L04 PREDICTION OF THE ACETIC AND FORMIC ACID FORMATION IN THE PAPER DURING THE ACCELERATED AGEING BY THE CHANGE OF OPTICAL PROPERTIES

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Introduction

The deterioration of paper as it ages is a serious problem for archival and library communities throughout the world[1]. The most important chemical reactions that occurs during the ageing of paper is the acid-catalyzed hydrolysis of cellulose in paper fibers[2–4] and oxidation of cellulose by oxygen.[2,5–7] The natural ageing processes in the paper lead to the formation of several low molecular weight compounds. Organic acids are spontaneously generated in the natural ageing of all cellulose–based papers, including alkaline papers. Easily detectable concentrations of formic (methanoic), acetic (ethanoic), lactic, glycolic, oxalic and a few others also unidentified acids accumulate within a few months of manufacture in paper stored under ambient conditions[8]. In another work Shahani[9] analyzed papers aged naturally and accelerated by ageing for carbohydrate species using ion chromatography and aliphatic acids such as formic and acetic, which we have discovered to form in surprisingly abundant concentrations, by capillary electrophoresis. In earlier works, which showed us that acidic degradation products tend to accumulate inside polyester encapsulations and other enclosures, and thereby hasten the ageing of the paper[10,11]. To stop the degradation and save millions of the books that are stored in archives different technologies of deacidification and fibre strengthening were invented[12] and considerable efforts have been devoted to find a new additives such as scavengers of free radicals, natural and synthetic compounds, inorganic compounds, solvent and improved original technologies of deacidification.[13–15]

The advantage of the optical methods in the visible part of the spectra consists in their non destructive character. Visually evaluated colour information are widely used in common praxis and in everyday life for grading, production control, sate, decisions of consumers, aesthetic and economical value evaluation, in utilisation, renovation and recycling of lignocellulosic materials and products. The objectively measured quantitative colour information are antropomorphous in nature (human-like, understandable and sometimes or to some extent proportional to the human perception).[16–19]

Experimental

Raw material

Commercial groundwood newsprint paper (grammage 45 g m^{-2}, liquor pH: 4.5–5.0) containing mechanically bleached, groundwood (55 %), bleached sulphite pulp (20 %), catch trash fibres (15 %) and clay (10 %) was used in all experiments.

Accelerated Ageing at 98 °C

Paper were conditioned for 24 hours at T = 23 ± 1 °C, RH = 50 ± 2 % by the norm TAPPI T 402 om-93. Twenty papers (sheets of paper in size A4 format) were put into PET/Al/PE bag which was subsequently completely sealed off. This bag was put into another PET/Al/PE bag which was also completely sealed off and was again put into third (final) sealed PET/Al/PE bag. Finally sample sheets were in the package consisting of three sealed bags put one in another. The bags with samples were put into the thermostat for 0, 1, 2, 3, 5, 7, 10, 15, 20, 30 and 60 days at temperature 98 ± 2 °C.

High Performance Ion-Exchange Chromatography

Approximately 2 g of the paper were accurately weighed and 15 ml of water (Millipore) was added. The mixture was mixed during 2 hour and filtered through 0.45 μm filter. Amount of 20 μl filtrate was injected into the analytical column. The used HPLC system consists of a DeltaChrom SDS 030 isocratic pump, a 7125 Rheodyne injector with a 20 μl injection loop, a thermostat Model LCT 5100, a Knauer variable wavelength detector (set at 210 nm), and CSW32 software for peak identification and integration.

Chromatographic separations of acids were performed with column Polymer IEX H-form (250 × 8 mm I.D., 8 μm). The mobile phase consisted of 9 mmol dm^{-3} sulphuric acid. The column temperature was 20 °C and the flow rate of the mobile phase was 0.8 ml min^{-1}. Formic and acetic acid were detected with spectrophotometric detection at 210 nm. The retention times were 9.7 ± 0.2 min. for formic acid and 10.7 ± 0.1 min. for acetic acid. The identification of the acids in water extract of paper was based on comparison of their retention factors (formic acid k = 1.21 ± 0.03, acetic acid k = 1.44 ± 0.03).

