DE GRUYTER J. Preserv. Libr. Arch. Mater. 2026; aop

Christa Hofmann*, Viktoria Thaller, Maria Katharina Plate, Dubravka Jembrih-Simbürger, Maurizio Aceto, Karin Whitmore, Johannes Bernhardi, Sonja Schiehser and Antje Potthast

Copper Green Pigments in 17th Century Atlases

Kupfergrünpigmente in Atlanten des 17. Jahrhunderts

https://doi.org/10.1515/res-2025-0027
Received October 10, 2025; accepted March 12, 2026; published online June 1, 2026

Abstract: In a conservation project at the Austrian National Library, the condition of green colouration with copper-based pigments on printed maps was assessed in 163 atlases from the 17th century. The pigments of the atlases were characterised by copper indicator papers, XRF, and FORS. The condition of the cellulose fibres was studied with optical microscopy, SEM, and cellulose analysis with carbonyl group labelling. Based on the study of painters' manuals for the green colouration of maps, test specimens were prepared, treated and submitted to accelerated ageing. The test specimens were evaluated visually, with optical microscopy, colour measurements,

***Corresponding author: Christa Hofmann**, Conservation Department, Austrian National Library, Josefsplatz 1, 1015, Vienna, Austria, E-mail: Christa.Hofmann@onb.ac.at
Viktoria Thaller, Conservation Department, Austrian National Library, Josefsplatz 1, 1015, Vienna, Austria, E-mail: viktoria.thaller@onb.ac.at
Maria Katharina Plate, Konservierung-Restaurierung von Papier und Archivmaterial, Schönbrunner Straße 242/1/13, 1120, Vienna, Austria, E-mail: maria-plate-papierrestaurierung@gmx.at
Dubravka Jembrih-Simbürger, Institute for Natural Sciences and Technology in the Arts, Academy of Fine Arts Vienna, Kelsenstraße 2, 1030 Vienna, Austria, E-mail: d.jembrih-simbuerger@akbild.ac.at
Maurizio Aceto, Dipartimento per lo Sviluppo Sostenibile e la Transizione Ecologica, Università\ degli Studi del Piemonte Orientale, Piazza Sant´ Eusebia, 5, 13100, Vercelli, Italy, E-mail: maurizio.aceto@unipo.it. https://orcid.org/0000-0001-6360-3632
Karin Whitmore and Johannes Bernhardi, University Service Centre for Transmission Electron Microscopy (USTEM), TU Wien, Stadionallee 2/057-02, 1020, Vienna, Austria, E-mail: karin.whitmore@tuwien.ac.at (K. Whitmore), johannes.bernhardi@tuwien.ac.at (J. Bernhardi)
Sonja Schiehser, Institute of Chemistry of Renewable Resources, BOKU – Universität für Bodenkultur Wien, Muthgasse 18, 1190, Vienna, Austria, E-mail: sonja.schiehser@boku.ac.at
Antje Potthast, Institute of Chemistry of Renewable Resources, BOKU – Universität für Bodenkultur Wien, Muthgasse 18, 1190, Vienna, Austria, E-mail: antje.potthast@boku.ac.at. https://orcid.org/0000-0003-1981-2271

and cellulose analysis. The addition of alum and vinegar to solutions of verdigris produced degradation on flax-hemp paper comparable to the degradation observed on copper-green colouration in 17th century atlases. Nine atlases with severe degradation caused by copper-green pigments were selected for treatment with the complexing agent benzotriazole and for stabilisation with precoated Japanese tissue papers that contained the antioxidant tetrabutyl-ammonium bromide.

