

Iron gall ink-induced corrosion of cellulose: aging, degradation and stabilization. Part 2: application on historic sample material

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Abstract Degradation of cellulose in historic paper by iron gall ink is a synergistic process of both, acid hydrolysis caused by acidic ink ingredients and oxidation catalyzed by free iron and/or copper ions. The interplay of both reactions was studied according to the CCOA method on historic paper samples. Only minute amounts (few mg) of the samples were required to obtain profiles of naturally present and oxidatively introduced carbonyl groups, which was done by group-selective fluorescence labeling in combination with determination of the molecular weight distribution by GPC-MALLS. In the present study naturally occurring degradation pathways in historic sample papers have been investigated. Different extents of oxidative degradation were shown

for paper with and without ink. A typical pattern of the molecular weight distribution in naturally aged papers was identified, the peculiar feature being a distinctive shoulder in the region of low molecular weight, roughly between 25,000 and 5,000 g/mol corresponding to a DP between 150 and 30. This pattern was a typical attribute of degraded natural samples: any artificial aging procedures aimed at modeling natural aging processes must thus attempt to reproduce this feature. Although the historic samples had been more severely oxidized than model papers, the inhibition of further oxidation and hydrolysis by the calcium phytate/hydrogen carbonate treatment was evident and could be proven for the first time on the molecular level. Also on plain paper without ink application the oxidation was suppressed and the molecular weight was stabilized on a high level.

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Introduction

The role of transition metal ions in paper has been studied for a long time, emphasizing the catalytic role of even trace amounts of different transition metal ions (Williams et al. 1977; Brown and Abbot 1995; Šelih et al. 2007; Shahani and Hengemihle 1986).

Paper conservation has to deal with inks and pigments that contain significant amounts of iron or copper components, because complexes or salts of iron or copper form the writing or drawing substance. Consequently these writing and drawing media that often induce degradation of cellulose are an important threat for paper documents of all kinds, ranging from letters in archives to drawings in collections of graphic art (Banik 1997; 1999; Banik and Stachelberger 1984; Banik et al. 1988).

Historic iron gall ink is typically composed of two main ingredients, iron(II)sulphate and a vegetable tanning agent, mostly gallotannin extracts from gall apples. Considering the broad variety of available recipes to produce it and all kinds of possible impurities in historic source materials for iron gall ink preparation, investigation of this writing and drawing material is faced with a hardly reproducible system which makes studies in iron gall ink corrosion quite difficult to handle (Zerdoun Bat-Yehouda 1983). As many different metals are contained in historic inks as impurities the term metallo-gallate inks will be used in the following when talking about historical inks.

Seeking an explanation of the mechanism behind this type of degradation and the necessity to develop treatment options against it, a synergistic model to explain deterioration caused by metallo-gallate inks has been put forward. According to the synergistic model, acid hydrolysis is caused by sulfuric acid that is a by-product of ink complex formation, and autoxidation is due to free iron ions that degrade paper-based items. Treatment options should therefore inhibit the two different degradation mechanisms. Translated into conservation treatment of objects that suffer from metallo-gallate inks, a deacidification, i.e. neutralization of existing acids in the paper, and a chelating step to inactivate the transition metal ions are needed for a successful treatment. This approach has been investigated in depth (Neevel 1995). Many research works dealing with the treatment of inked model papers has been performed to further establish the beneficial use of the calcium phytate/ calcium hydrogen carbonate treatment (Kolar et al. 2005; Kolar et al. 2003; Reißland 1999). Degradation of two different types of ink, unbalanced iron gall ink and unbalanced iron gall ink plus copper sulphate applied on model papers was inhibited by a calcium phytate/calcium hydrogen carbonate treatment (Potthast et al. 2008). Whether

this beneficial effect can also be found on naturally aged paper samples remained to be clarified.

Hence, in this study, historic samples have been analyzed to elucidate aging and degradation pathways in naturally aged papers. One set of sample material has been used to clarify the naturally occurring degradation phenomena without any treatment or artificial aging procedure applied. A second set has been divided into two halves, one of them being treated with the phytate system, the other one being left untreated. In order to evaluate the effectiveness of the treatment, the second sample set has than experienced accelerated aging to observe long term stability.

Material and methods

Fluorescence labelling

Carbazole-9-Carbonyl-Oxy-Amine (CCOA) labelling of carbonyl groups was performed as described earlier (Potthast et al. 2003; Röhring et al. 2002a, b).

