to a higher yellowing index with respect to the green ones, put in evidence more intensive degradation of the paper on the right, with strong differences between the central and upper areas.

4.2. Deterioration of Inks

One of the great advantages of the QHSI technique is that using the same digital measurement data, different regions of interest (ROIs) can be freely defined and re-defined on the document at any stage of the analysis.

In this way it is possible to use the extracted spectral data in multiple ways, depending on the research targets at hand. Figure 2 shows a spatial study, of deterioration effects of a metal gall ink on paper, realised using the so-called Modified Spectral Angle Similarity (MSAS) mathematical algorithm to map areas with similar spectral response towards a series of ROIs defined within the ink area.

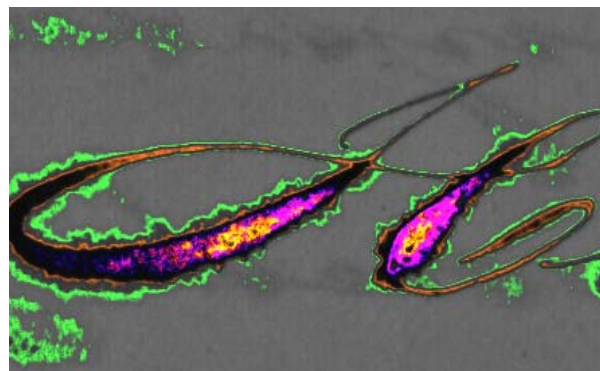


Figure 2: Pixels having similar spectral characteristics, extracted by a partial or total analysis of the datacube, are represented in a unique pre-selected colour obtaining a spectral mapping of the recorded object. In this case yellow, green, orange, blue and pink have been used to put in evidence areas with similar spectral response showing differences in the ink itself and in the substrate affected by its degradation.

4.3. Forensic Study of Palaeographic and Diplomatic Elements

Intrinsic and extrinsic elements of documents are sometimes not easy to identify, as they might be - purposefully or not - obscured. Preliminary tests have shown that hyperspectral imaging can help to enhance the visibility of such elements reducing the handling of the originals to a minimum. Good results have also been achieved in the study of extremely deteriorated objects, such as carbonised and erased materials where the enhancement of text was the primary goal.

5. The Bihanneⁱ Project at Het Nationaal Archief

Het Nationaal Archief has recently started an experimental project in combination with a systematic analysis of original documents displayed in the internal exhibition area. The aim of this project is mainly to realise and measure a set of artificial samples containing a large number of combinations of different substrates, writing materials, conservation treatments, induced damages, and ageing parameters. The analysis of these measurements is expected to result in more than 10,300 spectral curves. This large amount of data will be used to investigate the sensitivity of quantitative hyperspectral imaging in relation to the detection of spectral variations in archival documents to quantify aging processes and damages commonly found on archival units, such as foxing or biological and physical alterations. The second main goal of this project is the improvement of spectral analysis procedures to obtain good spectral mapping to be used in forensic applications.

First results of this study are expected for the beginning of 2009.

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(i) The name of the research project at Het Nationaal Archief has been chosen in memory of our dear colleague Bihanne Wassink who recently passed away.

NON-DESTRUCTIVE DETERMINATION OF CELLULOSE FUNCTIONAL GROUPS AND MOLECULAR WEIGHT IN PULP SHEETS AND HISTORIC PAPERS BY NIR-PLS-R

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A fast and non-destructive method to evaluate the condition of pulp and paper was developed. Partial least square regression (PLS-R) models based on near infrared (NIR) spectra and reference values for molecular weight, carbonyl group content, and carboxyl group content were calculated for pulp hand sheets and rag papers. Being an indirect method, reference methods are necessary to obtain the reference values for calibration. These reference methods may be time consuming, expensive or not applicable to the material in question. Consequently, they are used only for calibration, and will then be replaced by NIR spectroscopy which afterwards provides the same parameters in a fast, inexpensive and non-destructive way.^{1,2} Group-selective fluorescence labelling of carbonyl and carboxyl structures with subsequent gel permeation chromatography (GPC) analysis was used as a (destructive) reference method to provide three chemical parameters of cellulose: the carbonyl group content, the carboxyl group content, and the molecular weight, which were correlated with the NIR data.^{3,4}

Band assignment of NIR-spectra is rather complicated due to many broad and overlapping bands corresponding to overtones and combinations of fundamental vibrations appearing in the mid infrared region. Pre-processing of spectral data is useful to account for differences within the set of sample papers,⁵ especially for historic rag papers that are obviously different in colour and thickness. Derivatives, multiplicative scattering correction, vector normalization and straight-line subtraction, or combinations thereof, were found to be appropriate for the present problem. Before and after pre-processing, the spectra have been visually examined for unusual features. Depending on visual pre-selection, and further detection of unsuitable samples (called outliers) that were later found during modelling, different numbers of spectra for each parameter were used for the models.

In this study, 110 pulp hand sheets were used and gave satisfactory models with high correlation coefficients (up to 0.97) during validation; whereas the test set validation (external validation) results were always better than those of cross validation (Table 1).⁶

Modelling of 267 historic rag paper samples was more demanding due to inherent variability of the material. Nevertheless, PLS-R models for the carbonyl group content,

carboxyl group content and molecular weight with good correlation coefficients (up to 0.93) and low errors for cross validation using average spectra of different paper samples were obtained (Table 2).

For carbonyl group content models with good correlation coefficient was also obtained without previous averaging.

Joint models using both pulp hand sheets and rag papers were calculated for carboxyl and carbonyl group contents. The resulting correlation coefficients were lower than the single models (Table 3).

Table 1: Parameters of cross validation (CV) and test set validation (TS) on pulp hand sheets.

Parameter		Offset	Slope	r1	RMSECV2/ RMSEP3
Molecular weight	CV	29 kg/mol	0.84	0.90	37 kg/mol
	TS	20 kg/mol	0.87	0.93	23 kg/mol
Carbonyl group content	CV	1.3 µmol/g	0.91	0.96	2.7 µmol/g
	TS	0.7 µmol/g	0.87	0.97	2.2 µmol/g
Carboxyl group content	CV	5.8 µmol/g	0.64	0.77	3.3 µmol/g
	TS	1.3 µmol/g	0.88	0.91	2.2 µmol/g

2 RMSECV: Root Mean Square Error of Cross Validation.

3 RMSEP: Root Mean Square Error of Prediction.

Table 2: Parameters of cross validation on rag papers.

Parameter	Offset	Slope	r1	RMSECV2
Mw	32 kg/mol	0.85	0.92	34.6 kg/mol
Carbonyl group content	3.0 µmol/g	0.87	0.93	4.7 µmol/g
Carboxyl group content	3.6 µmol/g	0.84	0.91	2.1 µmol/g

1r: correlation coefficient.

2 RMSECV: Root Mean Square Error of Cross Validation.

Table 3: Parameters of test set validation of joint models obtained from pulp hand sheets and rag papers.

Parameter		Offset	Slope	r1	RMSECV2/ RMSEP3
Carbonyl group content	CV	4.5 µmol/g	0.77	0.86	4.5 µmol/g
	TS	4.4 µmol/g	0.78	0.86	5.3 µmol/g
Carboxyl group content	CV	8.4 µmol/g	0.58	0.74	3.2 µmol/g
	TS	7.4 µmol/g	0.64	0.79	3.1 µmol/g

1r: correlation coefficient.

2 RMSECV: Root Mean Square Error of Cross Validation.

3 RMSEP: Root Mean Square Error of Prediction.

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X-RAY DIFFRACTION ANALYSIS OF PAPER SAMPLES - INVESTIGATION OF THE EFFECTS OF WATER, DEACIDIFICATION TREATMENTS AND ARTIFICIAL AGEING ON CELLULOSE CRYSTALLINITY

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1. Introduction

Aqueous conservation treatments of paper materials are often studied by examining changes of paper properties providing mainly macroscopic information e.g. changes in pH, colour, degree of polymerization and mechanical properties.^{1,2}

The aim of this research project was to study the effect of washing, deacidification treatments and artificial ageing process on nano-structural properties of cellulose.

X ray diffraction images of paper samples were obtained in order to determine the important nano-structural properties that may be reflected in macroscopic alterations of paper/cellulose properties. Recent studies with historical paper samples had suggested that crystallization may be an important factor in the ageing of cellulose fibres.³

2. Experimental

Several different analytical methods: XRD, SEM-EDS, CIE L*a*b* colourimetry, pH determination and IC (Ion chromatography) were used to study paper samples and water based treatment solutions. This paper presents results of X-ray diffraction studies. Other research results are summarized elsewhere.^{4,5}

The NanoSTAR facility at Cardiff University, with a sample to detector distance of 4 cm, gives wide-angle X-ray diffraction (WAXD) images allowing features of cellulose structures of between 0.22 and 3.0 nm to be observed. A 0.154 nm X-ray beam is generated by a Kristalloflex 760 X-ray generator (Bruker AXS, Germany) and focused using cross-coupled Göbel mirrors and a 3-pinhole collimation system. A HI-STAR 2D detector is used for data collection. The calibration standard was calcite. Details of scattering system and data reduction can be obtained. One analysis of paper by X-ray diffraction is the assessment of paper crystallinity.⁶

Two methods of assessing paper crystallinity, were labelled the crystallinity index (CI) and crystallinity ratio (CR).⁷ These methods make use of two key values: the height of the (200) reflection, labelled I_{\max} , and the height of the scattering at 2.25 nm^{-1} corresponding to diffuse scatter from non-crystalline matter, where scattering is not due to peak maxima, labelled I_{\min} . The CI and CR are calculated as:

Crystallinity Index, $CI = (I_{\max} - I_{\min}) / I_{\max}$,

and

Crystallinity Ratio, $CR = 1 - I_{\min} / (I_{\max} - I_{\min})$.

Old "rag" paper samples, which contained mainly pure flax fibres, were taken from margins of a book from the year 1831. New paper samples were Whatman no. 1, which are pure cotton fibres.

The washing process with Millipore Elix III purified water and deacidification treatments (1 g paper/100 ml solution) with 0.02 M $\text{Ca}(\text{OH})_2$ or 0.04 M $\text{Mg}(\text{HCO}_3)_2$ took 30 min each. Artificial ageing of paper samples was performed at 80 °C and 65% RH for two weeks in a Binder Climate chamber.

3. Results and Discussion

Figure 1 shows the 2D high-angle X-ray diffraction pattern of a new untreated paper reference sample at a sample to detector distance of 4 cm, allowing dimensions in the region of 10 - 0.2 nm to be resolved. The 2D image was converted to the 1D linear profile of intensity (I) versus scattering angle, represented as reciprocal nanometres.

The main scattering peak of cellulose (200) is highlighted as I_{\max} . I_{\min} at 2.25 nm^{-1} is also highlighted as it was required in crystallinity calculations.

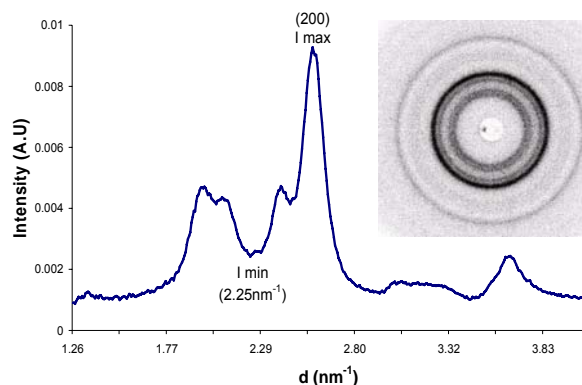


Figure 1: On the top a 2D X-ray diffraction image of a new untreated Whatman paper sample. On the bottom a 1D linear trace of the 2D X-ray diffraction image.

For the studied samples the CI and CR values have been calculated and are presented in Tables 1 - 4.

Table 1: Crystallinity Index and Crystallinity Ratio of old paper samples. Crystallinity Index Std dev ± 0.0109 , Crystallinity Ratio Std dev ± 0.0241 .

Old Paper samples	CI	CR
Reference (untreated)	0.660	0.484
Reference (untreated)	0.668	0.504
Washed in deionised H ₂ O	0.669	0.506
Washed in deionised H ₂ O	0.672	0.512
Treated with Ca(OH) ₂	0.667	0.502
Treated with Ca(OH) ₂	0.689	0.549
Treated with Mg(HCO ₃) ₂	0.586	0.293
Treated with Mg(HCO ₃) ₂	0.651	0.463

Table 2: Crystallinity Index and Crystallinity Ratio of the new paper samples. Crystallinity Index Std dev ± 0.0049 , Crystallinity Ratio Std dev ± 0.0092 .

New Paper samples	CI	CR
Reference (untreated)	0.725	0.621
Reference (untreated)	0.721	0.612
Treated with Ca(OH) ₂	0.732	0.634
Treated with Ca(OH) ₂	0.729	0.629
Treated Mg(HCO ₃) ₂	0.723	0.618
Treated Mg(HCO ₃) ₂	0.720	0.611

Table 3: Crystallinity Index and Crystallinity Ratio of the artificially aged old paper samples. Crystallinity Index Std dev ± 0.0220 , Crystallinity Ratio Std dev ± 0.0458 .

Aged Old Paper samples	CI	CR
Reference (aged)	0.721	0.613
Reference (aged)	0.714	0.600
Washed in deionised H ₂ O	0.671	0.510
Washed in deionised H ₂ O	0.676	0.522
Treated with Ca(OH) ₂	0.671	0.510
Treated with Ca(OH) ₂	0.670	0.507
Treated with Mg(HCO ₃) ₂	0.704	0.580
Treated with Mg(HCO ₃) ₂	0.670	0.507

Table 4: Crystallinity Index and Crystallinity Ratio of the artificially aged new paper samples. Crystallinity Index Std dev ± 0.0066 , Crystallinity Ratio Std dev ± 0.0120 .

Aged New Paper samples	CI	CR
Reference (aged)	0.744	0.655
Reference (aged)	0.742	0.652
Treated with Ca(OH) ₂	0.732	0.635
Treated with Ca(OH) ₂	0.751	0.668
Treated with Mg(HCO ₃) ₂	0.742	0.652
Treated with Mg(HCO ₃) ₂	0.735	0.639

The conclusions from these data are:

- During ageing, crystallinity may increase.
- Naturally aged rag paper samples have a lower crystallinity when compared with the new Whatman paper samples.

- Treatments do not appear to have any pronounced effect on crystallinity with the exception of the aged old rag paper samples.
- Washing and deacidification of rag paper prevent further crystallization during ageing.

There is one key feature that is of interest in these samples, namely the samples treated with Ca(OH)₂. In these samples it is clear that calcite deposits remain on the paper. The X-ray diffraction image shows a clear ring of sharp points at the highest angles (Figure 2).

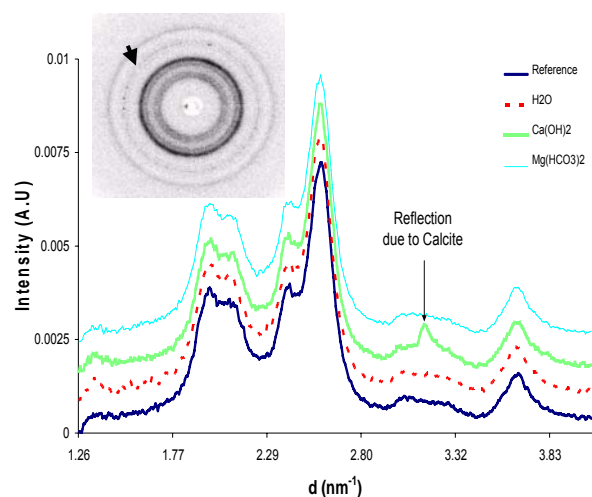


Figure 2: On the top X-ray diffraction image of old paper treated with Ca(OH)₂. Calcite reflection has been labelled with an arrow. 1D linear trace of the 2D X-ray diffraction images for the old paper samples set. Calcite reflection due to treatment with Ca(OH)₂ has been labelled. (Linear traces offset).

The presence of the calcite reflection is most likely a remnant of the processing with Ca(OH)₂, and has been observed in other materials which are subjected to treatment with Ca(OH)₂.⁸

4. Conclusions

Results show that aqueous conservation treatments, washing and deacidification have the effect on crystallinity of artificially aged rag paper cellulose. Anyhow, examination with other, more complex papers which contain different cellulose fibres e.g. wood fibres, lignin and additives, still remain the subject of further studies.

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CHARACTERISATION OF THE SLOVAK NATIONAL LIBRARY COLLECTIONS

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1. Introduction

The Slovak National Library in Martin is the oldest, largest and most significant research library in Slovakia. The library collection is comprised of 4.5 millions of documents. In other Slovak libraries - scientific, public, special and academic - about 43.6 millions of library units are kept.¹ The network of state archives in the Slovak Republic keep altogether 22.345 archival fonds and the collections represent about 157.700 running meters of material in total.²

The extensive cultural heritage of rare books and archival information on paper carriers is endangered by destructive effects of abiotic and biotic factors that result in its irreparable loss.^{3,4} The present preservation capacity of the Slovak Republic is insufficient and the capacities for mass preservation of books and archival materials do not exist. The first step of successful preservation and stabilisation is careful identification and quantification of their current state. The object of our research is to describe the composition of model books,⁵ to judge the physical and chemical properties, and then to suggest a flexible application for conservation of stocks in the Slovak National Library.

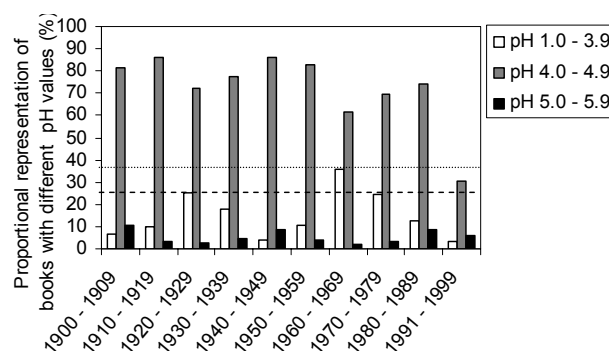


Figure 1: Proportional representation of model book acidity per decades of the 20th century. The share of books with pH > 6 is insignificant.

2. Experimental

The model library was created from 2.500 excluded books from the 20th century from the Slovak National Library. The standard surface pH measurement was used (STN 50 0374).⁶ Determination of pH was performed in the following way: 5 µl deionized water added to the surface of sample, pH was determined on the surface using by a flat-surface combined glass electrode.