Keywords: copper green pigments; colouration of maps; atlases; conservation treatments

Zusammenfassung: In einem Konservierungsprojekt der Österreichischen Nationalbibliothek wurde der Zustand von grüner Kolorierung mit Kupferpigmenten auf gedruckten Karten in Atlanten des 17. Jahrhundert erfasst. Die Grünpigmente wurden mit Kupferindikatorpapieren, RFA und FORS charakterisiert. Der Zustand der Cellulosefasern wurde mit optischer Mikroskopie, REM und Cellulose analyse untersucht. Nach dem Studium von Malerhandbüchern für die Kolorierung von Karten wurden Probekörper hergestellt, behandelt und beschleunigt gealtert. Die Probekörper wurden visuell, mit optischer Mikroskopie, Farbmessungen und Cellulose analyse ausgewertet. Der Zusatz von Alaun und Essig zu Lösungen von Grünspan führte zu einer Schädigung von Flachs-Hanf-Papier ähnlich jener auf kolorierten Karten aus dem 17. Jahrhundert. Von 163 Atlanten wurden neun mit schweren durch Kupfergrün verursachten Schäden für eine Behandlung ausgewählt. Braun verfärbte, brüchige Stellen wurden mit dem Komplexbildner Benzotriazol lokal behandelt und mit beschichteten Japanpapieren stabilisiert. Der Klebstoff enthielt das Antioxidans Tetrabutylammoniumbromid.

Schlüsselworte: Kupfergrünpigmente; kolorierte Landkarten; Atlanten; Restaurierungsbehandlungen

1 Introduction

During conservation work on atlases for the Map Collection of the Austrian National Library, frequent changes of green hues on coloured maps were observed, which exceeded the changes observed on green pigments in watercolours and illuminated manuscripts. The brown discolouration on maps is accompanied by the degradation of the paper carrier, a phenomenon that is especially pronounced in bound atlases. These observations gave rise to the idea of conducting a survey of atlases with coloured maps from the 17th century. The aim of the survey was to characterise the materials, to assess the risk of degradation and to develop solutions for conservation and preservation.

Intaglio prints were hand-coloured for aesthetic reasons and, in the case of maps, also for enhanced readability (Figure 1). The methodical colouration of borders and territories developed in the 17th century (Enzel et al. 2021). During this period, Amsterdam was the renowned centre for cartography where the profession of map painters and colourists emerged. It became customary for the publisher to commission the application of colours on demand. Coloured atlases were sold at higher prices. The colouration of maps was undertaken in specialised workshops as well as within the domestic environment (van der Linde 2020). Colours were applied in translucent washes to define territories and borders, whilst ensuring that the printed ink lines remained visible. The predominant colours observed in 17th century atlases of the Map Collection were yellow, blue, green, and red. Black was derived from the print, with white occasionally utilised for highlighting or as an additive with other pigments.

Until the 19th century, the selection of green hues was constrained to copper-based pigments, organic green colourants, or the mixture of yellow and blue pigments. In painters' and colourists' manuals, verdigris is predominantly stated for green. The synthetic pigment was normally manufactured by subjecting metallic copper to acetic acid in the presence of oxygen at elevated temperatures. The resulting blue-green pigment is a copper corrosion product, most typically a copper acetate compound (Eastaugh et al. 2004). Depending on the recipe and the preparation method, the pigment can be a mixture of different copper compounds (Banik