General analytics GPC-MALLS-RI

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; autosampler, HP 1100; column oven, Gynkotek STH 585; fluorescence detector, TSP FL2000; multiple-angle laser light scattering (MALLS) detector: Wyatt Dawn DSP with argon ion laser ($\lambda_0 = 488 \text{ nm}$); refractive index (RI) detector: Shodex RI-71; Data evaluation was performed with standard Chromeleon, Astra and GRAMS/32 software.

GPC method

The following parameters were used in the GPC measurements: flow: 1.00 mL min^{-1} ; columns: four PL gel mixedA LS, $20 \mu\text{m}$, $7.5 \times 300 \text{ mm}$; fluorescence detection: $\lambda_{\text{ex}} = 290 \text{ nm}$, $\lambda_{\text{em}} = 340 \text{ nm}$ (CCOA); injection volume: $100 \mu\text{L}$; run time: 45 min. *N,N*-dimethylacetamide/lithium chloride (0.9% w/v), filtered through a $0.02 \mu\text{m}$ filter, was used as the mobile phase. Historic rag paper samples are completely soluble in DMAc/LiCl.

Standard deviations

The standard deviation for carbonyl group determination is below 5%, for the weighted average molecular weight approximately 5% and for number average molecular weight around 10%. These values are based on long-term determinations of standard pulps.

Laser ablation

Paper analysis was performed by means of direct laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). A 266 nm laser system (LSX100, Cetac technologies, Omaha, Nebraska) was coupled to an ICP-MS (Perkin Elmer DRC, Perkin Elmer, Canada). The ablated material was transported by a 1.0 L min^{-1} Argon gas flow directly into the ICP-plasma after passing a glass wool filter of approximately 5 mm length which was directly placed into the tubing after the laser cell.

The LA-ICP-MS scan was performed before and after calcium phytate treatment. Starting on non-inked paper, crossing the ink line and ending on paper without ink again, a line of 4 mm was scanned with a spot size of 50 μm in order to study the distribution of calcium, iron and copper ions.

Historic letters

Historic paper samples influenced by metallo-gallate ink are rather widely available compared to, e.g., historic samples of pure copper corrosion. We have analyzed a number of letters from the 18th and 19th century with metallo-gallate ink writings on paper from unknown background to gain insight into typical characteristics of historic documents suffering from degradation caused by transition metal ions applied as inks. Three examples are given to illustrate different types of naturally occurring degradation caused by inks on paper. They are referred to as no. 296, no. 298 and no. 300. Per sample three sub samples were taken to get a rough spatial distribution of the damage (Fig. 1). One sub sample was cut out directly from the inked areas named “ink line”, a second one from paper adjacent to the ink line named “next to ink line” and a third from paper in at least 1 cm distance from inked areas named “edge”.

The papers were analyzed without further treatment or aging to study naturally occurring aging and degradation processes.

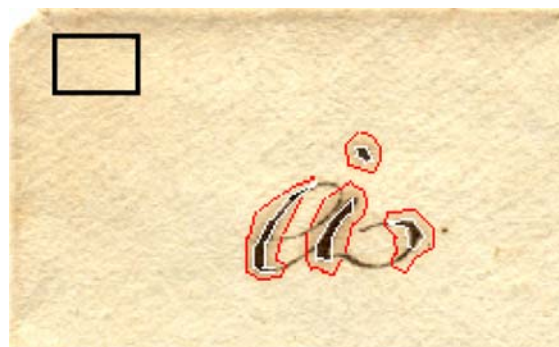


Fig. 1 Detail describing sub sample preparation from sample no. 296. The sub sample from the little black square in the upper left part is referred to as “edge” being a reference illustrating natural aging procedures without the influence of ink. Sub sample “ink line” is described using a white line that surrounds entirely inked areas on the paper sample, sub sample “next to ink line” is described using a red line and covers paper areas directly next to ink application

“K”-samples

Another set of naturally aged papers with metallo-gallate ink was used for testing the phytate treatment on original paper. They are referred to as “K” samples. The sub sampling scheme is found in Fig. 2.

As it is extremely difficult to exactly define historic papers of unknown origin the analysis was performed on one sheet of paper that was divided into different sample sets to prove the efficiency of the treatment.