Determination of folding endurance was carried out according to STN ISO 5626.⁷ The Schopper device was used for folding endurance measurement at the load of 0.5 kg.

3. Results

The whole collection is described by the following general information: date of edition, weight of document, size, and damage of document.

pH values were determined in the whole range (pH 1 - 14). There are no books with pH > 6 at the beginning of the 20th century. A significant amount of books with pH > 6 was found only after 1970.

The results presented in Figure 1 demonstrate that the most acidic books are from the 1920s, the 1960s and the 1970s. There are over the 97% of model books with pH value below 4.9.

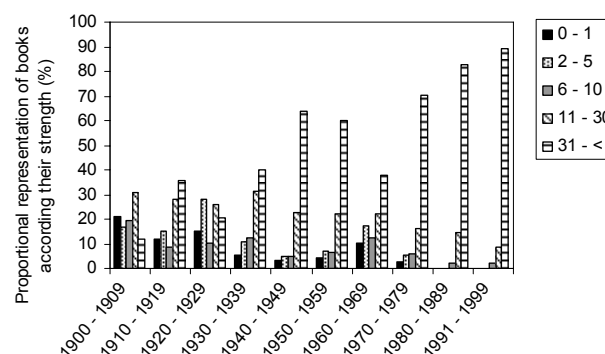


Figure 2: Proportional representation of model books' folding endurance per decades of the 20th century.

The strength of model books was measured as folding endurance. A similar observation as for pH was observed also for mechanical permanence (Figure 2). The exceptions are the 1970s, in spite of a great majority of acidic books, their permanence and stability is sufficient. Among them there are only 8% of very brittle books. The most brittle books were found until 1960s years; then their stability is higher. The higher stability of books from the end of century is related to the time of their production and raw materials used in manufacture.

At the beginning of the twentieth years the manufacture rationalisation and production modernisation took place.⁸ It is related to an increase in paper production, and to an increase in the use of groundwood as the main raw material for paper production.

Table 1 shows the percentage of acidic brittle books from the 1920s, 1940 s and 1960s respectively. The amount of acidic and fragile books from the 1940s years is approximately 2 times lower than that from the critical years of the 1920s and 1960s.

Table 1: Percentage of books from the 1920s, 1940s and 1960s according to their pH and strength.

Decade	1920s			1940s			1960s		
pH/folding endurance (%)	1.0 - 3.9	4.0 - 4.9	5.0 - 5.9	1.0 - 3.9	4.0 - 4.9	5.0 - 5.9	1.0 - 3.9	4.0 - 4.9	5.0 - 5.9
0 - 1	26	11.3	14.3	8.3	3	3.6	20	5.1	0
2 - 5	50.7	21.2	0	16.7	4.1	10.7	31.1	9.6	0
6 - 10	11	10.4	0	0	5.6	3.6	17.8	10.3	0
11 - 30	6.8	32.1	42.9	41.7	32.4	14.3	17.8	25.6	0
31 - <	5.5	25.0	42.9	33.4	64.9	67.8	13.4	49.4	100

4. Conclusion

On the basis of the survey, analysis and evaluation of tested model books collection, it can be concluded that:

- Papermaking technology in the 20th century (except 1990s) led to 80% - 90% of books printed on acidic paper.
- In order to create proper priorities for preservation of these books historical and time specification of their production must be taken into account.
- Paper strength directly depends on its acidity and quality is a crucial factor for selection not only for mass conservation treatment but also for other conservation technologies.
- In order to search for and to propose a suitable technology for mass conservation, it is necessary to take into account all factors and selection of documents should be adapted to the preservation priorities of the appropriate library and of the country as a whole.

5. Acknowledgement

The authors express their thanks to the Ministry of Education of the Slovak Republic - project KNIHA.SK 661/2003.

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STRENGTHENING AND DEACIDIFICATION OF ACIDIC GROUNDWOOD PAPER WITH THE TERNARY SYSTEM CHITOSANE-METHYL-HYDROXYETHYL-CELLULOSE - CATIONIC STARCH IN $\text{Mg}(\text{HCO}_3)_2$ AQUEOUS SOLUTION

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1. Introduction

Paper materials undergo degradation during their lifetime. There is a continuous search for new methods of lifetime prolongation and/or preservation of their useful properties.

The known deacidification agents for conservation of books and documents increase the pH and introduce an alkaline reserve, but they do not strengthen degraded paper. The use of cellulose derivatives¹⁻³ and starches^{4,5} is well known in the restoration and conservation practice. Chitosane is an environmentally friendly, antibacterial polysaccharide.⁶

This work deals with strengthening and deacidification of acidic groundwood paper with the ternary polymer system: chitosane - methyl-hydroxyethyl-cellulose - cationic starch in $\text{Mg}(\text{HCO}_3)_2$ water solution.⁷

2. Experimental

The following two paper samples were used:

- Newspaper with a basic weight of 45 g/m^2 , groundwood, unsized, cold extract pH 5.7 (NP).
- Writing paper, groundwood, with a basic weight 66.9 g/m^2 , cold extract pH 4.5 (WP).

Polysaccharides used in the modification mixture (TECH) preparation: low-molecular weight poly(D-glucosamine) chitosane (Aldrich), water soluble cellulose derivative methyl-hydroxyethyl-cellulose Tylose MH 300, cationic potato starch derivative Empresol N (Emsland-Stärke GmbH). Neutralisation solution $0.04 \text{ mol/dm}^3 \text{ Mg}(\text{HCO}_3)_2$ was prepared as an aqueous solution of MgCO_3 saturated with CO_2 .

The paper samples were subjected to treatment with the mixture for 10 min and dried. The samples modified in such a procedure were subjected to dry accelerated ageing at 105°C for 0, 3, 6, 12, and 24 days.

Mechanical properties of the modified materials, tensile strength (lt)⁸ and folding endurance (ω)⁹ were determined.

By monitoring the pH of the cold extract,¹⁰ changes in acidity were followed. The treatment efficiency was evaluated on the basis of mechanical permanence improvement index $S_{X,t}$, described as a ratio of measured property value ($X = \text{lt}$ or ω) of modified/unmodified (control) sample at a certain time of accelerated ageing (t):

$$S_{X,t} = \frac{S_{\text{modified},t}}{\omega}$$

- If $S_{X,t} > 1$ – permanence increased,
- If $S_{X,t} < 1$ – permanence decreased,
- If $S_{X,t} = 1$ – is it not changed.

3. Results and Discussion

By applying the modification system, the strengthening effect ($S_{\text{lt},0} = 1.21$ for NP and 1.28 for WP) is achieved, together with an improvement in the breaking length during the whole period of accelerated ageing (Figures 1 and 2). This effect was verified for both tested paper kinds.

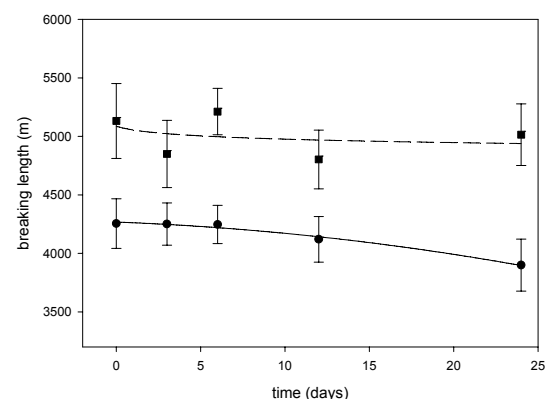


Figure 1: Dependence of breaking length during accelerated ageing for samples modified by „TECH“ (■) and control sample (●) of NP.

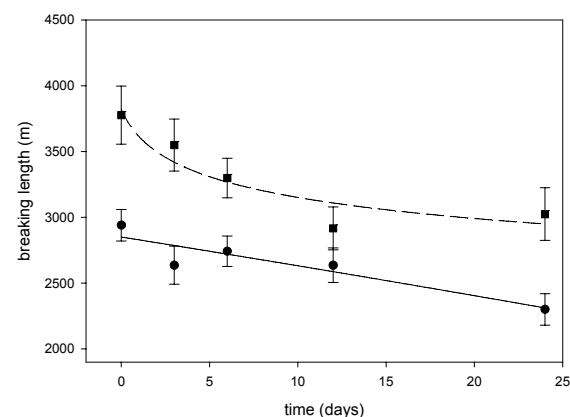


Figure 2: Dependence of breaking length during accelerated ageing for samples modified by „TECH“ (■) and control sample (●) of WP.

Paper samples modified using this system demonstrated an increase in folding endurance ($S_{\omega,0} = 2.36$).

The stability of this parameter increases with the time of accelerated ageing, particularly for the paper WP ($S_{\omega,12} = 18$) which is illustrated in Figures 3 and 4. Very low values of folding endurance should be taken into account in rationalizing the behaviour of this untreated paper kind.

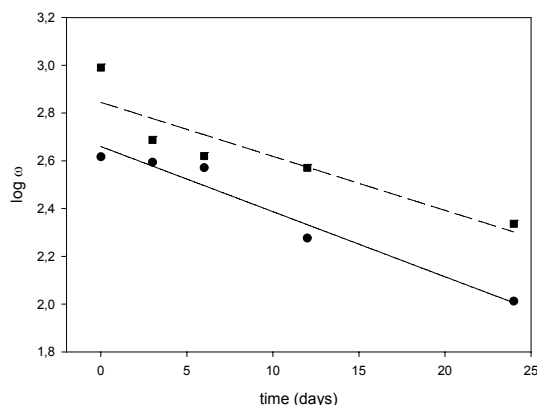


Figure 3: Dependence of logarithmic values of folding endurance during accelerated ageing of samples modified by „TECH“ (■) and control sample (●) of NP.

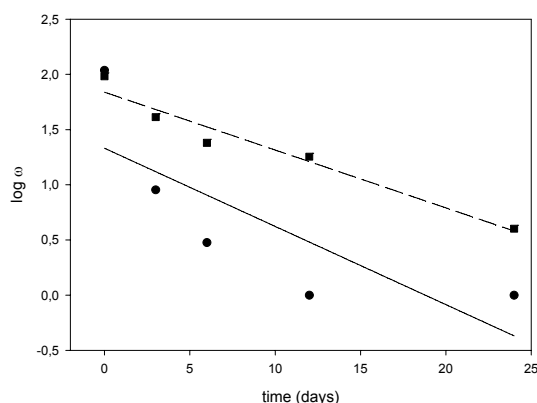


Figure 4: Dependence of logarithmic values of folding endurance during accelerated ageing of samples modified by „TECH“ (■) and control sample (●) of WP.

It is known that degradation processes occur at a higher rate in acidic wood paper and that pH decreases during ageing. By applying the modification system TECH, an increase in pH value was achieved when compared with a control sample in both types of newsprint papers (from 5.7 to 7.7 by NP and from 4.5 to 7 by WP). The pH value is kept constant during the accelerated ageing and does not decrease in the treated paper below the value of 7.

4. Conclusions

Application of above mentioned modification system caused an increase of tensile strength (lt) and folding endurance (ω) of paper samples and permanence of these properties after the accelerated ageing. Also, this ternary polymer system has a strengthening and stabilization effect.

The modification system provides preparation of paper samples with sufficiently permanent pH.

5. Acknowledgement

The authors thank Ministry of Education of the Slovak Republic for a support granted to the project No. 2003 SP200280301 Kniha^{SK}.

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ASSESSMENT OF THE EFFECT OF VARIOUS BLEACHING AGENTS ON FOXING STAINS

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1. Introduction

Foxing can greatly affect the visual appearance of artworks on paper. Whether and how to remove the stains from an artefact are some of the most sensitive decisions the conservator has to take. Despite our limited knowledge of the foxing phenomenon various bleaching methods are often applied. In addition, some studies of various bleaching methods indicate that they may cause extensive degradation and discolouration of the artefact. The risk associated with the techniques is even greater if transition metals, such as iron and copper are present in the paper. They can participate in the processes leading to foxing, as well as interfere with the bleaching processes. It is known that iron and copper catalyse decomposition of chlorine-based bleaches, as well as hydrogen peroxide and various borohydride salts.¹ During decomposition of hydrogen peroxide extremely reactive radical species are formed which cause undesired oxidative decay of the cellulose that results in loss of mechanical properties of paper and its discolouration.

The purpose of this study was to investigate the effects of different types of bleaching agents on real paper samples damaged by foxing.

2. Paper Samples and their Preparation

Paper samples with foxing stains were selected from five 19th century books. Fibre analysis of the paper was performed according to SCAN-G3:90 and SCAN-G4:90 standards. The results indicate that the papers were made either from rag cotton or bleached cellulose pulps or their mixtures.

Several paper samples were tested for the presence of iron and copper ions using laser ablation-ICP/MS technique.² Only two paper samples contained increased amounts of iron on foxing stains in comparison to surrounding paper (paper sample No. 4 15x, and sample No. 5 200x higher iron content on foxing stains).

Prior to bleaching, all samples were pre-treated (procedure a) by washing in distilled water and solution of calcium bicarbonate. The samples were washed in two consecutive baths of distilled water for 30 min. Wet samples were then immersed into two consecutive baths containing 0.01 mol L⁻¹ aqueous solutions of Ca(HCO₃)₂ for 30 min.

The following bleaching solutions were used: 3% hydrogen peroxide solution with pH raised to 9 with diluted ammonia³ (procedure b), 0.05% calcium hypochlorite solution with pH adjusted to 10 using aqueous sodium hydroxide³ (procedure c), 1% sodium tetrahydroborate solution (prepared 1 h prior to bleaching)⁴ (procedure d), 2% sodium dithionite solution with pH raised to 7.4 with sodium hydroxide^{1,4} (procedure e), 0.1 mol L⁻¹ EDTA in 2% sodium dithionite solution^{1,4} (procedure f), and 0.1 mol L⁻¹ EDTA in 3% hydrogen peroxide solution¹ (procedure g).

The pre-treated samples were bleached with hydrogen peroxide, sodium hypochlorite and sodium tetrahydroborate according to procedures described in the literature.¹⁻³

Sodium dithionite, its mixture with EDTA and hydrogen peroxide in combination with EDTA were introduced into the paper during a 30-min immersion. The papers were subsequently rinsed in distilled water twice for 30 min.

After the bleaching procedures had been carried out, wet samples were deacidified by immersion in two consecutive baths containing 0.01 mol L⁻¹ aqueous solutions of Ca(HCO₃)₂ for 30 min.

The samples were taken out the bath, placed on a polyester sheet (Mylar) and air dried.

Untreated, pre-treated and bleached samples were artificially aged at 90 °C and 65% relative humidity (RH) in a Vötsch VC 0020 ageing oven for 27 days.

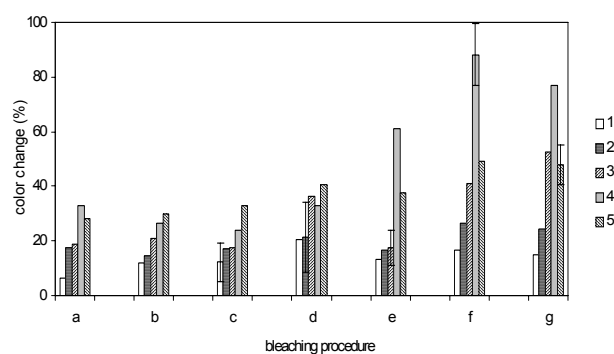


Figure 1: The changes of L* values of CIE L*a*b* colour space of foxing stains on aged paper samples (1 to 5) in percentage according to the colour of foxing stains of aged untreated sample. Samples were pre-treated (a) or bleached with different bleaching agents (b to g). Error bars represent the standard deviation (N = 5).

3. Results

Six different bleaching solutions were used. Two belong to the group of oxidative bleaching agents, two are reductive bleaching agents and the last two are combinations of a complexing and a bleaching agent.

The colour changes of foxing stains and paper support after application of bleaching solutions were followed using scanned images due to small area of investigation.⁶ L* values (brightness) of CIE L*a*b* colour space were determined with Photoshop 7.0 software.

The effect of different bleaching solutions on colour stability of stains and paper support during thermal ageing was evaluated, as well.

The results indicate that in comparison to untreated control all tested solutions improve the colour of foxing stains and their stability during thermal ageing of samples. After accelerated ageing the differences in colour of bleached foxing stains on paper samples, which were within a small range, became more obvious.

- Washing and deacidification improves L^* values of CIE $L^*a^*b^*$ colour space for up to $10 \pm 3\%$ in comparison to untreated sample. After accelerated ageing the pre-treated samples were up to $33 \pm 12\%$ more stable during thermal degradation than the untreated sample (Figure 1).
- Application of both oxidative bleaches improved the colour of foxing stains on paper samples from $8 \pm 3\%$ to $27 \pm 5\%$. On most of the samples, foxing stains were completely discoloured. During bleaching of paper with hydrogen peroxide, oxygen is formed. This may cause physical disruption of fragile paper fibres, which was observed on some of the samples. Bubbling of the upper layer of paper also appeared on one sample after the use of hypochlorite solution. Foxing stains re-appeared on most of the samples after accelerated ageing was performed. The results of colour stability are comparable to deacidified samples. Application of hydrogen peroxide and calcium hypochlorite can not be recommended, taking into account the short-term effect of bleaching and possible physical disruption of paper.
- Sodium tetrahydroborate is considered to be the only sufficiently effective reductive bleaching agent. When applied correctly, it may also decrease degradation of cellulose and improve brightness stability of pulps. Sodium dithionite, also a reducing agent, has a mild brightening effect on paper to which it is applied. Dithionite was selected because it may reduce iron content in the paper by way of chemical reduction of insoluble iron(III) species to soluble iron(II). Most of the samples were efficiently discoloured after the solution of sodium tetrahydroborate was applied. In comparison to samples treated with oxidative bleaches, the colour stability of samples was slightly better. Blistering was also observed on some of the samples. Sodium dithionite was the least efficient in discoloration of stains without iron ions, as it could be predicted. It is more efficient on samples with an increased iron content.
- A combination of dithionite with chelating agent such as EDTA, the extraction of iron into the bleaching solution is supposed to be faster. EDTA may also be used for stabilization of hydrogen peroxide during bleaching of paper.

The most effective - before and after artificial ageing - was the combination of EDTA and sodium dithionite for iron containing samples. Colour stability of other three samples is comparable to the results obtained after application of sodium tetrahydroborate. Efficiency of hydrogen peroxide combined with EDTA is comparable to mixture of dithionite and EDTA. Because of the bubbling appeared on one of samples (Figure 2) it can not be recommended for treatment of original artefacts.