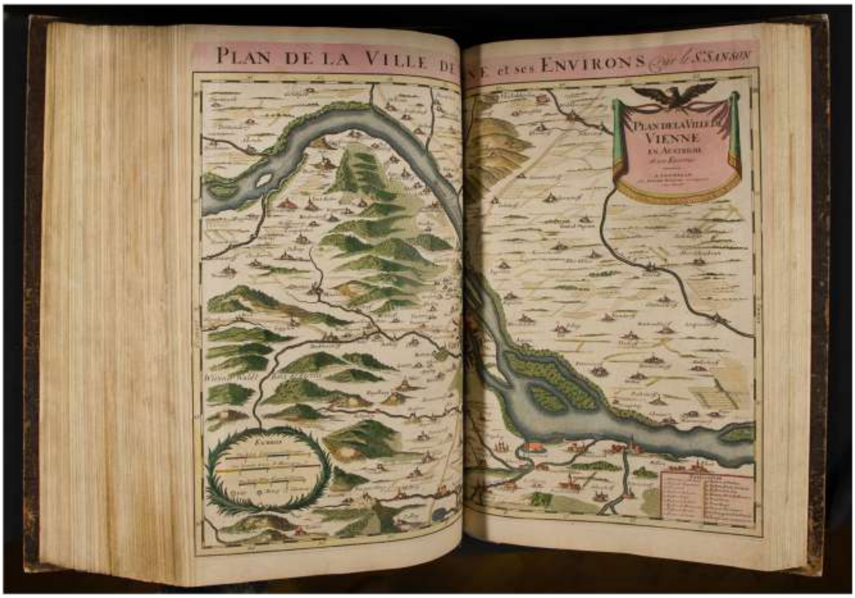

Figure 1: Coloured map of Vienna and its surroundings, map 166 in Atlas FKB 273-5.

and Ponahlo 1982; Henniges et al. 2005; Malešič et al. 2020). Verdigris can be produced in neutral and basic form. A study by Brostoff and Ryan suggests that the prevalent form of verdigris was “neutral”: $Cu(CH_3COO)_2{\cdot}H_2O$ (Brostoff and Ryan et al 2020; Brostoff et al. 2020). The aged pigment is difficult to characterize (Henniges et al. 2005; Brostoff and Ryan 2020). The addition of J. Schlüter, M. Edney, D. Lange et al. organic green and yellow colourants, such as sap green or saffron, has been demonstrated to be an effective method of tempering the vivid blue-green tones of verdigris as described in painters’ manuals (Theophilus 1999; Boltz von Ruffach 1913; Thompson 2018). In the comparison of recreated colour recipes on paper with miniatures in 15th century manuscripts, mixtures of verdigris with organic green and yellow colourants (Eastaugh et al. 2004) could be observed (internal report, Conservation Department, Austrian National Library).

Historical painters’ manuals describe a wide variety of recipes for a “wash”, a translucent liquid colour, from verdigris for the colouration of prints (Lindenbergh 1742). In most cases, the pigment was mixed with white wine vinegar and/or water. In some versions, the blue-green coloured vinegar was used to paint, after straining out the pigment grains, while other recipes involved the addition of tartrate, alum, and gum Arabic (Jordan 1531; Salmon 1685; Gautier 1708).

Since atlases were compiled by publishers for customers, 17th century atlases may contain maps of varying paper qualities. Paper was not produced specifically for intaglio printing until the 18th century (Stijnman 2012). Prior to this, printers had to select suitable paper themselves. For intaglio printing, the paper had to be white, smooth, and have little or no sizing (Stijnman 2012). Printed maps were probably partially or completely sized before colouring. In their manuals, Salmon (1685) and Lespinasse (1801) recommend treating the paper of a print with alum water before colouring. Presumably, the application of alum (potassium aluminium sulphate) was done before colouring the map at the colourist’s workshop. Alum could also have been added during the paper making process: to harden the gelatine, to avoid mould growth in gelatine sizing (Brückle 1992), and to prevent the sized sheets from sticking together (Petersen 2020). Fei-Wen Tsai found evidence of alum in Dutch coloured maps of the 16th and 17th century that she ascribes to alum-induced degradation of unsized paper (Tsai 1992). Brostoff et al. detected high amounts of potassium and sulphur on selected hand-coloured maps of a Ptolemy’s atlas from 1513 and attributed the elements to alum-hardened sizing from a later treatment (Brostoff et al. 2011).

Verdigris in its different chemical compositions (Brostoff and Ryan 2020) can shift colour from green to brownish tones. In the process of ageing, the colour change indicates chemical reactions mostly caused by copper ions contained in the pigments and humidity. Copper ions catalyse the oxidative and hydrolytic degradation of cellulose fibres (Henniges et al. 2005; Malešič et al. 2020). During this process, the paper coloured with copper-green pigments becomes brittle and easily breaks when it is handled. Alterations of paper caused by verdigris are especially pronounced on hand-coloured maps. The addition of vinegar and alum in the paper and pigment preparation as well as the application in form of a dilute wash might enhance degradation processes on maps. In an atlas, the folded maps are generally mounted on paper guards with animal glue. Brittle and degraded paper in this area of the binding is prone to damage caused by the mechanical stress while turning the pages and due to the strength and thickness of the paper guard (see Figure 13).

