Gelatine sizing of paper and its impact on the degradation of cellulose during aging: a study using size-exclusion chromatography
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Citation for published version (APA):
The issue of permanence and durability of paper is one of the major concerns in cellulose research and paper conservation. From the perspective of conservation research, the understanding of the long-lasting properties of paper begins with the investigation of the characteristics of papers in good physical condition that have best survived the passage of time. In European papermaking history, this is the case with early papers, which for the most part, present far better state of conservation than papers of more recent origins. Several facets that could explain the longevity and stability of paper have been investigated in the past, but one that has been largely neglected to date is the process of sizing. Papers dating from the fourteenth to the eighteenth centuries, in addition to having been fabricated from good quality fibres which partly explains their durability, have also in common that they were sized almost systematically with gelatine. The present study is dedicated to the investigation of the role of gelatine in pure cellulose paper. The research is approached mainly from the angle of polymer chemistry. The impact of gelatine sizing upon aging on the molecules of cellulose, and the changes incurred by varying the sizing material are studied. The analytical technique selected is size-exclusion chromatography (SEC), which is employed in the characterisation of both cellulose and the gelatine, and in the investigation of their degradation upon aging. Model papers were fabricated for this purpose, but the study also includes the characterisation of naturally aged papers.

A methodology was developed for dissolving paper in lithium chloride/\textit{N},\textit{N}-dimethylacetamide (LiCl/DMAC), a solvent that was chosen for its non-degrading quality and its compatibility with the SEC columns packing. In order to better comprehend the solvation mechanism, the structure of cellulose and the characteristics of the molecule that condition its accessibility to reactants are presented in the first chapter. In the second chapter, the techniques available to date for the analysis and the characterisation of cellulose are evaluated, and the solvents most currently associated with these methods are reviewed. In order to understand the choices made in the present study, the advantages of SEC for polymer characterisation and those of LiCl/DMAC as a solvent for cellulose are detailed.

The procedure developed for the dissolution of cellulose involves as a first step the activation by solvent exchange, with a water/methanol/DMAC sequence, followed in a second step by dissolution in 8\% LiCl/DMAC at 4\(^\circ\)C. The experiments carried out in order to perfect this method are presented in Chapter 3. A study of the stability of the cellulose solutions in the actual experimental conditions showed that no degradation occurred during the solvation process and confirmed the non-aggressiveness of LiCl/DMAC.
As detection is a crucial aspect of SEC, the detection modes that are available and the type of information each one provides are reviewed in Chapter 4. The principles and the advantages of the detection using multiangle laser light scattering (MALS) coupled with differential refractive index (DRI) are outlined. A section is especially dedicated to the detectors set-up, and to the determination of the parameters required for the characterisation of the molar mass distribution (MMD) of the polymer, the calculation of the molar mass ($M_m$) averages, and the root mean square (rms) radii averages. Among these parameters is the refractive index increment ($dn/dc$) of cellulose in 0.5% LiCl/DMAc. The precision and reproducibility of SEC/MALS/DRI for the analysis of cellulose are evaluated in order to validate the method. MALS also allowed for the characterisation of the polymer in solution. The conformation of cellulose in LiCl/DMAc was determined to be random coil, and a study of the solvent efficiency showed that LiCl/DMAc was a good solvent in the chosen conditions.

The SEC/MALS/DRI method for what is referred as ‘directly dissolved cellulose’ or DDC in LiCl/DMAc is compared in Chapter 5 to two other methods currently used for cellulose analysis. These are viscometry in cadmium triethylene diamine dihydroxide or Cadoxen, and SEC using low-angle light scattering (LALS) and ultra-violet detection of cellulose derivatised to tricarbanilates or CTC. The values of the $M_m$ averages of cellulose obtained with these different methods and the discrepancies on these values are discussed on the basis of the precision of each methodology and the action of the solvents on the polymer. As DDC yielded the highest $M_m$ averages values and viscometry the lowest, several hypotheses are presented in order to account for these differences. Each method is also discussed on the basis of its suitability to characterise the aging-induced degradation of the paper.

In Chapter 6, SEC/MALS/DRI is applied to the study of cellulose from model papers and naturally aged papers. Firstly, the degradation of pure cellulose papers upon heat and humidity aging is characterised. Hydrolytic scissions seem to occur more or less randomly on the cellulose chains. The role of the gelatine sizing in the aging-induced degradation of the papers is evaluated, whether these are laboratory sized, commercially sized or historic samples. Although not always in a significant manner, the presence of gelatine is generally shown to be beneficial to the papers, as evidenced by the lower rate of aging-induced depolymerisation of the cellulose, especially in the high molar mass molecules. However upon aging, the gelatine induced some discolouration of the papers as well as a decrease in their pH, which varied with the type of gelatine, its purity and its concentration in the papers. It was found that the purest grade gelatine, i.e. the photographic gelatine type B, made from cattle bones, induced less yellowing and less acidification of the paper than the food/pharmaceutical grade gelatine type A, made from fish, and of lowest quality.

In Chapter 7, the method of analysis developed is applied to the study of model papers sized with both gelatine and alum (aluminium potassium sulphate hydrate). In this study, alum is found to considerably accelerate the rate of hydrolysis of cellulose upon aging.
Gelatine shows a marked protective role towards cellulose, as the alum-induced degradation of the paper is significantly hampered in the presence of gelatine. Additionally, the alum dramatically increases both the acidity and the discolouration of the papers upon aging. In that respect, compared to the results obtained from the determination of the $M_r$ with SEC/MALS/DRI, neither the pH nor the colour measurements are found to be good indicators of the state of degradation of papers that contain both gelatine and alum. However, for those papers containing only alum and prepared as reference in the evaluation of its impact, pH is found to correlate well with the changes in $M_r$. Both parameters display an asymptotical decrease with the alum concentration, and a threshold value situated between 1 and 1.5 g L$^{-1}$ of alum is determined beyond which no changes in either pH or $M_w$ (weight-average molar mass) can be detected. This limiting value of $M_w$ was found to be 150,000 g mol$^{-1}$.

Finally, the degradation of gelatine in the model papers is characterised in Chapter 8. In this study, a SEC method using UV detection with a photodiode array is developed in order to evaluate the impact of the paper components, such as cellulose and alum on the degradation of the protein upon aging. The application of this method shows that gelatine undergoes hydrolysis and that a characteristic low-$M_r$ fraction forms. The type A gelatine exhibits a faster degradation rate than the type B. The aging leads to a decrease in the extraction yields of gelatine from the paper, with the formation of very high-$M_r$ polypeptides, which is attributed to crosslinking. The presence of alum below 1 g L$^{-1}$ is found to have no impact on the degradation while above that concentration the hydrolysis rate of gelatine is increased.