4. Conclusions

To minimize the potential risks associated with the use of bleaching methods, the object has to be thoroughly examined prior to any intervention. Most important is to know whether iron or copper ions are present in the paper. Results indicate that if iron ions are present in the paper, treatment with complexing agent EDTA and sodium dithionite efficiently discolours foxing stains and improves their colour stability. The effect of hydrogen peroxide and calcium hypochlorite on discoloration of foxing stains is only a short-term one. After some time, the stains will probably re-appear. For the artefact with no transitional metals present, either washing and deacidification or application of sodium tetrahydroborate might be a better decision.

The results obtained enabled us to select the most appropriate method for treatment of foxing stains on two original contemporary etchings containing high amounts of iron ions.

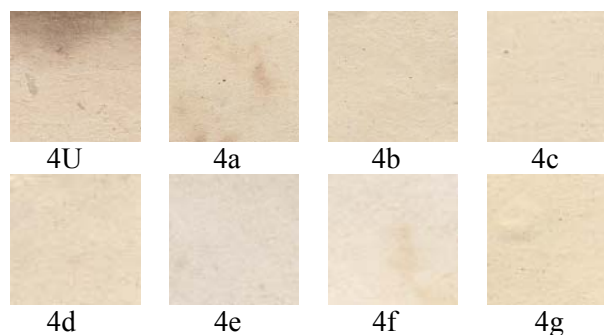


Figure 2: Scanned images of untreated sample No. 4 (U), pre-treated sample (4a) and the same sample after application of different bleaching procedures (4b to 4g).

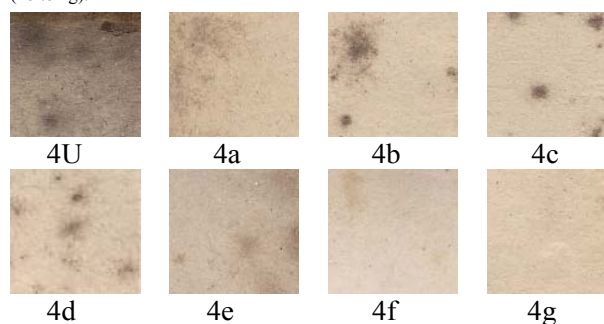


Figure 3: Scanned images of sample No. 4 after accelerated ageing.

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EFFECTS OF PREVIOUS TREATMENTS ON THE DRAWING “THE HOLY FAMILY UNDER THE OAK” FROM THE CROATIAN NATIONAL AND UNIVERSITY LIBRARY

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1. Introduction

Despite apparent similarities, works of art on paper are very different depending on the purposes for which they were made. Graphic works, such as drawings, can present difficult conservation problems because the paper substrate is part of the image. Thus, the colour of paper and its texture contribute to the visual appeal of the object, and study of the paper and its preservation is of great importance. The knowledge of drawing techniques, materials involved and their stability is essential for successful long-term preservation.

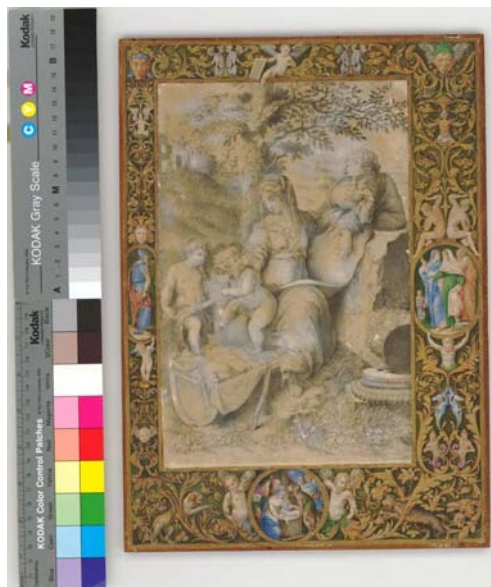


Figure 1: *The Holy Family Under the Oak*, drawing on paper, tempera on parchment, 359 × 254 mm, Graphic Arts Collection, National and University Library, Croatia.

The object under investigation is the drawing on paper *The Holy family under the Oak* with the miniature work on parchment *Gloria in Excelsis Deo* as part of the surrounding border design attributed to Juraj Julije Klović (known worldwide as Giulio Clovio - Croatia), the greatest Croatian miniaturist (Figure 1).

The drawing based closely on the *Madona della Quercia* by Giulio Romano (Prado Museum, Madrid) was made by an unknown artist (Andrea del Santo?). It is considered that both works can be dated to the first half of the 16th century.¹

Nearly three centuries later one of the past owners took two works and merged them together into the new composite artwork on wooden support. During the 19th century it was exhibited several times (exhibition stickers on the back side of the wooden board). Unfortunately, very little is known about the history of this artwork. Soon after its arrival to Croatia in 1991, the drawing was housed in the official residence of the President of the Republic of Croatia. Today it is stored in the National and University Library in Zagreb.

It is evident that the art object was subjected to conservation in the past and the resulting alterations have to be considered in relation to previous treatments. The damage due to past insect infestation of the wooden support (such as shavings, bore-holes etc.) is quite visible. One of the most serious conservation problems seems to be the thin whitish-grey surface deposit layer localized around the old repairs on paper substrate. The appearance of deposits on the paper surface has aesthetic implications and it indicates that chemical changes might have occurred.

Finally, in order to evaluate the artwork condition with respect to the drawing itself, and the reasons for surface destruction, scientific studies were undertaken. The technical investigations, identification and partial characterisation of the materials and alteration products were performed by visual observations and simple diagnostic tools while preserving both the physical integrity of the object and its appearance. Several non-destructive and micro-destructive techniques were applied in combination, in order to obtain as much information as possible.²

2. Experimental

The study was focused on the definition of drawing technique and paper degradation phenomena. The initial work included the observation of the surface with photography techniques (in the UV/VIS/IR) and stereomicroscopy. Visual observations were important starting points in the examination of drawing, but they could not identify all degradation processes. Therefore, stereomicroscopy was used to provide information on surface texture and microstructure of the substrate and to help in identification of drawing technique. The use of UV induced visible-fluorescence was useful in detection of the old adhesives, some pigments and previously restored areas. UV examination was mainly aimed at identifying areas similar fluorescence features and, therefore, characterized by similar mixture of compounds. Additionally, the presence of adhesive in wooden putty was determined by infrared spectroscopy. More specific non-destructive analytical technique as X-ray fluorescence spectroscopy (XRF) allowed the identification of the composition of materials.

The portable XRF was very practical and valuable instrument not only for paper materials analysis, but also for analysis of pigments, fillers in the wood and etc.

Finally, in order to investigate the state of wooden support X-ray radiography was performed. Radiography has proven to be very useful for determination of hole distribution in the wood.

3. Results and Discussion

In this work some preliminary results are presented. Further discussion and conclusions will be presented in the future.

Black chalk and metalpoint were common drawing techniques in Renaissance Italy.^{3,4} To distinguish between these two methods, the drawing was examined with ordinary light, under magnification and the elemental composition was determined by XRF. The particular metal traces in drawing lines (areas) were not detected and there was no visible depressed line on paper surface which seemed to be without special preparation.⁵ According to the results of XRF analysis and microscopic examination the drawing media could be black chalk (composite of carbon and clay).

Visual examination of the drawing itself using a stereo microscope showed that the particulate deposit material on the surface was incorporated throughout the structure of the paper fibres. Attempts to remove it with a needle showed that they adhered strongly to the fibres. It was possible to distinguish elemental differences of the observed deposits by XRF. Figures 2 and 3 show different elemental contents in different greyish areas of drawings.

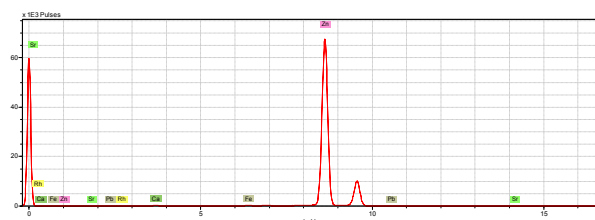


Figure 2: XRF spectrum of the whitish-grey deposit containing Zn (Zn-compound layer).

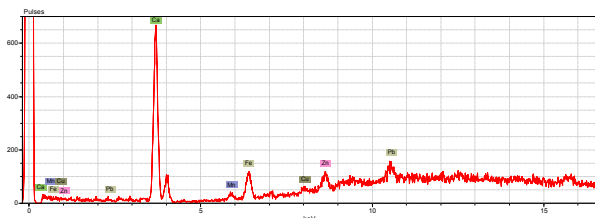


Figure 3: XRF spectrum of the whitish-grey deposit containing Ca (carbonate layer).

A common features associated to all greyish areas is that these areas fluoresce deep green light due to the presence of adhesives (proteins) when examined under long-wave UV. The areas of retouching on the miniature work under UV light appeared as dark areas.

X-radiograph of wooden support provided sufficient evidence of damage by insects. It also gave information on the size and number of the putty-filled holes which can be seen as white markings in Figure 4.

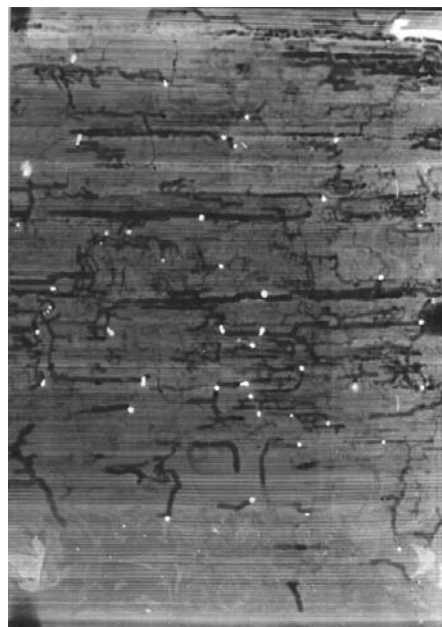


Figure 4: A detail of x-radiograph of the drawing support showing holes and connecting tunnels in wood support, suggesting that some of them were there before the drawing has been put on it. The visibility of the wood filling materials as white markings in the x-radiograph indicates a significant content of lead in them. The whitish areas of miniatures (left side of image) indicates a lead white-based pigments in paint layers.

FT-IR spectroscopy and XRF analysis showed that the fillers in wood consist of lead white and egg medium (Figure 5 and 6).

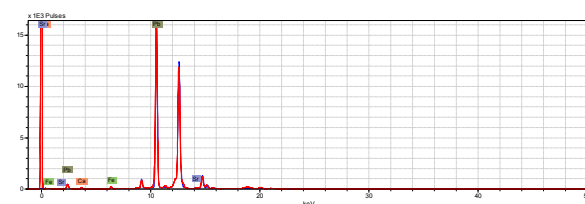


Figure 5: XRF spectrum of the white wooden putty containing Pb (basic carbonate lead white).

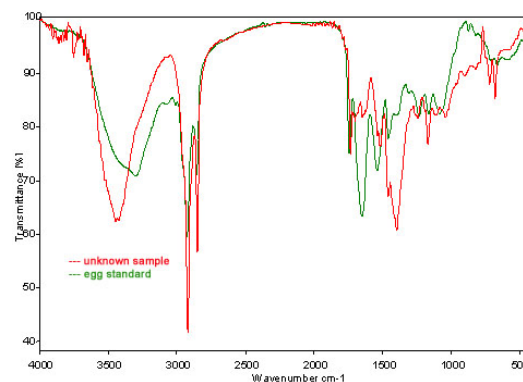


Figure 6: FT-IR spectrum of the wooden putty is compared with FT-IR spectrum of egg standard. The band at 1400 cm^{-1} is assumed to belong to carbonate.

Transition metals (Cu, Fe, Mn, Zn) were also detected in the paper substrate. Their presence could be due to possible metal migration out of the pigment layers and fillers. It has been proven that they have very important role in oxidative degradation of paper.⁶

4. Conclusions

The investigations provided the evidence of factors affecting the paper degradation (metal ions, migration of drawing/miniatures components, degradation products).

In order to determine the rate of degradation, further research is needed, especially on a micro-level.⁷ A lot of effort will go into improving paper stability.

5. Acknowledgements

Thanks to the colleagues from the National and University Library for their support and collaboration and M. Bošnjak and M. Klofutar from the Croatian Conservation Institute for technical assistance. Thanks also go to the all others who helped in discussions.

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ANALYSIS OF HISTORICAL PAPERS USING SEM/EDX

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1. Introduction

While Chinese and Arabic papermaking are famous in the world, nothing is known about Armenian papermaking which started in the 10th century AD. Until year the 1000 there were only ten manuscripts on paper known in Europe and four of them were Armenian. The differences in manufacture of Armenian paper have been discovered by studying the first Armenian manuscripts dated 981 and 989 AD and it was discovered that the paper was made in the city Ani, ancient capital of the Armenian kingdom.¹⁻³ In this city, also the first windmill was operated. Thus, Armenia was the third country in the world using paper for writing, after China and Arab countries. In the following centuries, paper was used mainly for production of manuscripts.

In this paper, SEM/EDX analysis of Armenian paper fragments of different periods are reported. Pyrolysis - gas chromatography - mass spectrometric studies of these samples and its written parts were performed.^{4,5} Using SEM/EDX technique we can also characterise samples in view of the composition of different parts having different morphology. The morphological structure of paper fibres can be investigated through the images collected by SEM (Scanning Electron Microscopy) while the elementary composition of the samples can be revealed by EDX (Energy Dispersive X-Ray Analysis) spectra. The variable pressure SEM technique proved to be particularly useful because it allows for a direct observation of paper and its chemical characterization without the need of surface coating and is therefore non-destructive.

2. Experimental

In this study, a Scanning Electron Microscopy LEO1450VP INCA300 model (SEM-EDX) equipped with an Energy Dispersive X-ray analyzer was used on the Whatman paper and on old (16th -19th century) paper samples. The elemental composition was carried out in an acceleration voltage of 20 keV, lifetime100s.

The analyzed papers were Whatman No. 1 (UK), i.e. pure cellulose, one sample of ancient paper dated 1567, partly with dark coloured ink, one dated 1641, one from the 16th century and another one from Venice dated 1885. The resolution of the instrument was 3.5 nm, the maximum magnification was 300000x.

3. Results and Discussion

As a model, Whatman paper made of pure cellulose and not subjected to any sizing procedure was used and the SEM image in Figure 1 shows large fibres and no degradation is observed.

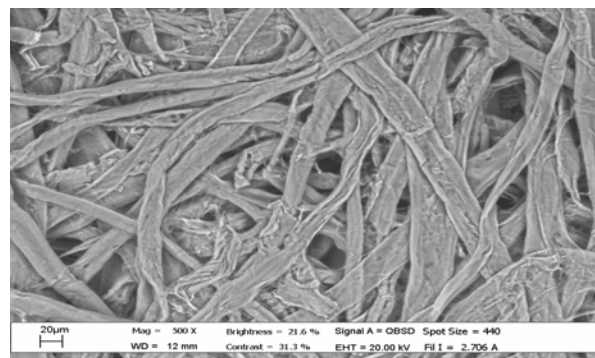


Figure 1: SEM image of Whatman paper.

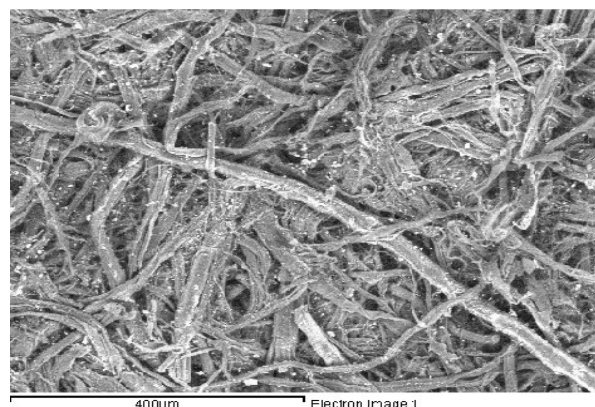


Figure 2: SEM image of paper dated 1567.

The fibres are homogeneous and seem to originate from rags, probably cotton. The fibre sizes are different and some seem to be broken. Some fibres exhibit encrustations which could be salt crystals. The presence of minerals in paper can often be the consequence of water used to produce it.

In Figure 3, the SEM image of the written part of the same paper, dated 1567, is shown. The fibres are covered in encrustations as in the previous image, but here they seem more compact, in the form of a matrix holding them together. It could be starch or gelatine, which were used as binders in inks. The lack of Fe and S, as evidenced by EDX analysis, excludes the possibility of an iron gall ink. The elemental composition reveals the presence of the same compounds in the unwritten part, apart from the presence of Mg.

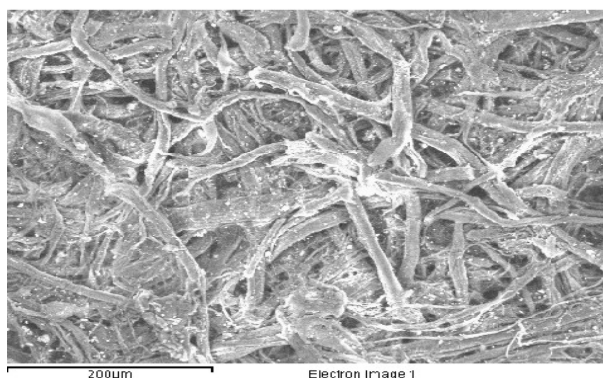


Figure 3: SEM image of a paper with ink dated 1567.

Figure 4 shows the SEM image of the paper from the 16th century. The light part of the image can be the consequence of the presence of sizing, which was thick. The EDX analyses showed the presence of Ba and S, as well as Al, Si and Ca.

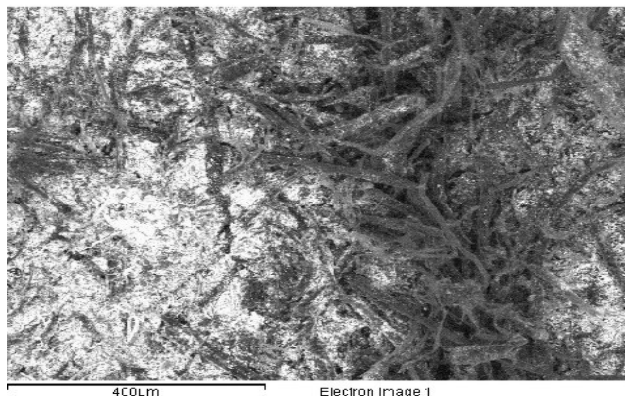


Figure 4: SEM analysis of the paper from the 16th century.