Treatment and aging

Historic papers (“K” samples)

Each piece was cut into half and each half into three different stripes. Half of the sample was treated with

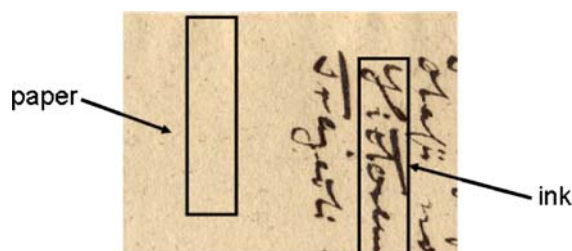


Fig. 2 Detail describing sub sample preparation from “K”-samples

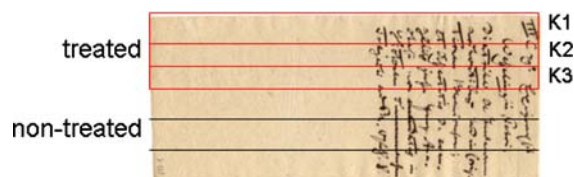


Fig. 3 Historic sample and sampling scheme

phytate, the other half remained as the reference. The treatment with calcium phytate/calcium hydrogen carbonate is based on studies of Neevel and Kolar et al. (Kolar et al. 2005; Neevel 1995) and was performed according to a treatment procedure developed in the course of a DFG research project (see references “Restauration...”), using calcium carbonate (Merck), and phytic acid (Mitsui Chemicals) in solution at a pH of 5.3 (Fig. 3). The pH was adjusted using 1.5% ammoniumhydroxide solution. The sample paper was immersed in a bath for 20 min, dried and sized with 0.15–0.2% gelatine solution using an airbrush. Details on the aqueous treatment are provided by Shirton (1987).

Each sample was then cut into three stripes, which have been submitted to different aging protocols (Fig. 3): K1: 1d pre-aged (70 °C, 50% relative humidity), 7d dynamic aging (55 °C, cycling humidity 35% and 85% relative humidity); K2: 1d pre-aged (70 °C, 50% relative humidity), 7d dynamic aging (55 °C, cycling humidity 35% and 85% relative humidity), 7d static aging (80 °C and 65% relative humidity); K3: non-aged reference.

It was thoroughly tested if there was an influence on the fluorescence labeling, especially of the gelatine, because it contains carbonyl groups. However, no influence could be measured, since the gelatine is completely dissolved during the activation procedure prior to cellulose dissolution in DMAc/LiCl and washed out. The presence of Fe and Cu ions did not show an effect on the CCOA labelling, which is done in Zn-acetate buffer.

Results and discussion

Different degradation patterns of metallo-gallate ink corrosion in historic papers

In the following, three typical examples of historic samples are given (sample 298, 296 and 300) to show in what different ways iron gall ink may change the

condition of paper during natural aging. Differences in the composition of ink and in historical storage conditions translate into significant differences of the way how the cellulose will degrade. These differences can be observed between the different samples, but also between different locations on one individual sample paper, depending on the spatial relation to the writing medium. In order to assess the contribution of oxidation or hydrolysis to the degradation observed, reducing end groups (REG) are plotted against log Mw. The total amount of carbonyls is the sum of reducing end groups (REG) and carbonyls introduced by oxidation. The former contribution can be calculated from the number average molecular weight (Mn) and is indicative for cellulose hydrolysis. Glycosidic bond cleavage by hydrolysis will shorten the cellulose chain and concomitantly generate a “new” reducing end. Contrary to that, oxidation causes generation of carbonyls along the cellulose chain, which is not necessarily accompanied by simultaneous chain breakage. This estimation assumes that all reducing end groups are present as such and not further oxidized, e.g. to the corresponding acid, and that the absolute value of Mn is correctly determined (error approx. 10%).

Sample no. 298 is slightly oxidized all over the molecular weight distribution, easily detectable when comparing $DS_{C=O}$ plots of all sub sample to DS_{REG} -plot. While in sub samples “edge” and “next to ink line” oxidation only plays a minor role, for the sub sample “ink line” a pronounced oxidation is detected in the molecular weight region below 10.000 g/mol. The molecular weight distribution (MWD) of sub sample “next to ink line” mainly follows the molecular weight distribution (MWD) of the “edge” sub sample, indicating that even though adjacent to aggressive metallo-gallate ink almost no decrease in molecular weight took place (Fig. 4, left). The increased amount of carbonyl groups in sub sample “next to ink line” as compared to the “edge” sub sample (Fig. 4, right) is mainly caused by chain scission. In this example ink corrosion is clearly detected, but its influence on chain scission is mostly limited to the ink line.