The objectives of the two-year conservation project at the Austrian National Library were as follows:

1. to survey the condition of maps with copper-based colouration in atlases including the influence of storage in bound volumes,
2. to characterise the pigments, the paper, and the influence of possible additives,
3. to treat endangered, degraded maps and to monitor the long-term effects of these treatments.

In conjunction with the Map Collection, atlases from the period between 1580 and 1720 were selected, as this was the period during which the production of atlases reached its zenith. The Map Collection at the Austrian National Library holds 220 atlases from this period, 163 of which contain hand-coloured maps. Most of the atlases were produced in Amsterdam, which became the centre of map and atlas production in the 17th century. These books have been stored together under similar conditions for at least 100 years. In bound volumes, the reactions of copper-containing pigments may be exacerbated by higher concentrations of degradation products, the migration of copper ions, and the mechanical stress caused by the binding structure and by turning the pages. The transfer of brown discolouration and mechanical damage in the gutter areas in atlases have been observed in previous interventions at the Conservation Department. The collection provides an opportunity to study the effects of previous treatments and develop long-term monitoring of new conservation efforts.

The project commenced with a condition survey that concentrated on green copper-based colouration. The coloured areas on the maps were characterised using copper indicator papers, X-ray fluorescence spectrometry (XRF), and fibre optic reflectance spectrophotometry (FORS). The analysis of fibre morphology in addition to scanning electron microscopy (SEM) and cellulose analysis with molar mass distributions and carbonyl group labelling has provided further insights into the extent of cellulose degradation. A review of the literature on the historical preparation and application of verdigris in washes on prints was conducted. Subsequently, test specimens with verdigris on paper were prepared and submitted to accelerated ageing to study factors that influence changes, such as the addition of vinegar and alum. The optional treatments involving complexing agents (benzotriazole, BTA) and antioxidants (tetrabutylammonium bromide, TBAB) were applied to unaged and pre-aged test specimens. In one particular sample set, the BTA treatment was combined with the reinforcement by precoated Japanese tissue papers that contained TBAB. The specimens were then compared with the historical maps and evaluated visually, by fibre morphology, colour measurement, and cellulose analysis.

Nine atlases with severely deteriorated copper-green areas, which were in imminent danger of loss, were selected for treatment. The primary objective of conservation efforts was to stabilise the prevailing condition and to forestall any further deterioration. The ensuing discourse shall encompass the primary outcomes of the condition survey, material characterisation, ageing study, and conservation treatment.

2 Results of Survey of Coloured Maps in 17th Century Atlases

Of the 220 atlases produced between 1580 and 1720 in the Map Collection, 163 contain maps with hand colouration. It is evident that the maps are generally composed of copperplate prints on rag paper, with occasional instances of etchings being utilised in conjunction. The atlases that were the subject of the investigation contained between 70 and 250 maps in each volume. The maps, which measure in general 530 mm × 620 mm, were folded in the middle, and then glued to a guard with which they were bound in the body of the book. Most atlases are bound in leather covers over wooden boards. Some have been rebound in paper over cardboard covers. In the atlases that were produced or dedicated to a specific client, the maps are more uniform regarding paper quality and colouration. In so-called collective atlases, maps of different origin and quality were assembled. In these bound volumes, the condition of paper and colouration varies widely. As we focused on the condition assessment of green coloured areas, we adapted the condition rating established by Alexandra Pahl in her master thesis (Pahl 2022), see Table 1.

The number of atlases in the different condition ratings is listed in Table 2. Of the 163 atlases examined, the maps in 125 (76.7 %) volumes were assigned condition ratings 0–III, while the maps in 38 (23.3 %) volumes received ratings IV–V (Table 2, Figure 2). This means that a majority of the coloured atlases seem to be in stable condition without immediate need for intervention like the reinforcement of brittle paper and tears when stored in a controlled environment. The green colour has changed, but the paper is still flexible and is not endangered by the binding structure. These books can be used in the reading room with due care.