The last sample, of which the SEM image is shown in Figure 5, is the Venetian paper from the 19th century. The fibres are thin, and could be cotton or linen. The lighter part of the image could be the consequence of the presence of a particular element, probably Ca deriving from the sizing process.

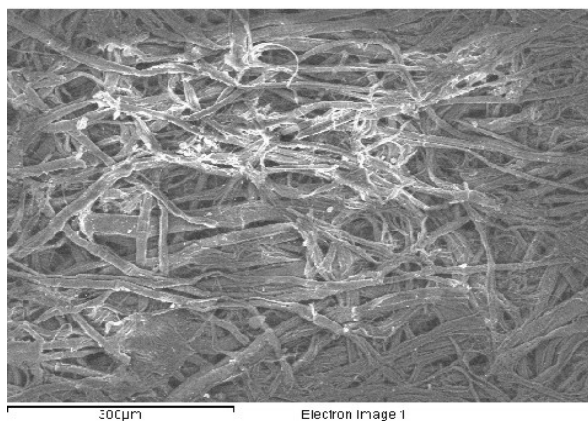


Figure 5: SEM analysis of the Venetian paper from the 19th century.

4. Conclusions

Observations using SEM/EDX technique showed that the samples had different composition and morphology and the presence of characteristic elements in papers and inks was revealed.

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POSTER PRESENTATIONS

PAPER STRENGTH AND ACIDITY OF MODEL COLLECTIONS

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1. Introduction

The strength of an information carrier plays the decisive role in the use of historical book collections in libraries and archives. There are many endogenous and exogenous factors influencing the strength of paper. Regarding the endogenous factors, we mean mainly the quality of material of which the paper was made and the technology of paper production. As for exogenous factors, acidic gas pollution, inadequate temperature, humidity in deposits, and irradiation with light influence paper strength negatively.¹

To avoid the loss of historic materials, it is necessary to remove acidity from paper, which represents the biggest threat. Considering the huge amounts of acidic materials (which have been produced for almost 150 years), technologies of mass deacidification are applied.² To put these processes into effect, all libraries or archives should analyse their collections - especially in view of the two fundamental factors indicating the risk to documents, i.e. acidity and strength.

2. Aim of the Work

- 1) Verify a screening method for measuring the strength of paper by applying the paper puncture tester® (ZT3P),^{3,4} to determine folding endurance using exact laboratory instrumentation; to find a relation that would enable us to convert puncture depth into folding endurance and vice versa.
- 2) Evaluate the influence of paper thickness on puncture depth ZT3P and determination of folding endurance.
- 3) Prepare a method for screening of paper strength and acidity with the aim to propose a system of categorizing objects into risk groups - RG.

3. Results

Paper endurance measured by ZT3P device was compared to folding endurance, and based on the correlation, risk groups⁵ were determined (Table 2). The SD values expressed as RSD for the measuring of folding endurance and the depth of puncture for individual paper thicknesses showed (Table 1), that the measurement of puncture depth provides more reproducible results (RSD from 10% to 12%) than the measurement of paper strength by means of folding endurance (RSD from 33% to 38%; for 0.155 mm thickness even 56%).

Table 1: Values of RSD and the range of uncertainty (\pm SD) for the determination of paper strength by ZT3P and folding endurance. RSD: relative standard deviation, SD: standard deviation.

Paper thickness (mm)	ZT3P		Folding endurance (number of double folds)	
	RSD	\pm SD	RSD	\pm SD
0.07	10	4.0	38	11
0.09	10	4.0	38	15
0.11	10	2.6	33	9.8
0.135	12	3.6	33	9.4
0.155	10	3.7	56	14

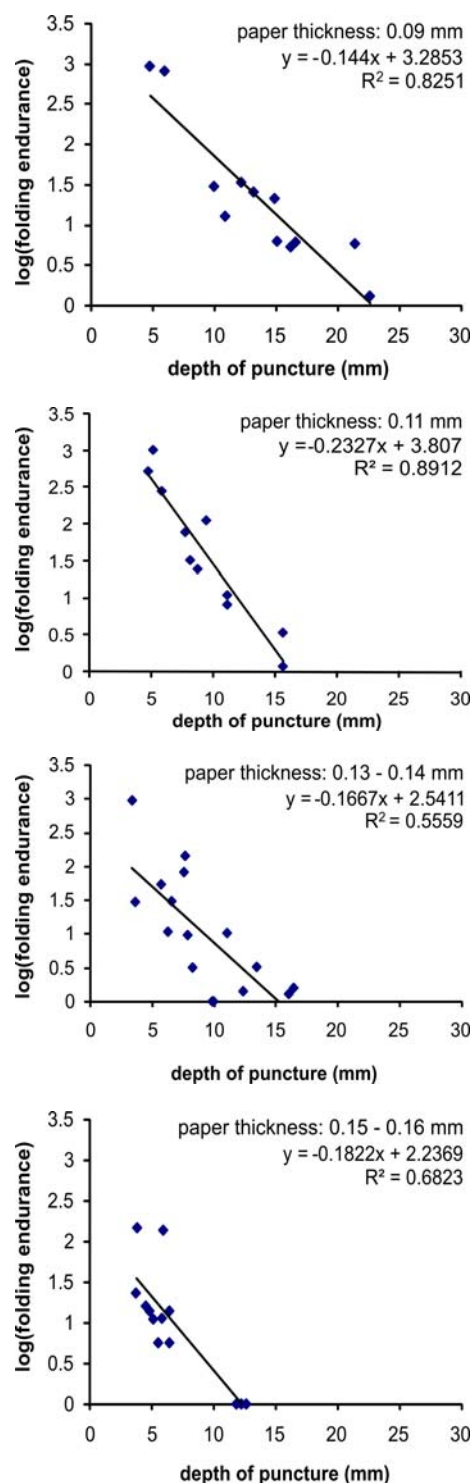


Figure 1: Relations between the double folds and the puncture depth for the paper thicknesses of 0.07 - 0.16 mm.

The relation between folding endurance and the ZT3P depth puncture is the same for all papers of the thickness between 0.07 and 0.16 mm. It is clear that the measurement of paper strength by ZT3P provides good results for not very firm papers, where the variance of values is considerably small. It is important to point out, that the discrimination ability of ZT3P is quite small for firm papers, for which even the natural variation of strength is high.

Table 2: Paper strength expressed in puncture depth and the corresponding classification into risk groups (RG).

Risk group	RG - I	RG - II	RG - III	RG - IV	RG - V
Folding endurance (DF)	0-1	2 - 5	6 - 10	11 - 30	31 - >80
Thickness of paper (mm)	Depth of puncture (mm)				
0.06	>27.0	19.8	17.1	14.4	<6.4
0.07	>25.4	19.3	17.1	15.1	<8.7
0.08	>23.7	18.5	16.5	15	<9.7
0.09	>22.0	17.3	15.4	14.3	<9.8
0.1	>20.2	15.8	14.1	13.2	<9.1
0.11	>18.4	14.2	12.6	11.7	<7.9
0.12	>16.8	12.7	11.1	10.2	<6.5
0.13	>15.3	11.2	9.6	8.7	<4.9
0.14	>13.9	9.8	8.2	7.2	<3.1
0.15	>12.8	8.8	7.2	6.1	<2.0
0.16	>12.2	8.5	6.7	5.8	<1.8
0.17	>11.6	8.2	6.3	5.5	<1.4
0.18	>11.8	8.1	7.2	6.7	<2.9

4. Conclusions

The relation between folding endurance and puncture depth can be described by an exponential equation, it is therefore useful to present it on a semi-logarithmic scale graphically. The method provides more reproducible results for analyses of less firm papers than for more firm papers regardless of their thickness (Figure 1). ZT3P puncture testing is therefore especially useful to discriminate the less firm papers, which is also the purpose of our work.

Based on determination of puncture depth, we also propose the definition of risk categories (RG).

By combining the RG categories and creating technological groups it is possible to define conditions for selecting documents (Table 2) for specific conservation processes.

5. Acknowledgement

The authors express their thanks to the Ministry of Education of the Slovak Republic - project KNIHA.SK 661/2003.

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QUANTATIVE AND QUALITATIVE CHANGES OF DEACIDIFICATION SOLUTION AND THEIR INFLUENCE ON THE NESCHEN "C-900" PROCESS

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1. Introduction

Acidity of paper documents is a very important issue for libraries and archives. It is considered that there are several reasons for accumulation of acids in paper.

Nowadays, there are several ways for tackling with this problem,¹ one of them is using the a machine produced by Neschen (Germany). In 2003, the Russian State Library bought this equipment for carrying out mass deacidification of paper documents, mainly newspapers.

In this paper, we discuss two main problems which we had to study during our work. The first one is evaluation of effectiveness of the method and the second one is connected with the quality of the deacidification liquid and the criteria for its use.

2. Materials and Methods

To evaluate the deacidification effect the following magazines and newspapers have been used:

- Sample 1 - German magazine printed in 1878, groundwood/cellulose - 60/40
- Sample 2 - the newspaper "Komsomolskya Pravda" printed in 1975, groundwood /cellulose - 90/10
- Sample 3 - German magazine printed in 1919, groundwood/cellulose - 30/70
- Sample 4 - covers of magazine "Niva" printed in 1915, groundwood/cellulose - 50/50

The composition of paper fibres was established using micro-chemical analysis with Herzberg reagent.

To evaluate the influence of changes in composition of the deacidification solution on paper we used paper samples with groundwood/cellulose - 60 / 40% and initial pH of 4.8 and deacidified them by liquid with pH = 7.4, 8.2 and 8.8 values. To evaluate the efficiency of the process the following parameters were measured: pH and mechanical properties. We controlled surface pH and pH of cold extracts according to the national standard (GOST 12523-77) before and after treatment, before and after artificial ageing in comparison with control samples. Artificial ageing was carried out according to the standard ISO-5630/3 (1986a). The samples were exposed to ageing for 72 h, 144 h and 12 and 24 days at 80 °C and 65% RH. This standard was chosen taking into account the properties of paper covered with magnesium

carbonate and the film of methylcellulose. Surface pH was measured with the pH meter Skincheck (Hanna Instrument), and the pH of cold extracts was determined using the pH meter Expert-001 (Ekonic-Russia).

The mechanical properties (tear resistance and tensile strength) of samples were measured using the instrument Zwick (Germany) at a deformation rate of 1.27 cm/min. Beforehand, the test samples were conditioned for 1 h at 22 °C and 60% RH. The tests were carried out in two directions.

The elemental analyses of the solution were carried out using ICP-MS method (mass-spectroscopy with inductively coupled plasma).

3. Results and Discussion

3.1. Evaluation of the Efficiency of Deacidification Process

Paper samples 1 - 4 were treated using the C-900 machine with a fresh deacidification liquid of pH = 7.2. As it can be seen (Table 1), the surface pH increased after deacidification. After ageing this parameter decreased for all samples but less in the treated ones than in the control sample. Bansa² stressed that in papers with higher initial acidity, the pH decrease after deacidification and subsequent aging is higher than for papers with a lower initial acidity. The same phenomenon was observed in our case. pH of the treated samples is higher than that of untreated even after ageing.

Table 1: Paper pH after deacidification and ageing.

	pH _{surface}	Samples			
		1878 sample 1	1975 sample 2	1919 sample 3	1915 sample 4
1	Control	4.97	5.85	6.3	5.47
2	Treated	8.04	7.89	7.9	8.08
After aging (72 h)					
3	Control	4.56	4.62	6.03	4.17
4	Treated	7.01	7.62	7.55	7.04

3.2 Mechanical Properties.

After deacidification, there are practically no changes in tear resistance of paper in both directions. For Sample 1 the increase of up to 12% was observed, in other cases there was a small decrease observed: from 2% to 21%. The last fact was observed also by Bansa² and it is, apparently, linked with extraction of water-soluble paper components during the process. The tensile strength increased for all samples, regardless of the direction. The changes in mechanical properties after deacidification depend on the composition and properties of the paper before treatment.

After artificial ageing, the tear resistance and tensile strength were usually higher for deacidified samples, with some exceptions in the case of sample 3 (tear resistance and tensile strength in the machine direction) and sample 4 (tear resistance in the cross direction).

During ageing, tear resistance for treated samples increased, and decreased in the case of control samples.

This phenomenon is usually observed³ - cellulose degradation takes place faster in control samples than in the treated samples, where the degradation process has been inhibited.

3.3 Quality Assessment of the Deacidification Liquid

During the work the composition of the deacidification liquid changes: it is enriched with the substances, which are washed out from documents, the colour changes from practically colourless to brown and the pH increases to 9.0.

The elemental analysis of this liquid determined by ICP-MS shows that it contains a high amount of heavy metals. The following relative increases were observed: Fe 90x, Ca 20x, Mn 10x, Cu 1.5x, Pb 2x, Zn 5x, Cr 1.75x, Al 2x.

One of the reasons for the observed pH change³ is also the transformation of the soluble magnesium bicarbonate to magnesium carbonate. In an old solution, the amount of soluble bicarbonate decreases, according to our results. For example, in a fresh solution with pH 7.2 the content of magnesium bicarbonate is 14.6 g/l, whereas in a used one with pH = 8.2, the content is only 6.4 g/l. The alkaline reserve measured according to GOST P (national standard) 10716-200 is the highest for sample treated with fresh liquid. Thus, the sample after treatment with a fresh liquid has an alkaline reserve of 2%. For the sample treated with liquid pH = 8.2 it less: 0.7% and for sample treated with liquid pH = 8.8 it decreases to 0.6%. In the last case, deacidification is only limited to the surface and not so effective. During accelerated ageing of the model documents deacidified using the liquid with different pH, it has become evident that the best result is obtained with a fresh liquid of pH = 7.2 (Figure 1). The pH of such samples is stable during accelerated ageing. The experimental data show that the pH of samples deacidified with liquid of pH 8.8, decreases faster and after 24 days of ageing the values of surface pH and the pH of cold extracts are the lowest, similar to those of the untreated sample. The pH of 8.2 of the treatment solution was taken as the boundary criterion for usage. If the pH increases beyond 8.2 the treatment solution should be renewed.

The periodic addition of CO₂ (gas) into the solution to restore the initial pH (7.2) usually takes 8 h and should be performed once per month. However, after the addition of CO₂ (gas), the liquid keeps its pH value for a much shorter time than a fresh one. The treatment solution needs to be entirely replaced 3 times per year.

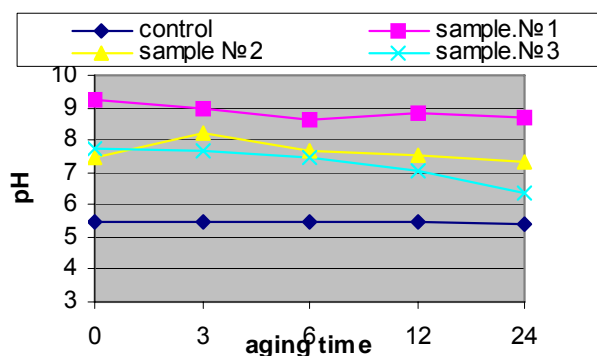


Figure 1: Changes in the pH of cold extracts of samples during ageing at 80 °C, 60% RH: Sample 1, treated with a solution of pH = 7.2, sample 2, treated with a solution of pH = 8.2, sample 3, treated with a solution of pH = 8.8.

4. Conclusions

The results indicate the following:

The deacidification treatment has a positive effect on paper: the tensile strength is increased, and pH increases up to 50%.

If the pH of the treatment solution increases above 8.2, the solution needs to be regenerated.

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STUDY OF ARTIFICIALLY AGED EXTRA-STRONG PAPER: COMPARISON OF TRENDS OBTAINED FROM KINETIC PROCESSING OF THERMAL ANALYTICAL CURVES

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It is a well-known fact that as a paper specimen ages the cellulose contained in it is gradually oxidized. We therefore investigated the possibility of constructing curves as a function of the ageing of cellulose, paper or wood items. In practice, this is a continuation of research we have carried out in recent years aimed at identifying the links between the breakdown of the cellulose and the physico-chemical parameters that allow it to be highlighted. For this purpose we used different techniques: enzymatic, electrochemical and thermal analytical.¹⁻³ The present communication illustrates the latest results obtained in this direction using thermogravimetric (TG and DTG, Figure 1) and differential scanning calorimetric (DSC) techniques, applied to the study of extra-strong (photocopier paper for office use) paper samples subjected to artificial ageing for various periods of time. In our more recent research on the subject,¹ among the various indicators tested, activation energy (E_a) values appeared the most promising for the purpose of constructing these curves. In the present study a comparison was made between the results obtained by application of three different methods for calculating the E_a of the oxidative thermal degradation of the cellulose contained in the paper specimens tested. In particular, three non-isothermal methods were applied: Arrhenius differential,⁴ Satava's integral⁵ and lastly Wyden and Widmann's method⁶ (Table 1).

Table 1: Algorithms utilized to calculate E_a : a) Arrhenius method; b) Satava method; c) Widen and Widmann method.

Method	Equation
a) Arrhenius	$\log da/dt = A e^{(-E_a/RT)} f(\alpha)$
b) Satava	$[g(\alpha)] = -0.4567 E_a / RT - 3.15 + \log(AE/R\beta)$
c) Widen and Widmann	$da/dt = e^{(-E_a/RT)} (1-\alpha)^n$

In practice, a comparison was made of the curve trends obtained by plotting the E_a values calculated using each of these methods against the duration of the sample ageing process carried out by means of photoirradiation in a weatherometer in the following experimental conditions: 58% RH, $T = 45^\circ\text{C}$, 750 h; spectral irradiance

$E\lambda = 0.6 \text{ W/m}^2/\text{nm}$, $\lambda = 310 \text{ nm}$. The trends obtained were found to be not completely monotonic. However, a reasonable correlation was found between the trends obtained using the Arrhenius and Satava methods, and partly also that of Widen and Widman. Some difficulty was found above all in the case of non aged paper the representative point of which was almost always anomalous in the trends obtained. It is still not completely clear to what extent this depends on the type of mathematical processing typical of the method used and how much it depends on the real differences in the physico-chemical characteristics of the cellulose in the sample of non aged paper versus the aged samples.