While in example no. 298 sub sample “next to ink line” follows mainly the “edge” sub sample in molecular weight distribution, in example no. 296 the molecular weight distribution of sub sample “next to ink line” is situated between the two other sub

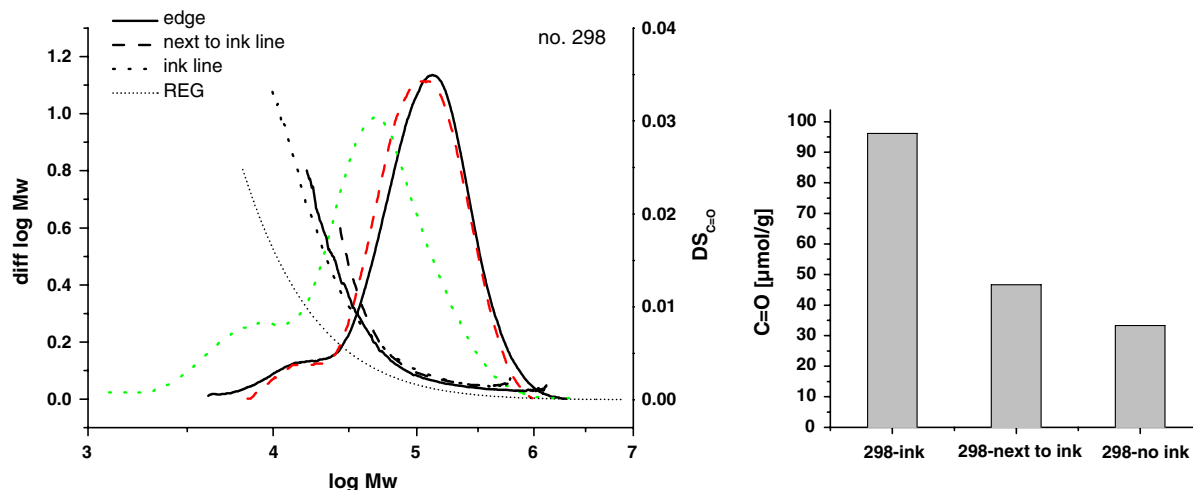


Fig. 4 Results for sample no. 298. Left: $DS_{C=O}$ and MWD: clear degradation is observed due to the action of the ink, nevertheless degradation is mostly limited to ink application. Right: Number of carbonyl groups in different paper regions

samples, indicating that the ink application has obviously influenced adjacent areas of the paper in terms of decrease in molecular weight (Fig. 5, left). In this case sub sample “next to ink line” seems to have a transition status which is an indicator for the aggressive influence of the applied ink even on paper that was not directly covered by it. Pronounced oxidation is found in all three investigated sub samples when comparing their $DS_{C=O}$ plots to the DS_{REG} plot. As the molecular weight distribution is shifted for sub sample “ink line”, heavy oxidation

has taken place, affecting also higher molecular regions. The carbonyl group content is more uniformly distributed, not having a sharp step between “ink line”, “next to ink line” and “edge” (Fig. 5, right).

In example no. 300 the molecular weight distribution of sub sample “next to ink line” is also situated directly in between “ink line” and “edge” sub sample like in example no. 296 (Fig. 6, left). Next to an overall oxidation of the sample no. 300, sub sample “ink line” shows a clear increase in