Table 1: Condition categories.

Condition category	Description
0	No apparent change
I	Verso blue green or green strikethrough, recto no visible colour change
II	Verso blue green/green or light brown strikethrough, recto beginning colour shift to yellow green.
III	Verso light brown strikethrough, recto colour shift to brown-green, sometimes haloes, browning at margin of wash, possible light-coloured transfer on adjacent pages.
IV	Verso dark brown strikethrough, recto brown discolouration, sometimes dark haloes, possible brown transfer on adjacent pages.
V	As IV, tears and breaks that may include losses

In the 38 atlases of category IV–V, where the green coloured areas show visible and physical degradation, we detected a wide range of phenomena. One frequent observation was that a high proportion of binder or adhesive seems to prevent colour change. In the gutter area where the map is glued to the guard with a protein adhesive, the green colour is sometimes better preserved (Figure 3). In areas with thicker paint layers that contain more binder, for example in cartouches and on title pages, the green pigment maintained its chromaticity. Printing ink or sizing can also help prevent the catalytic activity of copper ions. We assume that sizing, binder, or glue safeguards the cellulose fibres from the action of copper ions similar to presumed reactions of iron gall inks on paper (Kolbe 2004). Comparable phenomena are described in the investigation of the Ptolemy's *Geographia* in the Library of Congress (Brostoff et al. 2011). Low paper quality, weak paper sizing as well as the influence of high humidity seem to increase degradation. Considering the examination of painters' manuals referenced above and the observations made during the survey of atlases, it is proposed that verdigris was employed as a dilute solution, comprising minimal or no pigment particles, and potentially without the addition of gum Arabic (Lindenbergh 1742).

During the survey, we compared observations of previous treatments with the reports that we found on these interventions in the records of the Conservation Department. We noted that in general treatments undertaken in the 1970s and the early 1980s which introduced high amounts of moisture, often led to the formation of tide lines, the migration of degradation products, and the occurrence of further damage. In instances where a thick paper and a thick adhesive layer had been utilised for reinforcement, the brittle paper of the map was susceptible to breakage at

Table 2: Condition rating.

Condition category of green coloured areas	Number of atlases	Percentage of atlases
0	9	5 %
I	23	14 %
II	44	17 %
III	49	30 %
IV	24	15 %
V	14	9 %