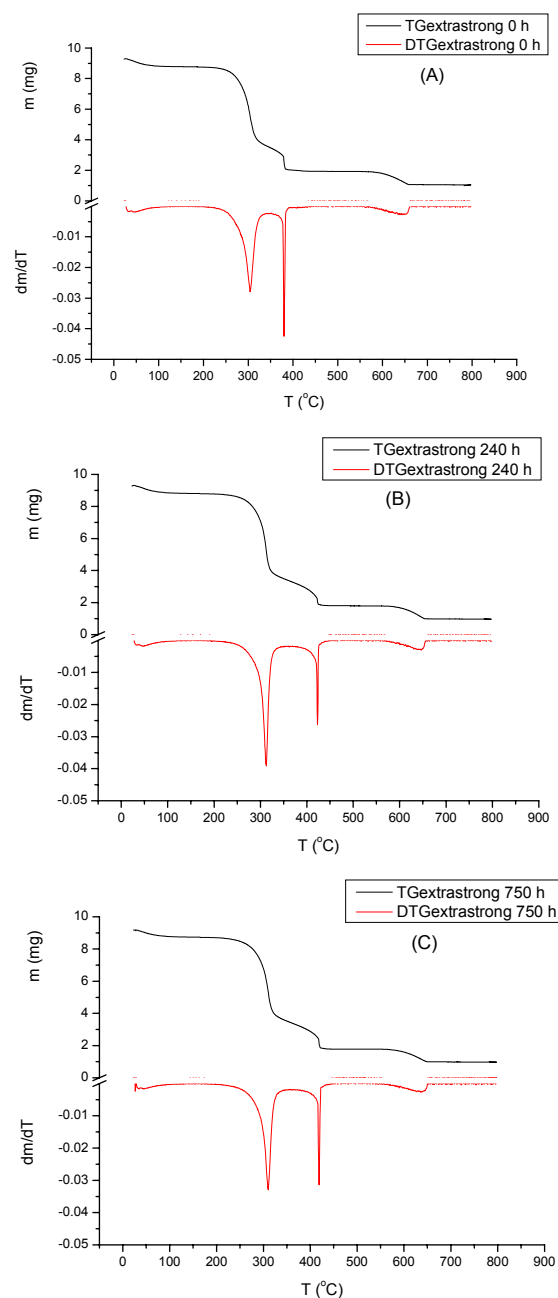


Figure 1: Typical TG and DTG curves of extra-strong paper: ageing time: A) 0 h; B) 240 h; C) 750 h.

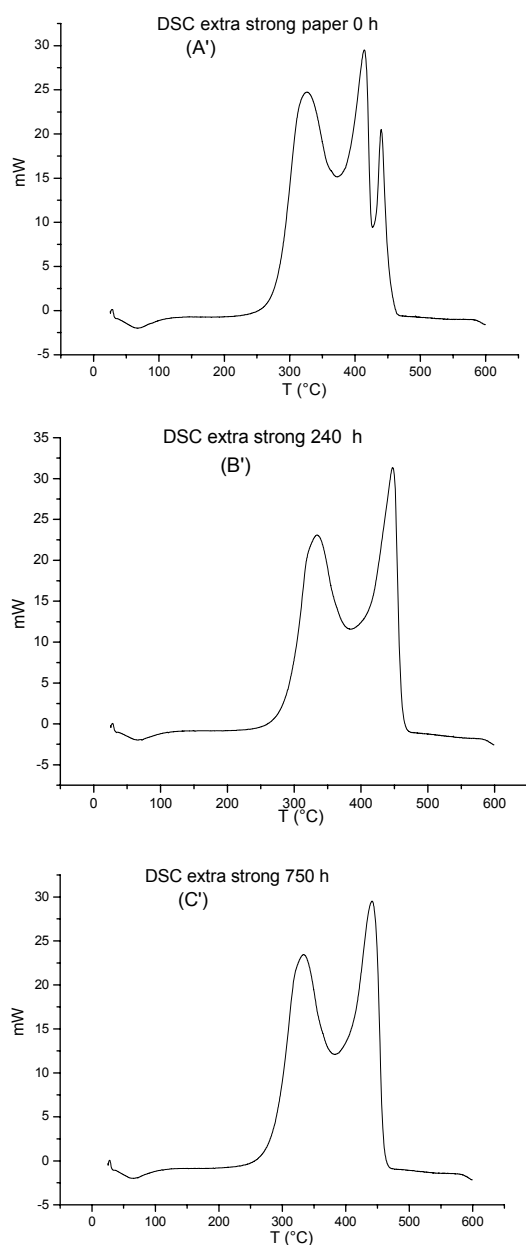


Figure 2: Typical DSC curves of extra-strong paper: ageing time: A') 0 h; B') 240 h; C') 750 h.

The data processes are essentially thermogravimetric ones although it was endeavoured for the first time to use the enthalpy values obtained using the DSC technique (Figure 2). The results are of course still preliminary as regards the curves obtained, based as they are on data obtained using these thermal analytical methods, and still do not represent a completely valid model that can lead to the construction of true archeometric curves. The results are nevertheless encouraging and are a stimulus for further research in this direction.

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DETERMINATION OF GELATINE IN HISTORIC RAG PAPERS BASED ON NIR/CHEMOMETRICS

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1. Introduction

Papers of different composition are differently sensitive to environmental parameters and it is well known that since the advent of modern papermaking the quality of paper decreased considerably and many paper-based objects from this era are now in an advanced state of deterioration. In order to develop a deeper understanding of the ageing behaviour of early European papers, new tools and techniques are still needed considering that such materials are not available in great quantity for testing and are often very inhomogeneous.

Gelatine was a common ingredient in papers from the 15th to 19th century, and while primarily used as a sizing agent it can enhance paper mechanical properties significantly. It was shown that there is a significant correlation between the condition of historic papers and the content of gelatine sizing.¹

2. Experimental

Near-infrared reflectance spectra were recorded using a LabSpec 5000 spectrometer (Analytical Spectral Devices, USA, Figure 1). The spectrometer was fitted with a Source Probe MugLite that features a tungsten quartz halogen light source with built-in DC current stabilizer circuitry. NIR spectra were captured over the range 350 - 2500 nm, using 50 scans. Each sample was analysed twice in duplicate and spectra for the duplicate runs were averaged.

The procedure of gelatine determination consisted of extraction and hydrolysis to obtain free amino acids and their subsequent liquid chromatographic determination using an Agilent 1100 Series HPLC system. Derivatisation of the obtained amino acids was performed by reacting with

9-fluorenylmethylchloroformate (FMOC). Derivates formed were separated at 40 °C on a Zorbax Eclipse AAA column (4.6 × 150 mm, 5 µm) and detected at 262 nm. Gradient elution was required to separate the FMOC derivates.



Figure 1: The portable NIR instrument used in this study.

3. Results and Discussion

We assembled a set of 96 papers dating between 17th and 19th century. The samples for analysis were taken from margins or areas without print, ink or discolorations on either side in order not to compromise the quality of analyses.

We have investigated and tested a combination of advanced chemometric methods, such as full-spectrum PLS (partial least squares) and genetic algorithm, to develop predictive models that enable us to provide high quality quantitative results when analyzing historic papers.² The model was calibrated against a reference chromatographic method (Figure 2).

The genetic algorithm (GA)^{3,4} evolves a population of n candidate solutions using operators inspired by natural evolution and genetics. In the GA implementation used in this study, each candidate solution is represented with a subset of frequencies of the size k where k is provided.

The initial population is generated at random according to the uniform distribution over all subsets of size k . Each iteration starts by creating a new population of subsets by applying crossover and mutation operators to the current population of subsets. Once the new solutions have been created, they are evaluated and the best n solutions from the previous population and a population of new solutions are selected to form the population in the next iteration.

The procedure is repeated (starting with crossover and mutation) unless user-defined termination criteria are met. For example, the run may be terminated when a maximum number of iterations has been reached.

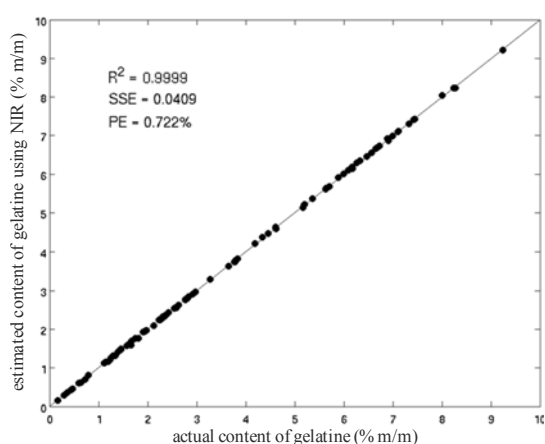


Figure 2: Ten-fold cross-validation was used to evaluate the quality of each subset in the initial population. Specifically, first the spectra were divided into 10 approximately equally sized groups where each group corresponded to a range of values of the target quantity (gelatine content). Then, the specific subset of frequencies was evaluated using any selection of 9 groups for fitting a linear least-squares model using only the selected frequencies on input and tested on the remaining group of data points. In this manner, the model was tested on different data than those used for learning. The average error from the 10 tests was then computed and the quality of the solution is estimated as the negative value of this error.

Using this state-of-the-art chemometric approach, we developed a new method for determination of gelatine in historical rag papers.

4. Acknowledgement

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NON-DESTRUCTIVE SURVEY OF BRATISLAVA ANTIPHONARIES COLLECTION - BRATISLAVA ANTIPHONARY II

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1. Introduction

The UNESCO programme Memory of the World, officially accepted and announced in 1993, is a very timely expression of a responsibility for the condition, preservation, reconstruction, scholarly treatment and refined humanistic utilization of significant monuments of the documentary heritage of the world. The digitization of valuable originals has become a unique method of virtually eliminating the ageing process. In this way their grand, an unknown world is opened to both specialists and laymen. It is a way to discover and appreciate the values humanity has produced. Making accessible the most significant Slovak monuments as a natural component of the cultural and documentary heritage of Europe and the world within the framework of the UNESCO programme Memory of the World, is a very necessary task. Historical, political as well as cultural developments that occurred in the geographical area of today's Slovakia were characterised by very diverse influences and interests, reflected in their penetration and specific transformations. In the field of book culture monuments and art, it is possible to follow already from the

early middle ages the dominant influence of Latin culture, adopted after the decline of Great Moravia Empire, primarily from western European centres of culture and learning.

Historical library of the Bratislava chapter represents a unique phenomenon in the context of written cultural heritage of Slovakia by its extent (more than 3000 volumes), antiquity (books from the 12th to 19th century) as well as by the content of period secular and religious literature. At the same time this library contains the most extensive, historically and artistically the most precious collection of medieval manuscripts in Slovakia. Numerous illuminations in antiphonaries of Bratislava serve as the basic information source to knowledge of development of medieval book illumination in the region of the Central Europe. A series of five antiphonaries "Illuminated codices of the Bratislava Chapter Library" was included into the UNESCO Memory of the World Register in 1997. Their digitisation and publishing on CD-ROMs was completed in 2007.

The publication of the first of these, the Bratislava Antiphonary II (also known as the Han Codex) for the first time, in a digital form on compact disk (CD-ROM), presents one of the most important monuments of book culture of Mediaeval Bratislava from the 15th century. The codex was insensitively divided into three parts during the inter-war period. Today these parts are kept in the Slovak National Archives, the City Archives Bratislava, and the City Museum Bratislava which keeps some illumination fragments. These fragments were brutally cut out from the original and stolen in the past; later on they were bought by the City Museum Bratislava. The publication on CD ROM virtually put together all parts of this Antiphonary and provides view to the complete original two-volume work. Despite their uniqueness no scientific and experimental search of antiphonaries from material and preservation point of view was made up to nowadays.

This work provides for the first time some results of XRF analysis and ink pH measurements of fragments and original volumes as well as their comparison from the viewpoint of dye and ink composition.

2. Experimental

X-ray fluorescence (XRF) analysis is a non-destructive technique widely used in the study of works of art. It provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. It is non-destructive and reliable, requires no or very little sample preparation and is suitable for solid, liquid and powdered samples. It can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level, depending on the quality and performance efficiency of the apparatus.

The measurements were carried out on the apparatus at the Department of dosimetry and application of ionizing radiation, Faculty of Nuclear Sciences and Physical

Engineering, Czech Technical University, Prague.

The apparatus consists of a small x-ray source and portable semi-conductor detector cooled by electric current.

For locating the analysed area about 1 mm² a pair of light diodes is used. The generator supplies a current of 100 µA and high voltage of 30 kV.

The incident X-ray radiation excites the characteristic radiation of the elements in the sample material providing the information about element composition. Each measurement lasted for 3 min. The present elements can be identified in the resulting spectrum expressing dependency of registered photons of characteristic radiation on their energy.

For pH measurements of iron-gall inks, non-bleeding pH indicator strips Merck (range 4.0 - 7.0), pH surface combination microelectrode MI-415-2, Microelectrodes, INC. USA and Jenway pH-meter, model 3510 (UK) were used.

3. Results and Discussion

Pigments of illuminations – an example (small fragment A49-MMB) is given in Figure 1.



Figure 1: XRF examination of the fragment A49-MMB.

The presence of Au in golden illumination is clearly confirmed; the presence of Fe points to iron-gall ink underneath. Calcium (Ca) is a component from parchment support (Figure 2, above).

The dominant element of blue colour is copper Cu; other elements i.e. Ca, Fe, Pb are present in lower amounts. The blue pigment is the most probably azurite (Figure 2, middle).

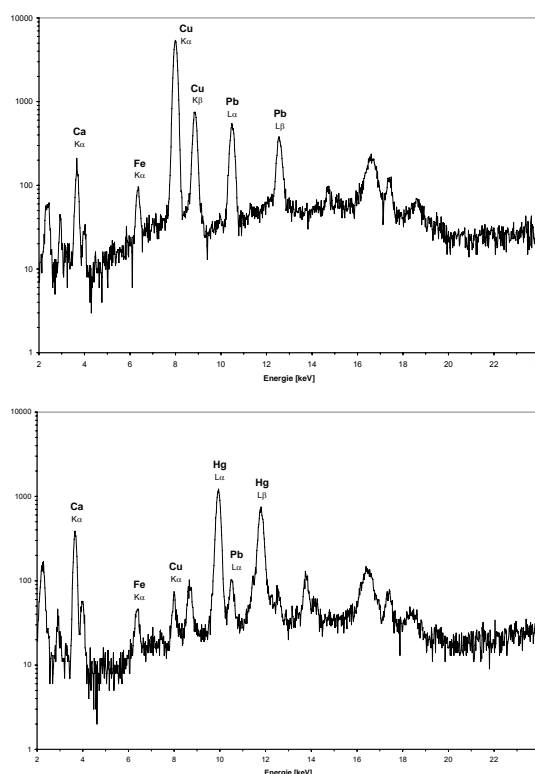
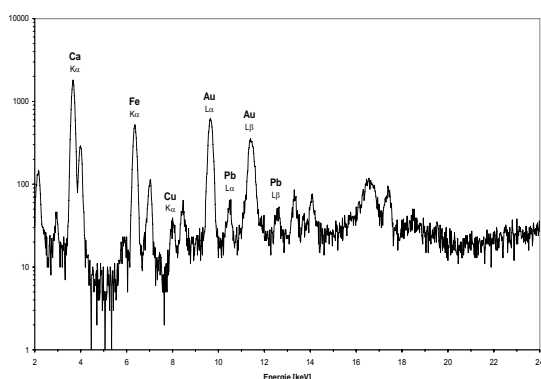


Figure 2: XRF spectra of pigments on the fragment A49-MMB.

High peaks for Hg point to use of vermillion (Figure 2, bottom).

4. Conclusion

This is the first attempt to analyse illuminations, writing inks and materials of the Bratislava Antiphonaries collection in order to gain, evaluate and provide information about their composition and possible damage influence on parchment support layer and illuminations themselves by XRF spectroscopy.

Some results on pigment layer composition of illuminations and writing materials are provided and several pigments have been clearly identified.

The analysis confirmed the presence of iron-gall inks from light brown through dark brown to black the pH in the range of 5.0 - 7.0.

Inks are in an excellent condition despite the fact that most of them contain rather high concentrations of Cu beside Fe.

More detail evaluation works are under preparation.

5. Acknowledgement

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OLD MASS DEACIDIFICATION PROCESSES. WERE THEY GOOD?

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The deterioration of paper due to acid hydrolysis is a major global concern. Worldwide there are different procedures designed to prevent acid hydrolysis. The methods are based on the chemical principle of acid neutralisation by reacting with alkaline compounds. However, this can vary in complexity, in both reaction and process. This review attempts to give a brief description about different procedures of deacidification which have been terminated and are even forgotten.

1. Introduction

It is well known that the main component of paper, cellulose fibres, was not originally designed for having a great durability.¹ Nevertheless, we would like to have paper based objects as permanent as possible. Permanence is mainly influenced by two factors - the impurities and the acidic species accelerating the deterioration of paper. Acidic species can be present due to the components used during the paper making process and/or due to air pollutants.² The latter was for example already mentioned by Wiesner in 1887.³

One simple solution to prevent paper against acids is to neutralize them acids by a simple chemical reaction: "an acid and an alkali results in a salt". Chemists were trying to solve this simple question by developing sometimes complex chemicals and/or processes.⁴⁻¹⁰

This review is based mainly on gray literature we could discover (reports, thesis work etc.) and the authors are aware that more literature on deacidification is available at (inter)national journals and probably even more in the non-published literature.

2. Some Forgotten Deacidification Treatments

2.1. Diethyl Zinc Process

This can be seen as the most promising and the most dangerous process ever. It was based on the volatile DiEthylZinc which was transferred chemically into Zinc Oxide (ZnO) in the presence of residual water and the acidic species present in the fibres. The serious first attempt for paper deacidification on a large scale was done by Akzo (later Akzo Nobel) under the supervision of the Library of Congress (LOC). It is the most complicated process in the deacidification world. The first research leading to the Akzo DEZ process was done by LOC.¹¹ The pH was between 7.2 - 7.3, which can be seen as not too alkaline for possible side effects. Furthermore, the alkaline

reserve was between 1.5 - 2.0 % ZnO. However, this process had some side reaction like ethylene can polymerize, and ethylene oxide or some alcohol compounds can be formed.¹² Furthermore, it was found that due to manmade-mistakes papers could show serious so called Newton rings or be chemically "burned".¹³ Therefore, a lot of research has been undertaken to optimize this process. For example Het Nationaal Archief in The Netherlands put an enormous amount of effort into the optimization,¹⁴⁻¹⁶ however the process was finally discarded.