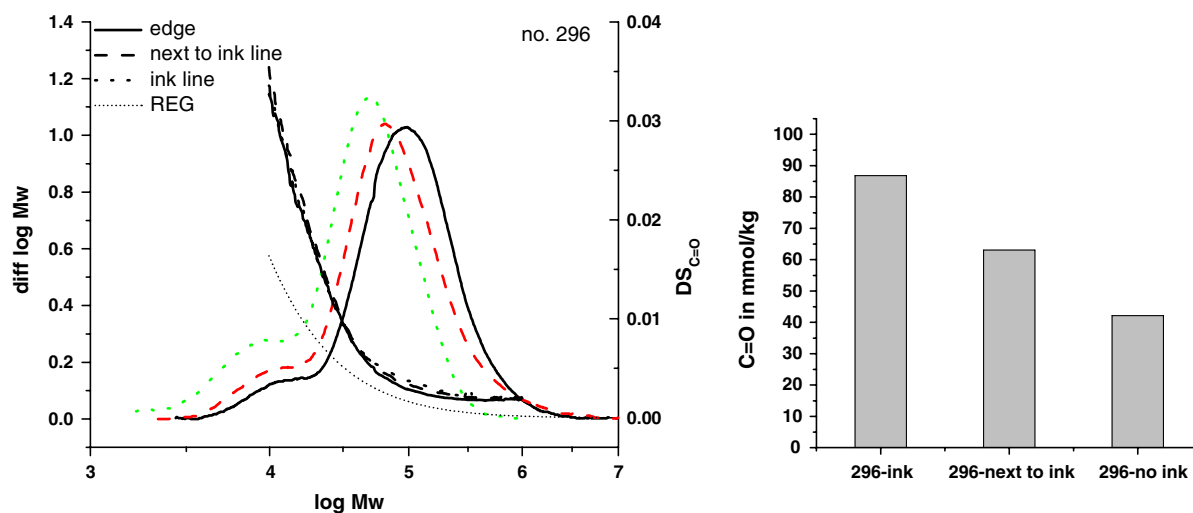


Fig. 5 Results for sample no. 296. Left: $DS_{C=O}$ and MWD: degradation is observed due to the action of the ink, also influencing areas next to ink line. Right: Number of carbonyl groups in different paper regions

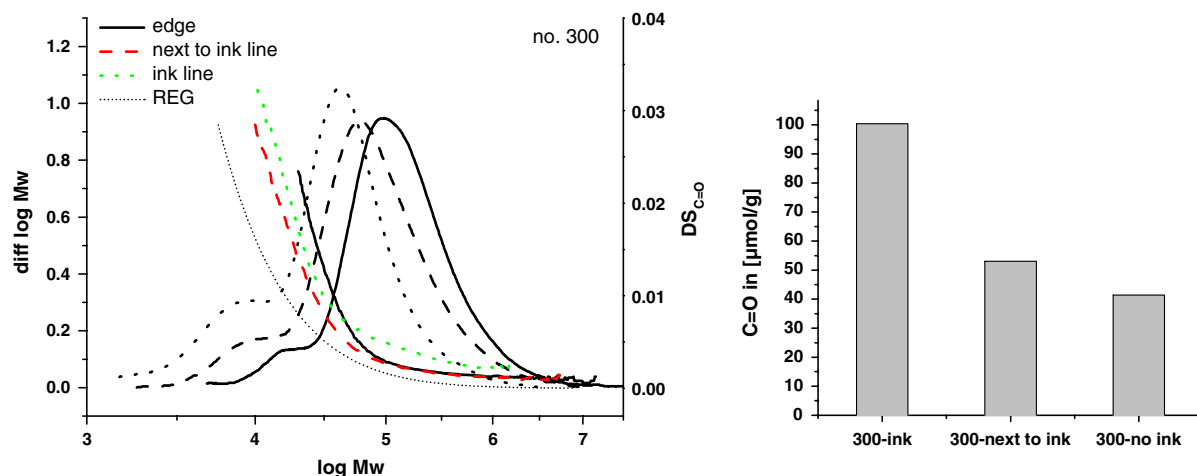


Fig. 6 Results for sample no. 300. Left: $DS_{C=O}$ and MWD: clear degradation is observed due to the action of the ink. Right: Number of carbonyl groups in different paper regions

oxidation rate. This oxidation obviously affects all molecular weight regions, even higher molecular weight regions. Considering the $DS_{C=O}$ plot of “next to ink line” that runs quite parallel to the DS_{REG} plot and a comparatively low increase in carbonyl group content (Fig. 6, right) a possible conclusion is a rather hydrolytic driven influence on the cellulose adjacent to “ink line”.