Calibration curves were constructed by performing a regression linear analysis of the peak area versus the concentration of acids. Based on a four-point calibration, a linear response (r = 0.99) was observed from the limit of determination to 20 mg ml^{-1} of studied acids. The limits of detection, defined as the lowest sample concentration, which can be detected (signal-to-noise ratio of 3 : 1) were 10.7 μg ml^{-1} for formic acid and 18.4 μg ml^{-1} for acetic acid. The limits of determination, defined as the lowest sample concentration, which can be quantitatively determined with suitable precision and accuracy (signal-to-noise ratio of 10 : 1) were 42.8 μg ml^{-1} for formic acid and 92.2 μg ml^{-1} for acetic acid.

Optical Properties

Changes in colour of paper surfaces due to ageing were measured using a colour measuring system ELREPHO DATACOLOR 2000. Brightness (B), yellowness (Ys), CIE-Lab L^*, a^*, b^* and ΔE parameters were measured at five spots on each specimen and average value was calculated. The precision in the optical properties determinations brightness are estimated to be less than ± 0.05 units. The Kubelka–Munk coefficient (k/s) describing the number of chromophores present in the paper was determined on the basis of experimental values for brightness[20].

Results

On the Fig. 1. are shown correlations between each pair of variables. Fig. 1 shows Pearson product moment correlations between each pair of variables. These correlation coefficients range between –1 and + 1 and measure the strength of the linear relationship between the variables. The second number in each location of the Fig. 1. is a p-value which tests the statistical significance of the estimated correlations. P-values below 0.05 indicate statistically significant non-zero correlations at the 95% confidence level.

The most evident signs of paper are yellowing and loss of mechanical strength[21]. During the ageing of paper, decreases the lightness, brightness, but on the other side increases redness and b^* coordinate, yellowness (Ys), total colour difference, Kubelka-Munk coefficient and also increases content of acetic and formic acid in paper. In modern papers the decrease of brightness is about 13–15 %, in historic papers is 3–16 %[22]. In our paper the initial value of brightness was 66.20 % ISO and after 60 days of ageing was decrease of brightness about 78 %.

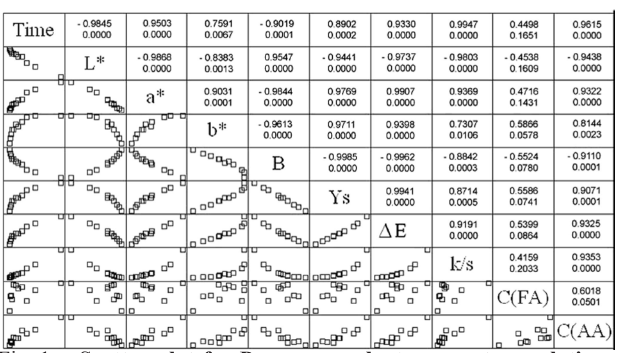

Fig. 1. **Scatter plot for Pearson product moment correlations between each pair of variables**

The acidic products formed during the accelerated ageing accumulate inside the paper and inter-sheet spaces of the books or archival files and it results in enhanced degradation[23]. On the basis of evaluation of carboxylic acids content (formic and acetic acid) was noted unambiguous increase of acetic acid concentration during the accelerated ageing and moderate increase of formic acid concentration. During the accelerated ageing was increased concentration of acetic acid from 0.361 on the value 4.798 $mg\,g^{-1}$ of paper (after 60 days). The content of formic acid during the accelerated ageing increases from 0.185 to 0.868 $mg\,g^{-1}$ of paper (after 60 days). All chemical reactions causing paper degradation are also responsible for the creation of chromophores, especially thermal oxidations and photo–Oxidations. Other reactions such as condensation, cross linking and dehydration due to heat and strongly acid environment, also produce coloured chemical compounds[23,24]. In principle, simple acid hydrolysis does not affect colour, but low-molecular-weight products are more prone to oxidation and colour formation than cellulose chains[23]. The yellowing of paper during the ageing procedure is attributed to the presence of chromophores formed by the degradation of paper components (cellulose, hemicellulose, lignin)[25,26]. The formation of macromolecular hydroperoxides in the cellulose backbone was evidenced previously in the research on paper ageing and the significant role of the produced radical species was postulated[25,26].

Correlations between optical properties and all other characteristics were mostly strong. Fig. 1. demonstrates that a few outliers did not drive the lack of correlation. It was seen earlier that a good correlation exists between C(AA) and time of accelerated ageing ($r = 0.9615$) and to a lesser extent between C(AA) and L^* (–0.9438), k/s (0.9353), ΔE (0.9325), a^* (0.9322), B (–0.9110) and Ys (0.9071).