2.2 Wei T'o Process

This is a liquid-phase mass deacidification process using Methoxy Magnesium Methyl Carbonate (MMMC) which was applied on paper using methanol and Chloro-Fluoro Compounds (CFC). The process has a variant called the Sablé process, developed by Flieder from CRCDG (Paris, France).¹³ The Sablé process developed further, while the Wei T'o process remains as it was conceived. After the treatment the pH of paper turns to approximately 8.5 - 9.5 with an alkaline reserve 0.7 to 0.8% magnesium carbonate. Treated books have an odour of freshly ironed cloths. In another report⁶ it was shown that the pH can be very high, 10.3. A higher folding strength after accelerated aging was found. A side reaction of MMMC leads to magnesium sulphide hydrates which can be mechanically degrading. The positive point for this deacidification is that the books were completely deacidified even in the gutters.¹⁷ However, cockling, yellowing, white residue, discolourations were found as well as up to 30% of treated books were not deacidified.⁷ In 1995 a new solvent was found [10], which was a hydrochloro-fluoro compound, yet still a CFC and the use of CFC was banned in 2000. Therefore, in 1996, the Wei T'o mass deacidification process in Canada reverted to its original 1970s procedure.⁴ This did show potential, but after reports¹⁸ on the weakening of papers after treatment it was not used anymore.

2.3 FMC

The FMC or FMC/LITHCO process was initially developed by the Lithium Corporation of America. The application of organometal components in Freon 113 was initially successful.^{5,19} Here, the reactive component was MG-3 (carbonated magnesium dibutoxy triethylene glycolate) which was later substituted with magnesium buthyl glycolate in heptane. Research showed that using the old composition the paper was deacidified well, however papers often had a curious smell.¹³

2.4 Paper Strengthening Process

The method consists of impregnating paper with a liquid mixture of acrylic and methacrylic monomers which are polymerised using low intensity gamma rays. This process is also known as the Graft-copolymerization process.²⁰ The end result is a paper/polymer composite in which some of the polymer is chemically bound to cellulose. The process has been modified to neutralize the acid in paper.

Testing showed that the strength increases up to 5 - 10 times for paper containing 15 - 20 percent by weight of polymer deposited on them.

2.5 Battelle Process

This process is actually not a forgotten one, as it developed to a successful process now known as the PaperSave process applied both in Switzerland and in Germany.

In 1987 the Deutsche Bibliothek instructed Battelle Ingenieurstechnik GmbH to invent a superior deacidification method. Beforehand, the Battelle process was a four stage process using Magnesium/Titanium carbonated ethoxides in alcohol with Freon134a as a co-solvent. But due to the environmental effect of freons the co solvent was needed to change. The first research in operation²¹ was done by the Swiss National Library in 1994; the solvent was changed by HMDO putting freons aside. It also shows some side effects like a residue of minerals (silicon), alcohol odour and burn stains.²² The Battelle process was privatised by ZFB in the year 1998 and from then it is known as the Papersave process. In 2000, Papersave was tested.²³ In the research done by CNC,²⁴ the homogeneity was not satisfying. The concentration of active compounds of the outside was twice as high as the inside. The latest research showed serious improvements of this process.²³

2.6 Polymer Electrolyte and the Electrolytic Conductance Method

This is the first method of removing acid from paper non-aqueously by ion conducting polymer.²⁵ Polyethylene oxide was chosen to be used on each paper sample for this experiment. Polyethylene oxide is known as a polymer electrolyte. The ion conductivity influences mobility of the charge carrier such as the molecular weight of the polymer, the concentration and ionic size of the added salt.

PEO solvent is strongly attracted to cations due to the strong association with oxygen atoms in the polymer chain. The maximum raise of pH was from 4.0 to 4.9. It is said that the pH can be raised to raise the mobility of the electrons, by raising the moisture level or increase the treatment time. The electrolytic conductance method utilizes a current voltage and is a non-destructive technique. However this system never became commercially available.

3. Discussion and Conclusion

It can be concluded that most of the developed deacidification processes were successful in neutralisation of acids. However, only neutralising is not enough, as the components should be environmentally friendly (no use of CFC) and not to complex (DEZ process). For simple processes less can go wrong including damage to the materials to be deacidified. The ideas behind the application of organometal components are chemically sound, however the application of solvents may results in unwanted side effects, such as odour formation.

During the European STEP project on Paper Ageing the evaluation of mass deacidification processes was included and the research group concluded in 1994 that all the investigated processes (DEZ, FMC, Sablé) fulfil the requirement of acidic paper deacidification. Minor negative side effects could be solved by optimizing the process parameters. It is a pity that most of these processes stopped for commercial reasons with the exception of the Graft-copolymerization process, which really failed.

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STABILITY OF ARYLMETHANE DYES ON PAPERS DEACIDIFIED BY THE BOOKSAVER PROCESS

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1. Introduction

A big amount of materials produced in the last 130 years on groundwood containing acidic papers have suffered a continuous degradation process which leads to a total loss of printed or written information. The reason for this is the instability of paper substrate and the low chemical and light stability of dyes which represent the main component of modern inks. Neutralization appears to be the most proper conservation method for such objects, with simultaneous formation of a sufficient alkaline reserve. An increase of pH of the paper substrate extends the lifetime but can damage written records mainly in unsuitable climatic conditions in a repository.¹⁻³

The aim of this study was to investigate the influence of relative humidity and pH of paper substrate on dyes. Non-aqueous deacidification was used hence no fixation was necessary.

2. Experimental

In this work, acidic, groundwood containing paper with no fillers, sizes or optical brighteners made in Slavošovské papierne was used. A part of samples was prepared on original (acidic) paper and another part on neutralized paper deacidified by Booksaver PAL method in Preservation Academy in Leipzig. The initial properties and properties after deacidification process are listed in Table 2. Samples of size 5 × 5 cm were prepared from non-modified acidic paper and also from deacidified paper substrate and were treated with several solutions of dyes.

Several dyes for treatment were prepared: Acid Green and Basic Red - 0.1% solutions in ethanol and Methylene Blue - 0.2% solution in ethanol and water (1:1). Papers were treated with 1 ml of the prepared dye solutions and dried in air.

The prepared samples were exposed to accelerated ageing in the climatic chamber SANYO Gallenkamp PLC (UK) at 80 °C and 3 different values of RH: 65%, 50% and 40% for 0, 1, 3, 7, 10, 18 and 30 days.

Non-aqueous deacidification (CSC) Book Saver is based on carbonated magnesium propylate dissolved in *n*-propanol as the deacidification agent and on 1,1,1,2,3,3,3-heptafluoropropane (HFC 227) as the carrier. It can be used for both mass deacidification and for individual objects and is supplied as a spray.

Table 1: Initial properties and properties after deacidification of paper.

Property	Acidic paper	Paper after deacidification
Brightness (%)	76.40	74.37
Opacity (%)	96.70	97.12
CIE L*	91.14	94.80
CIE a*	-1.07	-0.70
CIE b*	3.41	2.04
pH	4.40	6.94
Alkaline reserve (%)	-	0.67

3. Results and Discussion

Figure 1a shows that for Acid Green 16 on acidic paper the lowest colour difference during ageing was in the case of conditions of RH 50% (6.46), 40% (6.87) however for RH 65% it was 15.48. This can be explained by the change in *a** (12.97) towards less negative, i.e. from green to grey. Figure 1b represents results on Acid Green 16 on neutralized paper and the least noticeable ΔE^* colour difference was observed at 50% RH (6.22) while for other 2 ageing types the final colour difference value was 2 times higher.

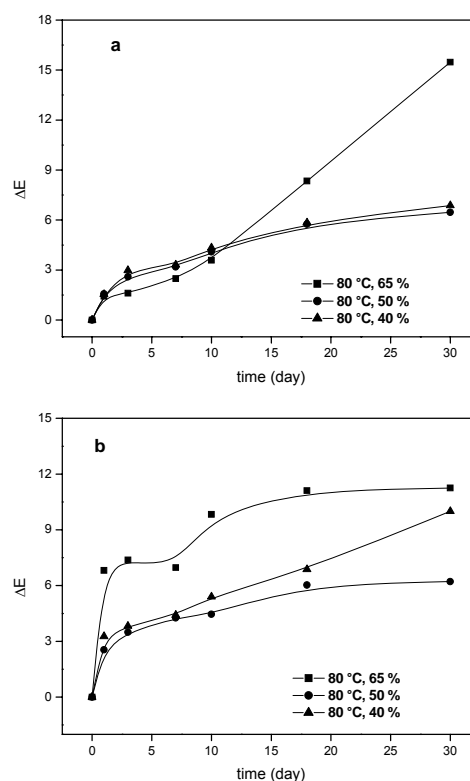


Figure 1: Comparison of ΔE^* of Acid Green dye during ageing at three different conditions, a - on acidic paper, b - on deacidified paper.

In Figure 2, the results obtained with Methylene Blue are summarised. On acidic paper, the highest colour difference ΔE^* was observed during ageing at RH 65% (15.77). ΔE^* was most considerably influenced by changes in L^* and b^* : significant bleaching of samples and a shift from blue to grey hues was observed. During ageing at 50% and 40% RH, much lower values of ΔE^* were measured: 6.52 and 7.64, respectively. Similar behaviour was noticed also for Methylene Blue on deacidified paper, although after ageing the values of ΔE^* were lower (Figure 2b). At 65% RH, the maximum value of ΔE^* was 14.53, at 50% RH it was 3.87 and at 40% RH, it was 5.68.

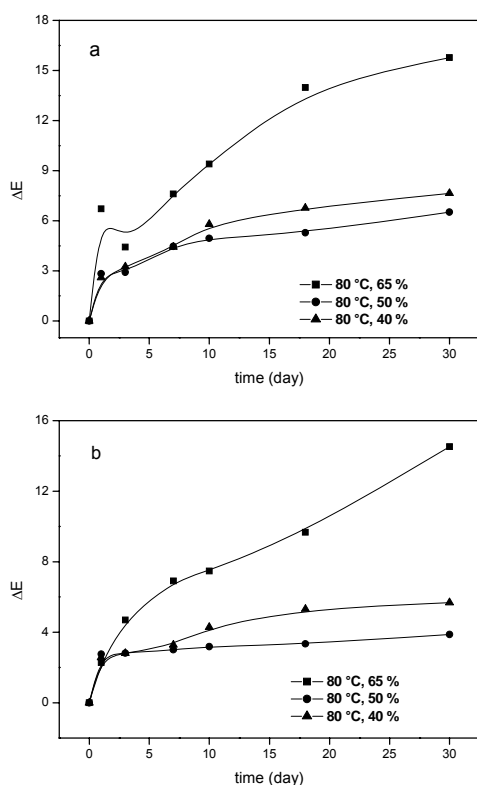


Figure 2: Comparison of ΔE^* of Methylene Blue dye during ageing at three different conditions, a - on acidic paper, b - on deacidified paper.

On Figure 3, the influence of ageing conditions on colour changes of the Basic Red 9 dye are summarised. The highest colour differences ΔE^* were measured during ageing at 40% RH (10.13) and 65% RH (8.51). The value of 5.88 was observed at RH 50%. The sample Basic Red 9 applied on deacidified paper (Figure 3b) showed less stability compared to the sample applied to acidic paper. The most obvious instability was noticed during ageing at 65% RH where ΔE^* was 27.71 which represents the highest total colour difference observed. The biggest contribution to the total colour difference was $\Delta a^* = 26.88$, which represented a shift from red to grey hue. During ageing at 40% RH and 50% RH, the lowest colour differences (12.66 and 11.29, respectively) were measured.

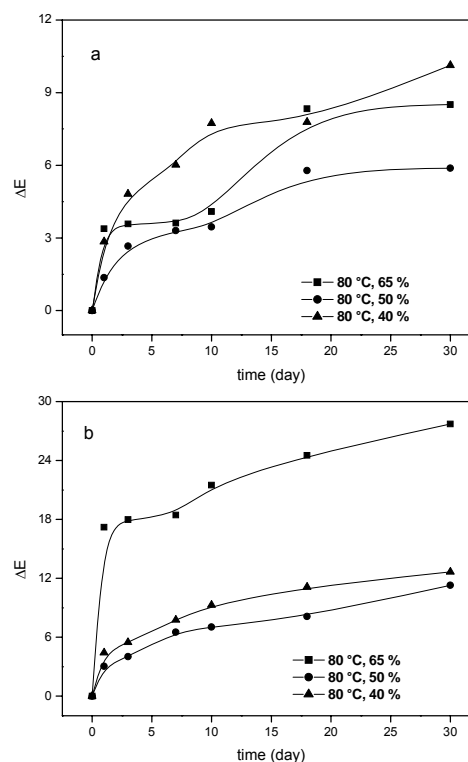


Figure 3: Comparison of ΔE^* of Basic Red 9 dye during ageing at three different conditions, a - on acidic paper, b - on deacidified paper.

4. Conclusions

This study investigated the influence of relative humidity (40%, 50% and 65% at 80 °C) and pH (acidic and deacidified paper) on optical properties of several arylmethane dyes (acidic Acid Green 16, alkaline Methylene Blue and Basic Red 9). ΔE^* was measured during ageing. The stability of arylmethane dyes on acid and deacidified paper with Booksaver method was compared.

A comparison of optical properties of acidic and alkaline dyes indicated a higher stability of the acidic dye Acid Green 16 on acidic as well as on deacidified paper. A lower value of RH (40 - 50%) during ageing was beneficial to colour stability and ageing at 65% RH influenced optical properties most negatively. Deacidification of paper improved optical properties during all 3 types of ageing and all dyes, particularly Methylene Blue. However, even after deacidification, ageing at lower RH (40 - 50% RH) was more appropriate.

5. Acknowledgements

This work has been supported by Slovak Grant Agency VEGA (project VEGA 1/0800/08) and project MVTs COST D42/08. We also thank the Ministry of Education of Slovak Republic for the support in the project KnihaSK No. 2003SP200280301.

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EFFECT OF ANTIOXIDANTS ON STABILISATION OF PAPER CONTAINING VERDIGRIS

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1. Introduction

Copper ions, which constitute certain historical pigments such as malachite and verdigris, catalyse oxidative decay of cellulose, leading to paper brittleness. The damage, referred to as "copper corrosion", endangers many historical manuscripts, drawings and maps.

To prevent oxidative decay of materials, antioxidants are employed. However, there is currently no available treatment, which would address the problem of copper corrosion. This is partly due to the solubility of the malachite and verdigris in water, which calls for a non-aqueous approach. Recently, an EC co-funded project InkCor proposed the use of bromide antioxidants for non-aqueous stabilisation of iron gall inks.¹⁻³ We have therefore decided to evaluate the effects of several antioxidants on the degradation of paper, with the copper pigment verdigris.

2. Experimental

Verdigris was produced according to the literature.⁴ 15 g of gum Arabic was dissolved in 25 mL of deionised water, after which 10 g of the pigment was added. The mixture was applied to the model paper, made from historical rag paper, using silkscreen printing technique. Samples were then pre-aged in a climatic chamber (Vötsch Climatic Chamber Type VC 0020) at 55 °C and cycling relative humidity (between 35% and 80% RH every 6 h) for two weeks. After pre-ageing, the samples were treated using a solution containing 0.05 mol L⁻¹ (C₂H₅O)₂Mg (denoted as MgEtO) and 0.03 mol L⁻¹ of antioxidant in ethanol. The following antioxidants were used: tetrabutylammonium bromide (TBABr), 1-benzyl-3-butylammonium bromide (BBABr), 1-ethyl-3-methylimidazolium bromide (EMIMBr), 1-butyl-3-methylimidazolium bromide (BMIMBr), 1-butyl-2,3-

dimethyl-imidazolium bromide (BDMIMBr) and 1-hexyl-3-methylimidazolium bromide (HMIMBr) and 1-hexyl-3-methylimidazolium chloride (HMIMCl). After the treatment, samples were aged at 80 °C and 65% RH.

Viscometry, which is a standard technique to follow cellulose degradation at 80 °C and 65% RH could not be used due to the presence of copper pigments. Instead, a method based on size exclusion chromatography of cellulose carbanilates⁵ was adapted for paper with copper pigment. Weight average molar masses determined in this way were divided by a molar mass of carbanilated glucosidic monomer to obtain the degree of polymerisation (*DP_w*), which was used to calculate the kinetics of cellulose degradation the Ekenstam equation.⁶

3. Results

The results demonstrate (Figure 1) that a successful stabilisation of paper with verdigris may be achieved using bromide antioxidants. Paper with verdigris treated with a solution alkali alone was 1.7 ± 0.3 times more stable than the untreated control. An addition of tetrabutyl ammonium bromide antioxidant to the treatment solution significantly increased paper stability (8 ± 2 times) as compared to the untreated control. A similar extent of stabilisation was observed in case of 1-benzyl-3-butylammonium bromide (BBABr), while imidazolium antioxidants were less effective. No negative side effects, such as colour change of the pigment or paper were observed.

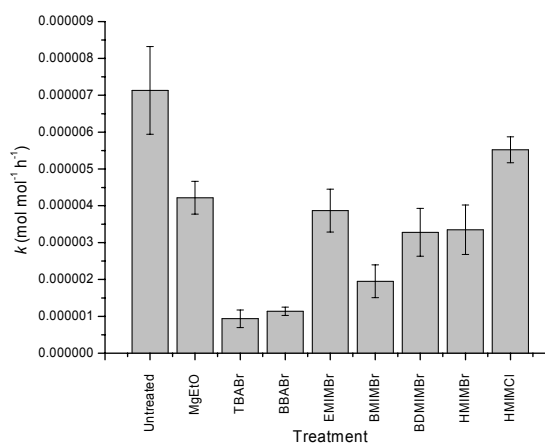


Figure 1: Degradation rate constants of untreated paper containing verdigris (Untreated) and the one stabilised using prototype non-aqueous treatments. The papers were aged for 168 h at 80 °C and the 65% relative humidity. Treatment solutions contained either alkali (MgEtO), or a combination of an alkali and antioxidants tetrabutylammonium bromide (TBABr), 1-benzyl-3-butylammonium bromide (BBABr), 1-ethyl-3-methylimidazolium bromide (EMIMBr), 1-butyl-3-methylimidazolium bromide (BMIMBr), 1-butyl-2,3-dimethyl-imidazolium bromide (BDMIMBr) and 1-hexyl-3-methylimidazolium bromide (HMIMBr) or 1-hexyl-3-methylimidazolium chloride (HMIMCl).