General features of natural aged cellulose samples

One common feature in all three historic samples shown here as well as in almost all of the historic paper samples we have analysed so far (about 300) is the distinctive shoulder in the region of low molecular weight (here 25000 to 5000 g/mol corresponding to a DP between 30 and 150). We consider this to be a typical attribute of naturally degraded historic samples (Fig. 7, left). This peak contains cellulose fragments formed after severe hydrolytic degradation as well as oxidation. Figure 7 right gives the refractive index signal (mass-proportional) and the carbonyl-proportional fluorescence signal. The region of the above mentioned shoulder shows nicely the high number of oxidized functions in the low Mw peak. This specific feature was not only found for this specific historic sample material, but can be considered a rather general element of naturally aged papers.

It is not always possible to reproduce this pattern under artificial aging conditions and attention should

be paid to the shape of the MWD obtained after accelerated aging.

Phytate treatment

Historic papers (“K” samples)

Before accelerated aging the samples were analyzed to make sure that no unwanted side effects occur during phytate treatment. In Fig. 8 molecular weight distributions before and after treatment are shown. Neither plain paper nor inked paper samples suffer from any detectable change in molecular weight distribution immediately after aqueous phytate treatment. No detrimental effects are observed by the treatment itself.

The data obtained for the historic samples are summarized in Fig. 9. Even though the historic samples have been more oxidized at the beginning of the treatment than model papers, the inhibition of oxidation and hydrolysis are clearly confirmed. Also on plain paper the oxidation is suppressed and the molecular weight is stabilized nearly at the original level. This was a rather unexpected effect at this point. Besides the neutralization of acids found in paper by calcium hydrogen carbonate treatment, the stabilisation of the plain paper by the phytate treatment raises the question to what extent trace amounts of metal ions are responsible for degradation during natural aging. Possibly the phytate treatment is able to strongly mask this ions to withdraw them

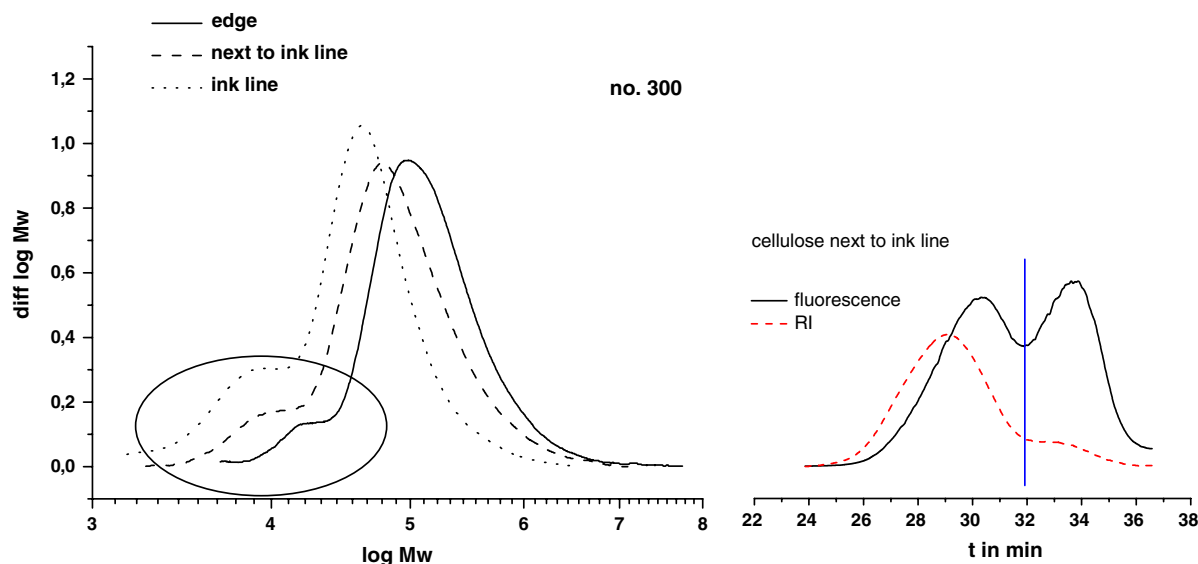


Fig. 7 Left: MWD of naturally aged cellulose taken from a historic letter showing the distinctive shoulder in the low Mw region that is gaining more importance when more damage

occurred in the analyzed paper. Right: RI and fluorescence signal for bulk material and low Mw shoulder

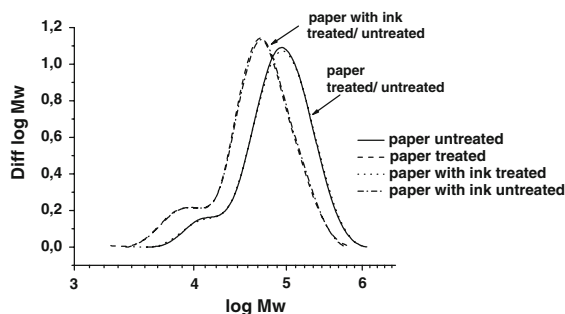


Fig. 8 Historic “K” samples before accelerated aging. The phytate treatment has no immediate negative effect on paper and on paper with ink

from any further interaction during aging. The mechanism for this stabilisation within plain paper still remains to be elucidated.