Whereas the values for C(FA) are poorly correlated with the optical properties and time of accelerated ageing and C(AA). The correlation between content of formic acid and all other characteristics was evaluated ($r < 0.61$). The weak correlation were between time of accelerated ageing at 98 °C and b^* coordinate (0.7591) and between b^* coordinate and k/s (0.7307).

We tried to achieve a quantitative linear correlation between optical properties of ageing paper and a property related to extent of degradation formation of acetic and formic acid in paper, respectively. For our multiple regression models, we have used the model set containing samples aged in the time interval from 0–60 days at 98 °C. The output shows the results of fitting a multiple linear regression model to describe the relationship between content of acetic acid (C(AA)) or formic acid (C(FA)) and 8 independent variables. The equation of the fitted model is

$$C(AA) = -23.5965 + 0.239192T + 0.354993L^* - 0.925779a^* - 1.82714b^* - 0.311187B + 2.17738Ys - 2.7564\Delta E + 0.850291k/s$$

Since the p-value is less than 0.01, there is a statistically significant relationship between the variables at the 99 % confidence level. The R^2 parameter indicates that the model as fitted explains 99.88 % of the variability in C(AA). By the method forward selection was evaluated new multiple linear regression model are presented Table I. The R^2 parameter indicates that the model as fitted explains 96.70 % of the variability in C(AA).

The equation of the fitted model for concentration of formic acid and optical properties and time of accelerated ageing is:

$C(FA) = -70.4895 + 0.0640916T + 0.667981L^* - 0.836883a^* - 2.84595b^* + 0.234988B + 1.19121Ys + 1.29359\Delta E - 10.578k/s$

Table I
Parameters and estimates of fitting of linear multiple regression model for concentration of acetic acid

Dependent variable: C(AA)			
Parameter	Estimate	Standard error	p-value
Constant	1.0985	0.1303	0.0000
Time	0.2119	0.0448	0.0015
k/s	–3.6854	1.1477	0.0124
$R^2 = 0.967$			

Since the p-value is greater or equal to 0.10, there is not a statistically significant relationship between the variables at the 90% or higher confidence level. The R^2 indicates that the model as fitted explains 92.95 % of the variability in C(FA). By the method forward selection was evaluated new multiple linear regression model which is presented in Table II. The R^2 parameter indicates that the model as fitted explains 34.4 % of the variability in C(FA).

Table II
Parameters and estimates of fitting of linear multiple regression model for concentration of formic acid

Dependent variable: C(AA)			
Parameter	Estimate	Standard error	p-value
Constant	0.2990	0.1648	0.1031
b^*	0.0209	0.0096	0.0578
$R^2 = 0.344$			

As was mentioned before, optical properties are physical properties which are often monitored by the conservators for the indication of chemical changes[27]. From this paper is obvious that brightness decreases during the ageing, probably because of formation of chromophore in cellulose, hemicellulose and lignin, and then it increases. In this work was confirmed that formation of acetic acid in paper depends on the time of accelerated ageing and on number of chromophores present in the paper which can be described by the Kubelka-Munk coefficient. The correlation between time of accelerated ageing, Kubelka-Munk coefficient and formation of acetic acid is strongly significant. Correlation between optical properties and time of accelerated ageing according to formation of formic acid is weak significant.

In this work was also confirmed that low-molecular product such as acetic acid have coherence with the colour information which is consequence of the accelerated ageing. Paper properties are interdependent[27] hence the change of optical properties relates with the change of chemical properties and fragility of pulp fibers during the accelerated ageing.

Conclusions

The aim of the work was to quantify the failure of acetic and formic acid estimation by optical parameters in models of ageing papers at 98 °C from 0 to 60 days. The results presented in the paper has shown that multiple linear regression model describes the relationship between acetic acid content and independent variables as time of accelerated ageing (T) and coefficient of Kubelka-Munk (k/s). The equation of the fitted model is $C(AA) = 1.0985 + 0.2119T - 3.6854k/s$.

The R^2 parameter indicates that the model as fitted explains 96.70 % of the variability in acetic acid content. For formic acid content the equation of the fitted model is $C(FA) = 0.299 + 0.0209b^*$. The R^2 parameter indicates that the model as fitted explains 34.40 % of the variability in formic acid content.

Low-molecular product such as acetic acid, have coherence with the colour information which is consequence of the accelerated ageing. Formation of acetic acid in the paper depends on the time of accelerated ageing and on number of chromophores in the paper.

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