4. Conclusions

It is demonstrated that paper containing corrosive copper pigment verdigris can be successfully stabilised using an alcoholic solution of a bromide antioxidant, e.g. tetrabutyl

ammonium bromide, and an alkali magnesium ethoxide. Although no negative side effects were observed, it is advised that the effects of the treatment solution on paper and pigment are verified on a number of historical papers.

5. Acknowledgement

The authors gratefully acknowledge the support of the Ministry of Higher Education, Science and Technology of Slovenia, Programme No. P1-0153.

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DETERMINATION OF ROSIN ACIDS IN PAPER

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1. Introduction

Abietic acid (AA) and dehydroabietic acid (DHAA) are the main components of colophony which was used as a sizing agent in paper production from ~1850 - ~1990. In order to precipitate the acids onto fibres, aluminium sulphate was used. It is commonly assumed that the use of aluminium sulphate led to a decrease in the paper pH, which led to the well-known low stability of rosin-sized paper. Another potential source of rosin acids could be ground softwood, which can be used in papermaking directly. In this work, we examine the content of rosin acids in paper through time and the relations between the content of rosin acids and pH. We also report on the development of an NIR/chemometrics method for determination of rosin acids in historical paper.

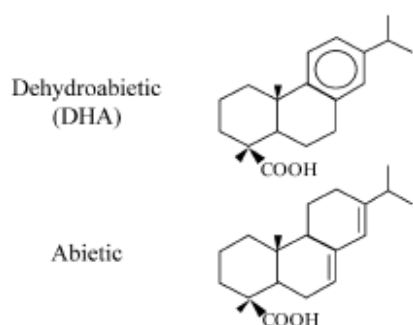


Figure 1: The two common rosin acids: dehydroabietic and abietic acid.

2. Experimental

For determination of rosin content, the samples were extracted in acidified acetonitrile and analysed using liquid chromatography with mass-spectrometric detection. The composition of the extraction mixture was optimised. We used a reversed-phase column and isocratic elution with mobile phase composed of acetonitrile and acetic acid. The quantification was achieved using external standard solutions.

We also collected spectral data in the reflectance mode using the Perkin-Elmer Spectrum GX FT-NIR spectrometer equipped with a 76-mm Labsphere RSA-PE-200-ID integration sphere coated with Infragold, with DTGS detector. Partial least squares method was used to correlate chromatographic and spectral data and the obtained correlations were satisfactory. Using this methodology, the SurveNIR reference material collection¹ was characterised.

3. Results and Discussion

The plot of rosin acid content vs. year of production (Figure 1) shows that there is a trend towards lower rosin content in more recently produced papers. The introduction of rosin into paper started around 1840 and reached the peak around 1900. Afterwards, the content of rosin acids begins to decrease slowly. However, even in contemporary papers, there may be rosin acids present, most probably as a consequence of the use of groundwood fibres in papermaking.

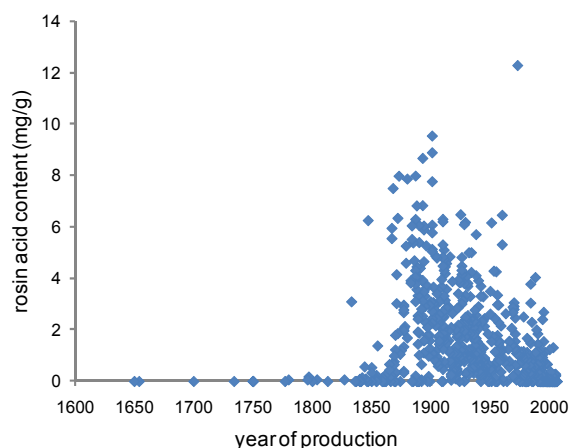


Figure 2: Content of rosin acids in historical papers through time (n = 1012).

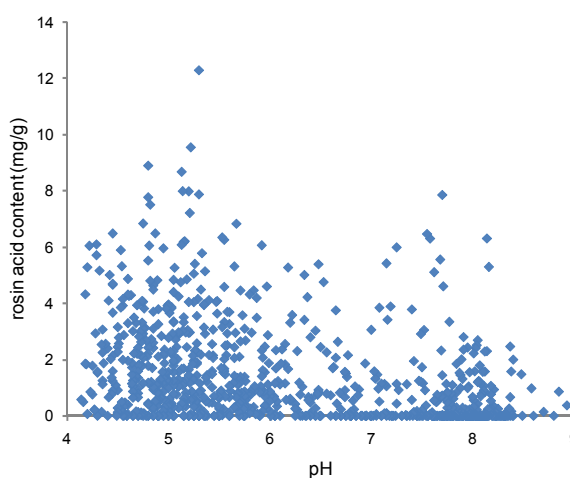


Figure 3: Relationship between rosin acid content and pH of historical paper.

A plot of rosin content vs. pH of the same papers shows that there is a dichotomous distribution - a group of samples with moderately alkaline pH is represented by deacidified historical samples and contemporary samples containing groundwood. From among the samples with $\text{pH} < 7$, there is a trend of decreasing pH with an increase of rosin acid content. Considering that rosin acids are carboxylic acids, their contribution to paper acidity should thus not be overlooked.

The data on rosin content obtained chromatographically were compared with FT-NIR spectra of the same samples using partial least squares (PLS) approach.² The resulting PLS calibration is shown in Figure 4.

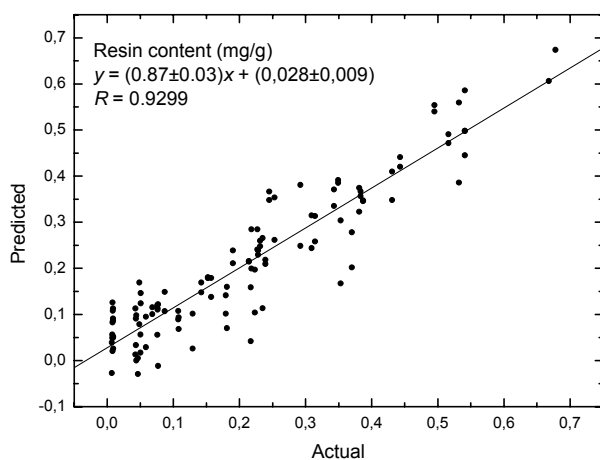


Figure 4: Correlation between rosin content - modelled by NIR ("Predicted") vs. measured ("Actual").

4. Conclusions

A chromatographic method for determination of rosin acids in historical paper was developed using mass-spectrometric detection. 1012 samples from the SurveNIR reference sample collection were analysed. The results demonstrate that the content of rosin acids in paper increases with age, reaching a peak at 1900. Rosin acids can also be determined in contemporary groundwood containing papers. Taking only acidic papers into account, there is a trend of higher acidity with higher rosin content.

An NIR/chemometrics method was developed for non-destructive rapid estimation of rosin content in historical papers.

5. Acknowledgements

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USE OF LASER AND OPTICAL DIAGNOSTIC TECHNIQUES ON PAPER: THE 'POMELNIC' FROM SUCEVIȚA MONASTERY, ROMANIA

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1. Introduction

During the Culture 2000 workshop taking place at the Sucevița monastery in Eastern Romania in 2006, a group of conservation and research experts was entrusted a document from the monastery's rich collection: to examine its material properties, state of preservation, and eventually to propose a suitable conservation strategy, using a variety of non-demanding techniques in situ. The document, 'Pomelnic', showed signs of extensive use (Figure 1). The age and composition was difficult to determine visually.

The object itself was glued onto a support, which was also very badly preserved.



Figure 1: 'Pomelnic', Inv. no. 25, examined at the Culture 2000 workshop in Sucevița.

2. Results and Discussion

Using colourimetry, the presence of at least four different inks was established. The composition of the black ink was of particular interest. The analyses done using laser induced breakdown spectroscopy (LIBS) showed that the peaks for iron were only slightly higher when inks were examined than when paper was examined (Figure 2). Additional analyses using iron-indicator paper strips indicated no presence of Fe(II), which means that it is very likely that the ink used was a carbon-based ink.

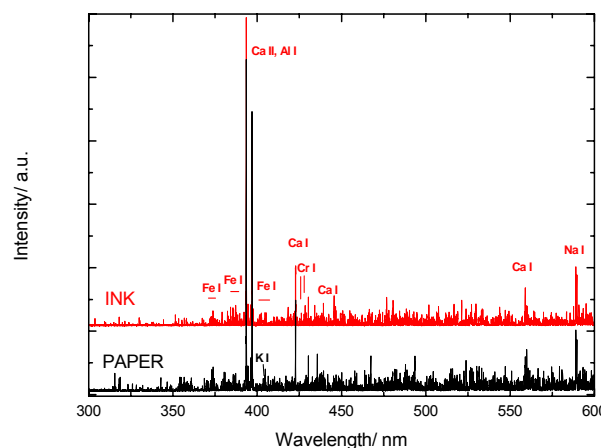


Figure 2: LIBS analyses of the ink and of the paper of 'Pomelnic'.

Analyses using the imaging camera indicated evidence of biological attack. Using micro-destructive determination of pH with a polyaniline-coated carbon electrode,¹ we established that the original document is very acidic

(pH 3.6), however, the material with which it was lined, was also acidic (pH 3.4).

Approximate dating of the document was possible basing on technological and historical evidence. The paper itself is machine-made and acidic, which means that it was probably produced after 1850. Historical analysis of the document showed that the document was used during ceremonies and that it contained names of dignitaries, who were already deceased at the time of its making. Close inspection of the text revealed that the names of three Austrian emperors appeared, i.e. Josif, Leopold and Franc (Figure 3). As they were probably successors, they were Joseph II (1741 - 1790), Leopold II (1747 - 1792), Francis II (1768 - 1835), while the successor Ferdinand I (1793 - 1875) was not mentioned. This means that the document was probably produced before 1875. In conclusion, the document was produced between 1850 and 1875.

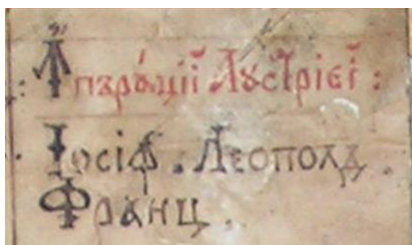


Figure 3: Names of Austrian emperors written on the 'Pomelnic'.

3. Conclusions

The document which was examined during the Culture 2000 workshop in Sucevița was a late 19th century manuscript, written using a variety of inks, as established using colourimetry. The inks were not iron gall inks, as demonstrated by LIBS and microchemical analysis. Using a micro-pH electrode, it was shown that the paper is acidic and is lined with another acidic paper and additionally with an acidic cardboard. Signs of biological attack were evident from fluorescence images. Using technological and historical evidence, the document was dated between 1850 - 1875.

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APPLICATION OF THE NEAR-INFRARED MOISTURE METER FOR CONTACTLESS MEASUREMENTS OF PAPER AND PARCHMENT

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1. Introduction

Moisture content is an important factor that influences the deterioration of artefacts made of organic materials: parchment and leather,¹ paper,² wood, textiles. The traditional method of measuring the moisture content in paper requires relatively large samples (about 2 g) and is destructive.³ Non-destructive methods used nowadays in paper industry are based on application of electromagnetic radiation (at radio frequencies), microwave technology or infrared sensors.⁴ Measurements with the infrared Moisture Content Analyzer (MCA) are contact less, non-destructive and can be performed through materials transparent to the IR wavelengths used by the meter (i.e. inorganic and organic glass). All this features make the IR moisture meter a valuable tool in cultural heritage studies, especially in situations where the access to object is limited (sealed frames and other enclosures).

The main purpose of our measurements was to measure the moisture content of paper samples aged in sealed glass tubes and to evaluate the possibility of using the MCA to measure the moisture content in parchment placed behind a protective Perspex cover. These conditions are usually met when paper or parchment objects are stored in frames.

2. Experimental

A non-contact instrument manufactured by Fibro System AB (Fibro MCA 1410 model)⁵ was used in our measurements. It measures moisture content using the 1940 nm water absorption band (the specific wavelengths absorbed by water are 1200, 1450, 1940 and 2950 nm).

The MCA 1410 gives readings in millivolts and had to be calibrated for a specific type of material and measurement arrangement used. The calibration procedure presented below was designed to allow for the measurement of moisture content in paper samples undergoing artificial ageing tests performed in accordance with the ASTM D6819-02e3 standard (ageing of paper in sealed vials). For all tests the model paper PAPER-1 (P1) supplied by TNO (Center for Paper and Board Research, Delft, Netherlands)⁶ was used.

Samples of P1 were prepared in the form of small scraps and as a roll with the dimensions fitting to the glass vials used

(Kontes hybridization bottles, approx. 150 ml of volume, diam. 3.5 cm, 14 cm high).

The samples of both kinds were placed in the climatic chamber (NCC 0130, NEMA Industrietechnik) and conditioned for 5 h at 90 °C at the chosen relative humidity in the range 10 to 75%. The MCA fibre-glass probe was fitted through the climatic chamber wall and mounted at a specific distance and angle to the paper samples placed behind the glass wall of an open vial. The moisture measurements were carried out in the arrangement identical to the one used for ageing in the closed vials in the laboratory oven.

When the conditioning period was over, the chamber was opened, and the paper sample in the form of scraps was immediately transferred onto the drying balance for the determination of its moisture content (Mettler-Toledo HR-83P).

3. Results and Discussion

3.1 Calibration of MCA

The values of water content as determined by drying balance were drawn against the readouts of MCA. The linear regression equation presented in Figure 1 describes dependence of MCA readouts on the moisture content for the tested paper (P1).

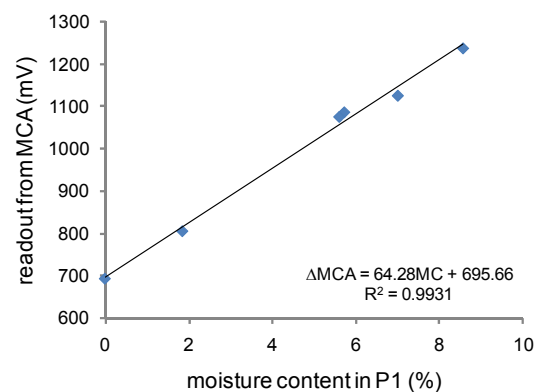


Figure 1: Calibration curve obtained for MCA 1410 at 90 °C.

The data collected during calibration of the instrument allow us to establish the relation between RH and moisture content in paper (MC) at 90 °C. This dependence, described by linear regression equation $\Delta MC = 0.0958 RH + 0.9391$, was used for the evaluation of relative humidity inside a closed vessel during artificial ageing of paper P1 performed in accordance with ASTM D6819-02e3 standard method. On the base of this estimation, it was found that RH in the vessel with P1 paper equals to ca. 59%.

3.2 Application of MCA - Paper and Parchment

Our research plan considered also an evaluation of the possibility to apply the MCA for measuring moisture content in paper or parchment placed behind a Perspex

(polymethylmethacrylate) cover, as glass and Perspex are frequently used in construction of protective cases for valuable artefacts.

A flat sample of paper P1 (4 plies) or parchment (1 ply) was attached to a piece of Perspex. This set was subsequently placed in the climatic chamber. The MCA probe was set in contact with the Perspex plate (at the side opposite to that of paper or parchment) at the angle of 70°. After closing the chamber, conditioning of paper/parchment was started.

The conditioning parameters were: (i) constant temperature of 23 °C, (ii) step-wise change of relative humidity (detailed information about the RH changes can be read from Figures 2 and 3).

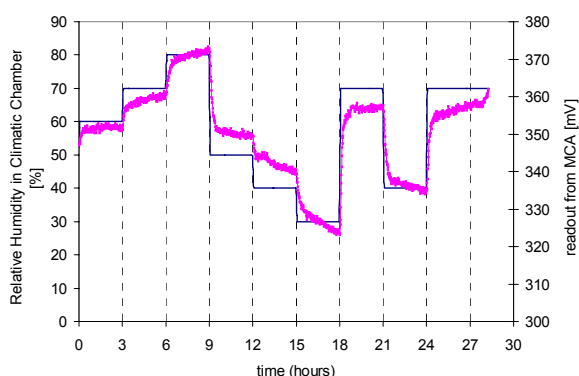


Figure 2: Changes of moisture content ($T = 23\text{ °C}$) in P1 paper placed behind Perspex, expressed as changes of MCA readouts (magenta-coloured line).

In Figure 2 one can observe the correlation between changes of relative humidity in the climatic chamber and the moisture content of P1 paper placed behind Perspex. In all steps the response in moisture content of paper P1 to RH changes was strongly delayed and the equilibrium moisture content was not fully reached.

A similar experiment was performed for a sample of historical parchment (cover from a 16th century book). Prior to the measurement with the MCA meter, FTIR spectra (Nicolet 5700) were collected for the tested parchment sample placed behind Perspex. The FTIR spectra were measured for the parchment sample preconditioned in a dry (105 °C for 5 h) and in a moist (72 h at 23 °C and 98% RH) atmosphere. The band utilized by the MCA 1410 for the detection of water was not obscured by the absorption bands of the Perspex or the parchment sample.

The results obtained with the MCA meter for the parchment sample conditioned in the climatic chamber with step-wise changes of RH are presented in Figure 3.

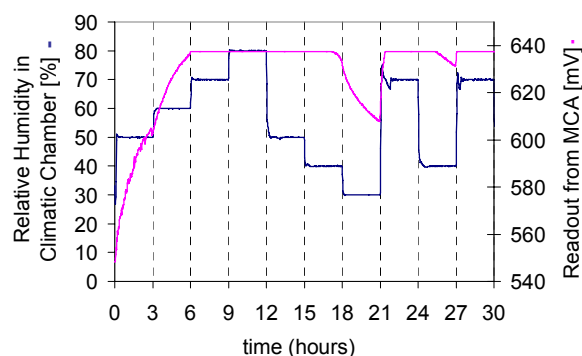


Figure 3: Changes of MCA readouts for parchment placed behind Perspex ($T = 23\text{ °C}$).

One can easily see that the response of MCA readouts to the RH changes are so delayed that they do not allow us to draw any conclusions on the moisture content of the tested parchment sample. The equilibration time needed for the parchment to reach the stable moisture content is of an order of magnitude greater than in the case of paper (as shown by P. Budrugaec and others⁷ approx. 300 h of conditioning are needed).