The extent of stabilization is also remarkably on inked areas. Between the two aging steps no further degradation is detected, both, carbonyl group content and molecular weight, have been stabilized at a value close the their starting values.

Distribution of metal ions

Using LA-ICP-MS the distribution of selected ions across the surface of a piece of paper can be determined. In Fig. 10 it can be observed that across

the ink lines, important amounts of iron and copper are detected, while calcium is only present in minor amounts evenly distributed within the paper surface. After calcium phytate treatment the amount of detectable calcium has increased considerably, but mostly within the ink line, following the distribution of copper and iron ions. The sharp increase and decrease in copper and iron ion content especially after the treatment additionally suggests that no important ion migration has taken place, even though this phenomenon has not been studied in detail in this context.

Conclusions

Analyzing a choice of historical papers containing metallo-gallate inks in detail reveals that metallo-gallate ink causes both, hydrolysis and oxidation, supposedly depending on the type and composition of metallo-gallate ink applied. In one example mostly hydrolytic degradation of ink was found that further was limited to the close vicinity of the applied ink. In another example the damage harmed also adjacent areas roughly 1 mm away from the ink applied. In this case a major influence of oxidation could be determined in addition. All historic samples had in common that a low molecular weight shoulder was observed. This shoulder increased upon more

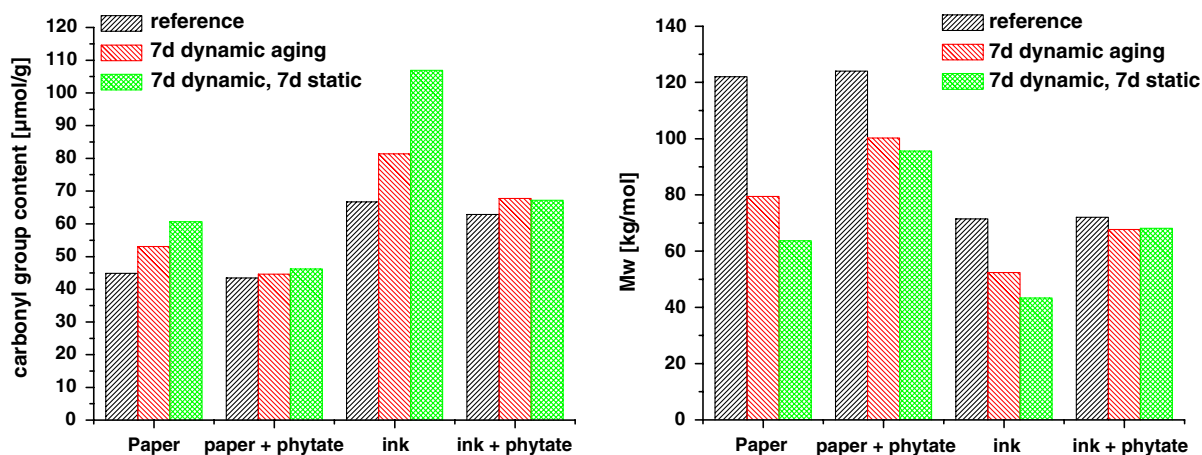


Fig. 9 Left: Carbonyl groups in the plain paper and ink covered areas after two aging stages. The reference sample was not aged. Right: Weight average molecular weight (M_w) in the

plain paper and ink covered areas after two aging stages. The reference sample was not aged