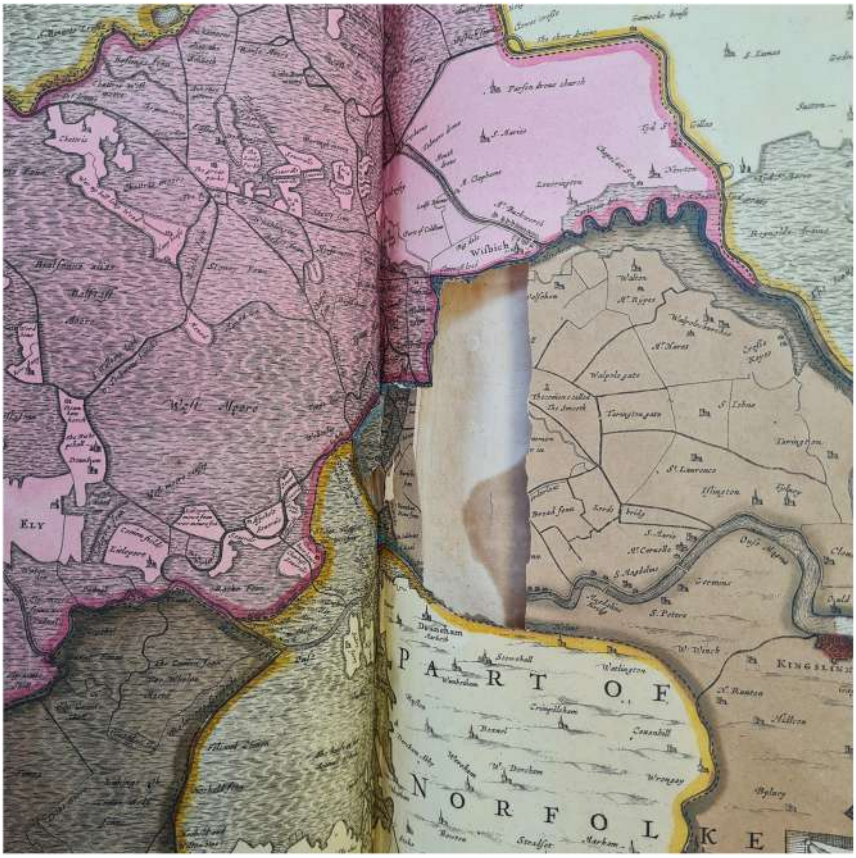

Figure 2: Detail of green colouration in condition category V, map of Lincolnshire from Atlas 393686-E KAR 3.

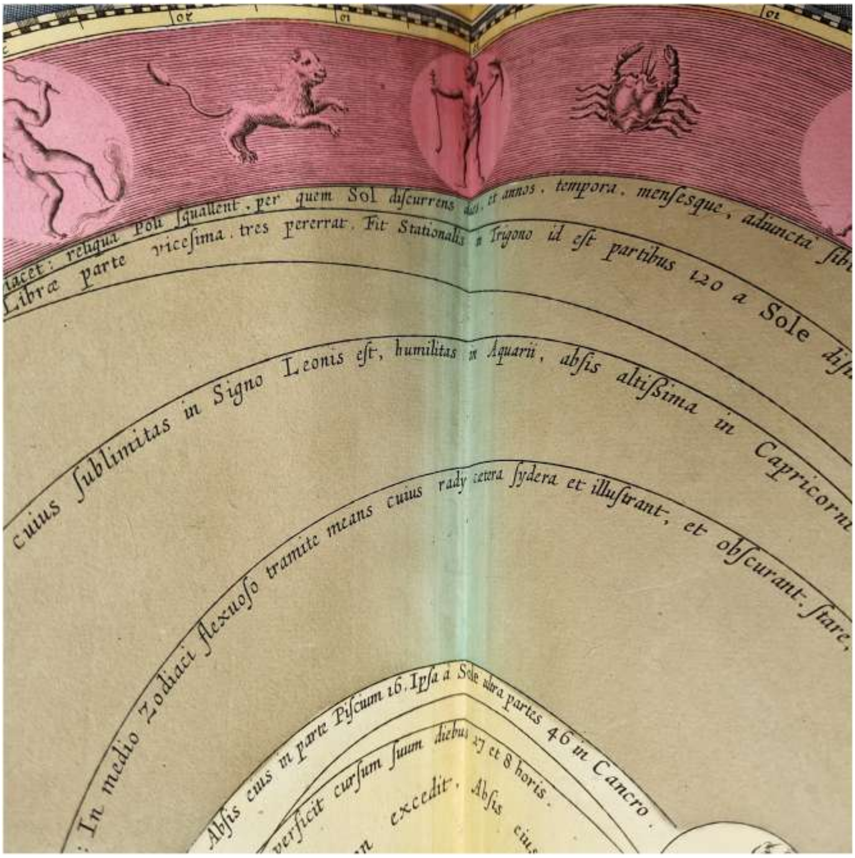

Figure 3: Detail of preserved green colour in the gutter area, where the map is glued to the guard, Atlas 393686-E KAR 1.

the border of the repair paper. The treatments that were executed during the late 1980s and 1990s utilising low moisture and thin Japanese papers appear stable.

In discoloured, brittle areas, mechanical stress caused breaks and subsequent losses. When the pages are turned, more stress is put in the area close to the gutter, especially when the binding is tight (see Figure 13). Thick, stiff paper guards and a high amount of animal glue used for hinging the maps in the atlas exacerbate the stress. Large, folded maps are likely to break in the folds. In some cases, it is no longer possible to open the folded map.