4. Conclusion

Using the NIR-based MCA instrument for the measurements of moisture content in paper requires its calibration. It has been shown that in the applied conditions, readouts of the MCA meter are proportional to the moisture content with a high correlation coefficient. One may calibrate the instrument at various temperatures and obtain a very convenient non-contact method suitable for measuring the moisture content behind a glass or other materials transparent to the near-infrared radiation. However it should be remembered that the signal measured by the MCA instrument is sensitive to the position of its probe against the measured object. It is to be expected that MCA measurements can be successfully applied also for other materials, but the calibration procedure should be adopted in order to allow for a proper equilibration of a tested material.

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THE PAPYULUM PROJECT: CHEMILUMINOMETRY FOR STUDIES OF MATERIAL OXIDATION

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1. Introduction

In the frame of the 5th Framework EU project Papyrus (2001 - 2005), chemiluminescence was introduced as a new research tool in studies of oxidative degradation of heritage materials. Chemiluminescence is weak light emission occurring during oxidation of organic materials and has been noticed during oxidation of many organic materials. In the frame of the Papyrus project the technique was mainly used for studies of paper oxidation, which was summarised in a book.¹

This work reports on the successful use of chemiluminescence in studies of a variety of heritage materials since the project was completed. While the studies of paper continued by investigations of oxidation phenomena in acidic papers, we also successfully applied the technique to studies of cellulose acetate and, most recently, parchment.

2. Experimental

Chemiluminometric experiments were performed using the Lumipol 2 chemiluminometer, manufactured at the Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia. A sample was placed onto an aluminium pan placed on an oven in the sample compartment. Dynamic ('ramp') experiments (temperature increased from 40 °C to 220 °C at the heating rate of 2.5 °C min⁻¹) were carried out. The measurements were performed in nitrogen atmosphere, maintaining a flow of 3 L h⁻¹. Pre-oxidation of samples was performed at different conditions, but typically in a flow of oxygen at 80 °C for 120 min, following which the temperature was cooled down to 40 °C and the atmosphere switched to N₂. After a 15-min period of annealing, the dynamic experiment in N₂ was performed in order to follow the formation of peroxide species formed during oxidation.

3. Results and Discussion

The importance of oxidation reactions in acidic paper is still of high interest. In an acidic environment, cellulose decomposes via the acid-catalysed hydrolytic mechanism. The relative importance of this well-researched degradation pathway decreases with increasing pH of the macromolecular environment, while the importance of oxidative degradation increases. In samples of acidic character, oxidation and acid-catalysed hydrolysis can take place simultaneously. Light emission is also observed, albeit less intensive than in alkaline samples (Figure 1). Chemiluminescence is so far the only technique providing the evidence of oxidation reactions taking place in acidic paper *in situ*.²

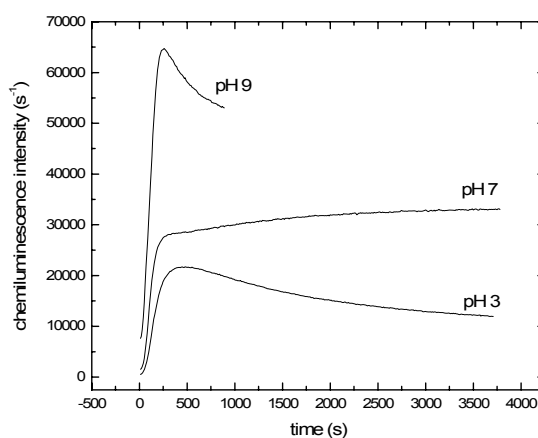


Figure 1: Isothermal chemiluminescence of cellulose samples (Whatman filter paper) impregnated with phosphate buffers of different pH as indicated. Conditions: 180 °C, O₂ atmosphere.

Although more stable than cellulose nitrate, acetate film deteriorates and releases acetic acid. This phenomenon is widely known as the "vinegar syndrome". Intensive research has shown that cold storage (0 - 5 °C, 30 - 40% relative humidity) is a viable preservation strategy, although some studies indicate that antioxidants may also have a positive effect, therefore, studies of oxidation of cellulose acetate are of interest.³

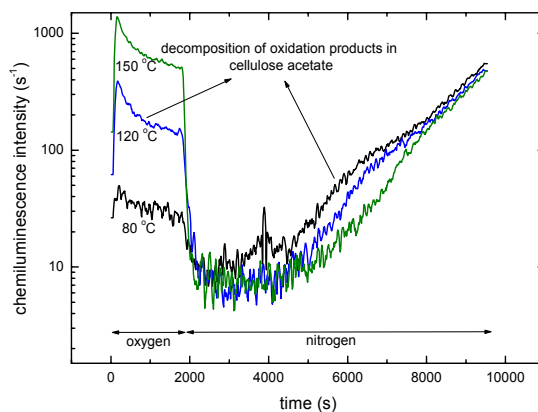


Figure 2: Isothermal chemiluminescence of cellulose acetate at different temperatures in O₂ atmosphere, as indicated. Following pre-oxidation, the atmosphere was switched to nitrogen and a ramp experiment was performed.

In Figure 2 we can observe that light emission accompanies degradation of cellulose acetate in oxygen atmosphere.

After the atmosphere is switched to nitrogen, the decomposition of peroxides formed as a consequence of oxidation, can barely be observed as a slight shoulder, indicating their very low stability.

In Figure 3, we can observe CL curves of non-pre-oxidised parchment showing an almost monotonous increase of intensity until a peak is reached at 170 - 180 °C. This peak is present in both oxidised and non-oxidised samples and its origin is at present the subject of further studies. The CL peak at 140 - 150 °C is of interest: it appears as a prominent feature after oxidation in both new and old parchment. In both proteinaceous and cellulosic materials, this peak is associated with peroxide content.

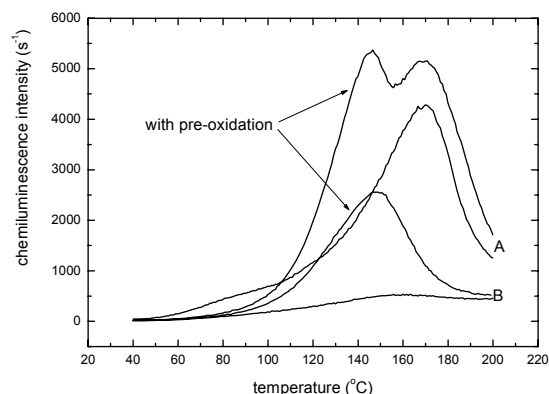


Figure 3: Dynamic chemiluminometric experiments with parchments in N₂ atmosphere with (O₂, 120 min) and without pre-oxidation. Sample A: modern parchment, sample B: historical parchment.

4. Conclusions

The use of chemiluminometry in studies of oxidation of historical materials continues to attract considerable interest. In the present work, we demonstrated that:

Chemiluminometry can be used to follow oxidation of acidic paper samples.

The technique provided the evidence of high instability of peroxides in cellulose acetate, the information being of importance when examining the use of antioxidants for stabilisation of this historical polymer.

Evidence of parchment oxidation was put forward indicating that this degradation pathway might be of particular importance during parchment degradation. Further research is under way to understand the nature of light emission of parchment.

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QUANTITATIVE APPROACH TO LASER ABLATION - ICP-MS ANALYSIS OF IRON GALL INK ON PAPER

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1. Introduction

The use of laser-based techniques for paper has largely been restricted to conservation or conservation science. A lot of research has been focused on laser cleaning, where laser radiation is used for removal of surface soiling.¹⁻⁴ In some of these studies, it was shown that during pulsed irradiation of paper (Nd:YAG, 1064 nm), interactions between surface deposit and cellulose may lead to thermal degradation of the substrate,⁵ while the use of pulsed UV lasers (Excimer, 308 nm) leads to photolytic degradation of cellulose.⁶ On the other hand, microprobe laser techniques have not yet been extensively used for paper analysis, mainly due to problems associated with quantitation. So far, LA-ICP-MS was used only for qualitative determination of elements in paper heritage objects, e.g. for revealing the distribution of transition metals across ink lines.^{7,8} In this work, we present quantitative LA-ICP-MS analysis of ink on paper, together with some studies of relative distribution of transition metals across ink lines. The main emphasis of this work was on obtaining quantitative information with the use of LA-ICP-MS - to obtain the content of elements in paper and ink.

2. Experimental

Since certified reference materials are not available, synthetic standards had to be prepared. The samples, containing 11 metals (Mg, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd), were prepared by immersing cellulose filter paper in solutions of metal chlorides of various concentrations and dried. The calibration samples were then analysed for metal content using a reference technique. ICP-MS following a microwave digestion procedure was used. For the LA ICP-MS work, a New Wave Research UP-213, Nd:YAG deep UV (213 nm) laser ablation workstation, equipped with the standard sample cell was used. LA workstation was coupled to Agilent® 7500ce ICP-MS, the same instrument that was used for analyses of microwave

digested standard samples, only in solution mode. Due to the improved transport efficiency and particle size distribution of the ablated aerosol, helium, rather than argon⁹ was used as the carrier gas from LA to ICP-MS. Previously prepared synthetic calibration samples (5 x 7 mm) were mounted onto microscopic glass slides with the use of self-adhesive tape. Helium, at 0.95 L/min, was used as the carrier gas in the ablation cell and argon at 0.75 L/min was used to make up the total gas flow to ICP torch. Six consecutive replicates of each calibration sample and the blanks were measured and the signal of ¹³C was used as internal standard, to minimize for the minor fluctuations and drift of the analytical system.

Laser ablation parameters were as follows: laser wavelength: 213 nm; beam diameter: 100 µm; beam travel speed: 25 µm/s; shot repetition rate: 10 Hz; laser fluence: 0.1 J/cm².

3. Results and Discussion

Using the parameters as above, enough material was ablated to provide a stable signal, while damage to the sample was minimized and barely visible. Calibration for all 11 elements was successfully performed, taking ¹³C as an internal standard. LA-ICP-MS could be qualified as a micro-destructive technique, provided that sample size is not a limiting factor. Thus, it is advantageous over other micro sampling techniques, mainly due to its high sensitivity and low detection limits.

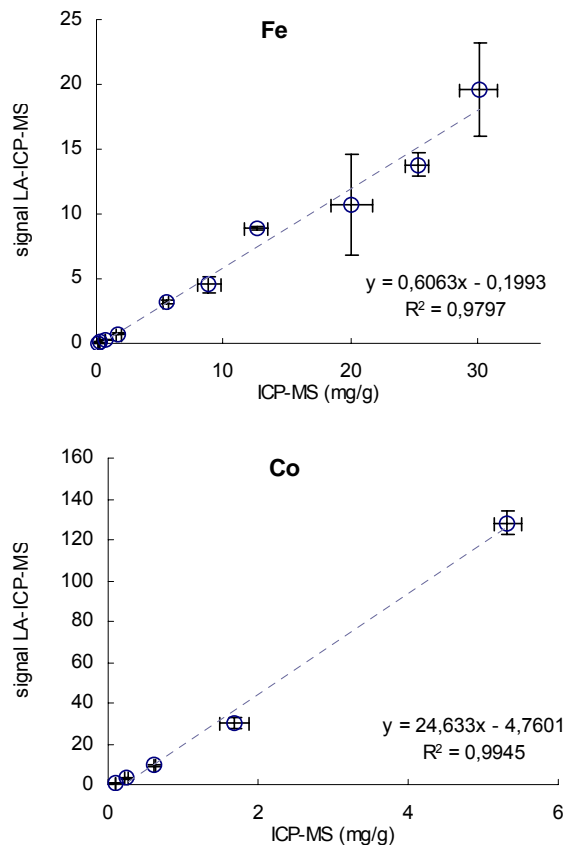


Figure 1: Examples of calibration lines (Fe and Co), obtained with the quantitative LA-ICP-MS approach.

Several case studies on historical documents, containing iron gall ink, were performed. The essential ingredients of this ink were gall nuts and vitriol and they are known to contain large amounts of transition metals. Their distribution, content and identity are important parameters for estimation of the ink stability. The described analytical approach, the quantitative LA-ICP-MS, can be used for monitoring these critical parameters.

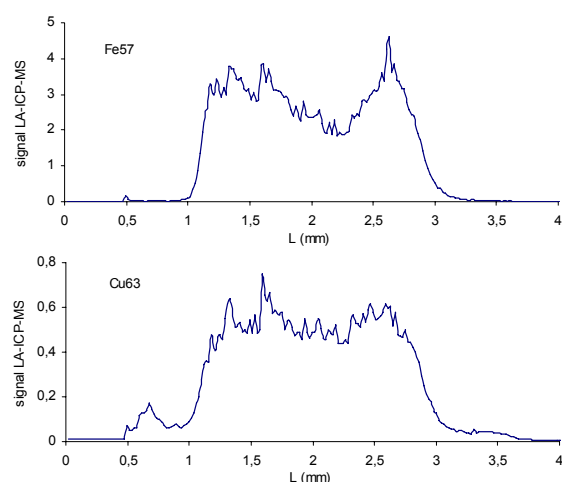
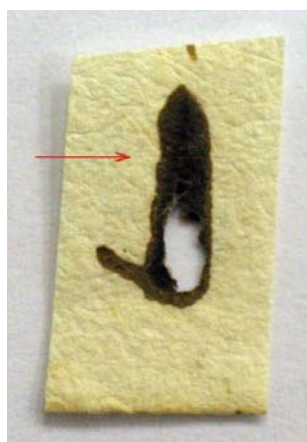


Figure 2: Examples of LA-ICP-MS scans across the iron gall ink line (top picture), with Fe and Cu distribution profiles. (Sample provided by Manfred Anders, ZFB - Leipzig, Germany).

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DETERMINATION OF MECHANICAL PROPERTIES OF COMMERCIAL PULP SAMPLES USING IR SPECTROSCOPY

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1. Introduction

We report on the use of near- and mid-FTIR in combination with multivariate data analysis for prediction of mechanical properties of pulps. More than 250 commercially available, predominantly bleached Kraft softwood and hardwood pulp samples were included in the study. The data were analysed using partial least squares in order to obtain correlations between the time-consuming standard reference methods and spectral data. Satisfactory correlations were obtained for drainability, tensile index, burst index and breaking length. Less satisfactory was correlation for tear index.

IR spectroscopy remains a very attractive analytical method in paper characterization, as it is non-demanding and non-destructive technique. In the mid-IR spectrum, polar covalent bonds have characteristic and well defined

absorptions bands. The fingerprint region is more complex and band assignment is usually more difficult. The NIR region is complex, overtones and combination bands dominate vibrational excitation and even spectra of chemically simple substances are rich in strongly overlapping bands. With the advancement of chemometric data analysis, the wealth of information contained in these spectra can be processed and several studies have been published on paper characterisation.¹⁻⁴ Our research so far focused on the use of NIR/chemometrics for the determination of chemical and mechanical properties of historical papers.^{5,6}

2. Materials and Methods

We used more than 250 pulp samples. After wet disintegration, the pulp samples were laboratory beaten using a PFI mill. Drainability according to the Schopper-Riegler method was determined at four extents of beating, and standard paper sheets with grammage of ~65.3 g m⁻² were prepared.

Tensile strength, tearing resistance, tear index and bursting length were determined using standard methods and FT-(N)IR spectra of the samples were measured.

A Perkin Elmer Spectrum GX (Waltham, MA) equipped with a 76-mm Labsphere RSA-PE-200-ID (North Sutton, NH) integration sphere coated with Infragold, with DTGS detector was used for measuring the spectra. The reflectance spectra were measured in the interval 6500 - 500 cm⁻¹, 128 scans per sample, using four layers of paper. We used partial least squares to correlate spectral information with the measured reference data. The samples were divided into two sets. One set was used for calibration and another one for validation of models. Spectrum Quant+ software (Perkin Elmer, Waltham, MA) was used to model the chemical properties.

Table 1: Summary of the parameters of PLS calibrations and validations of different mechanical properties of pulp (N - number of used samples, R² - square of correlation coefficient, SEE - standard error of estimation, SEP - standard error of prediction).

Sample	Pulp property	Wavenumber interval (cm ⁻¹)	Pre-processing	Calibration				Validation	
				N	R ²	SEE	SEP	N	R ²
All	Tensile index	6500 - 800	none	251	0.9466	5.8	5.9	20	0.9543
Hardwood	Drainability	6500 - 800	none	130	0.9349	3.6	3.7	14	0.8000
	Tensile index	6500 - 800	none	130	0.9583	5.1	5.3	14	0.9453
	Tear index	6400 - 1500	1 st derivative	130	0.9120	0.78	0.80	14	0.7378
	Burst index	6500 - 800	none	130	0.9898	0.24	0.25	14	0.9554
	Breaking length	6500 - 800	1 st derivative	130	0.9707	438	449	14	0.9128
Softwood	Drainability	6500 - 800	1 st derivative	107	0.9962	0.78	0.80	15	0.7327
	Tensile index	6500 - 800	none	107	0.9643	4.7	4.9	15	0.9438
	Tear index	6500 - 800	1 st derivative	107	0.9881	2.2	2.3	15	0.6022
	Burst index	6500 - 800	1 st derivative	107	0.9584	0.48	0.49	15	0.9603
	Breaking length	6500 - 800	none	107	0.9705	436	452	15	0.9539

3. Results

Using partial least squares (PLS), we were able to build the models for rapid determination of a number of mechanical properties based on FT-(N)IR spectra of standard paper sheets. Mechanical properties of paper are influenced by inter- and intra-molecular bonds, which are affected during the milling process. Due to these changes, vibrational spectra are also affected, and the minute changes can be evaluated using chemometric methods.

PLS models for all samples (hardwood and softwood) and separately for hardwood and softwood samples were calculated. Different spectra pre-processing was tested to improve the quality of calibration and validation: normalization, derivatisation, smoothing, baseline correction and use of different wavenumber intervals.

As shown in Table 1, there is only a slight difference in calibrations and validations if modelling of tensile strength is performed separately for hardwood and softwood samples or for all samples together. For almost all parameters the best correlations we obtained using both the near and mid-IR spectral range. Quite satisfactory calibrations for determination of drainability were obtained, but the validations are unsatisfactory. For tensile index, burst index and breaking length the both the calibrations and validations are satisfactory. PLS methods can thus be used for prediction of these parameters rapidly and reliably. For tear index calibration is acceptable but the validation is not, so this model can't be used for the quantitative determination of tear index.

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