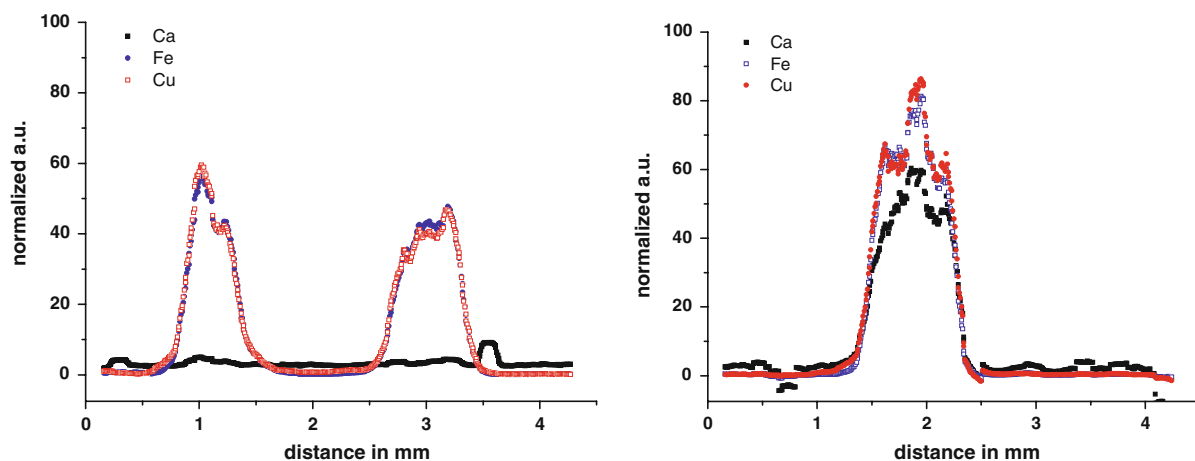


Fig. 10 Left: LA-ICP-MS scan above two inked areas of K-sample before treatment. During LA-ICP-MS the C12 signal was also recorded. As C-atoms monitor the ablation of cellulose surface it was used for normalization to account

for varying amounts of material ablated. Right: LA-ICP-MS scan above one inked area on a treated K-sample. Two different lines have been used to study ion distribution before and after treatment

pronounced degradation. This shoulder contains mainly cellulose degradation products below DP 150 with an elevated degree of oxidation.

Regarding the naturally occurring degradation mechanisms of the historic samples investigated, the stabilization of transition metal ion induced degradation in original papers needs to address both, hydrolytic and oxidative processes at the same time. As shown in previous experiments, calcium phytate, a chelating agent, in combination with calcium hydrogen carbonate to increase the pH, was successfully applied on model papers.

In the present series of experiments, the phytate treatment was very effective in stabilization against degradation caused by historic metallo-gallate inks, containing both, iron and copper ions. The beneficial effect of phytate is attributed to a strong chelation of metal ions of different kind and thus suppressing the generation of reactive species. In addition, the molecular weight distribution is well stabilized by phytate, showing an inhibition also against hydrolytic processes. The data clearly show the effectiveness of the phytate treatment also on historic paper samples, confirming the convincing results of the model compound study. This

successful treatment can directly be linked to a significant increase in calcium ion deposition in very close vicinity to iron and copper ions. Previous research has also shown that phosphate accumulates in the ink region after phytate treatment (Banik et al. 2002). It was therefore concluded that the phytate-iron complex has been formed preferably on the inked areas underlining the effectiveness of the treatment.

Interestingly, not only the processes related to ink corrosion are significantly slowed down but also processes related to the general aging procedure of plain paper like acid hydrolysis are positively affected. This observation can be associated with the neutralization of acids found in paper by calcium hydrogen carbonate treatment. The amount of calcium compound deposition was not quantified in this study. Nevertheless, according to LA-ICP-MS no major amounts of calcium salts were deposited next to the ink line. However, further research has to be performed to clarify the influence of trace amounts of metal ions in plain paper and the contribution of these metal ions to degradation during aging.

The main advantage of the applied analytical approach of functional group labelling followed by GPC is that the key parameters of cellulose aging and subsequent conservation treatments can be quantified. Especially when it comes to processes involving both, oxidation and hydrolysis e.g. reactions triggered by transition metal ions the applied methods allow for a more detailed description of the underlying degradation process of the cellulose molecule.

If the risk of aqueous immersion is acceptable for the historic object to be restored, a phytate treatment should be considered, because its beneficial effects on plain paper and especially on metallo-gallate ink damaged parts could be clearly demonstrated. Further investigations have to be conducted to better understand the action of the phytate in combination with calcium carbonate.

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