3 Material Characterisation by Analysis

The green pigments and the colour palette were characterised by non-invasive methods (copper indicator papers, XRF, and FORS). The aim was to correlate visual observations of pigments and papers with material analysis. Microsamples of fragments from degraded areas were investigated by optical microscopy. As we did not want to take additional samples from the maps, the samples were restricted to existing fragments. To assess the condition of cellulose fibres, microsamples of fibres from degraded, detached fragments were studied with optical microscopy and Scanning Electron Microscopy (SEM) in comparison with new rag paper and a microsample of uncoloured paper from the folded corner of one map. The molecular weight distribution and the carbonyl content of the historical microsamples was analysed with Gel Permeation Chromatography (GPC). The methods are described in Appendix B.

Further characterisation of green copper pigments was attempted with Raman spectroscopy and ATR-FTIR. Due to the high fluorescence of the cellulose and the dilute application of pigment washes, the aged pigment verdigris could not be clearly identified. Considering these limitations, the copper indicator paper appeared as useful, simple tool to confirm the presence of copper ions in the colouration.

3.1 Copper Indicator Papers

Non-bleeding copper indicator papers were prepared according to Hulthe (1970). A strip of indicator paper (Whatman No. 1) is wetted with one drop of deionised water and put in contact for 1 min with the pressure of the fingertip (in gloves) with the green coloured area on the recto side of the map to be studied. The tested area is supported with blotting paper in a polyester sleeve. In the presence of copper, the indicator paper turns orange. The test was recently evaluated by Jasna Malešič and proved to be more sensitive than other non-bleeding copper tests (Malešič 2025). The test was used on selected maps to verify the visual assessment of green colouration or degradation by copper containing pigments. The indicator papers confirmed the presence of copper on all the tested maps on the recto side.

3.2 X-Ray Fluorescence Spectrometry (XRF), Fibre Optic Reflectance Spectrophotometry (FORS)

The following areas were analysed with XRF point measurements and XRF scans (area: 10 mm × 10 mm): browned, degraded areas of former green colouration;

brown transfers on adjacent maps; blue-green washes in the gutter area and on well-preserved maps; and reference points in the uncoloured paper margin. The atlases used for this analysis were 393686-E KAR 2 and FKB 273-5 (see list of atlases and methods in Appendix A). The utilisation of organic colourants was the subject of investigation with FORS.

The XRF results confirm relatively high copper intensities in green and brown degraded areas. Figure 4 shows the XRF scan of a detail on the map *Italia* (393686-E KAR 2). The copper intensities are higher on maps where the blue-green colour of comparable application is preserved (results not shown). Furthermore, it can be seen that also low chlorine intensities are detected on the detail of map *Italia*. The lower chlorine intensities in the browned colouration attributed to verdigris compared to the surrounding area (Figure 4) are due to the fact that copper in verdigris acts as an effective absorber of lower X-ray energies, in this case low-energy Cl Ka X-rays. The origin of the low chlorine intensities has not yet been clarified. Tsai found chlorine on maps in a 17th century atlas from Amsterdam that she attributes to the use of sea water or salt-contaminated water during paper making (Tsai 1992) in the Netherlands. The place of paper production for the investigated map *Italia* could not be defined. Before intaglio printing, the finished sheets of paper are usually wetted in water (Neunteufel 2024). If the water used in Amsterdam during printing of the map was salt-contaminated, this water could be a source for traces of chlorine in the map. As shown in the distribution map for potassium, higher intensities of the potassium Ka line are measured in the brown areas than in the uncoloured paper areas. In general, low intensities of sulphur and potassium Ka lines in the paper indicate the application of alum (potassium aluminium sulphate). The higher amounts of potassium in the coloured area could point to a pre-treatment with alum before colouration. High intensities of potassium and sulphur in the investigation of maps of Ptolemy's *Geographica* were ascribed to alum-hardened sizing and attributed to a later treatment of selected maps by Brostoff et al. (2011). The detection of copper in

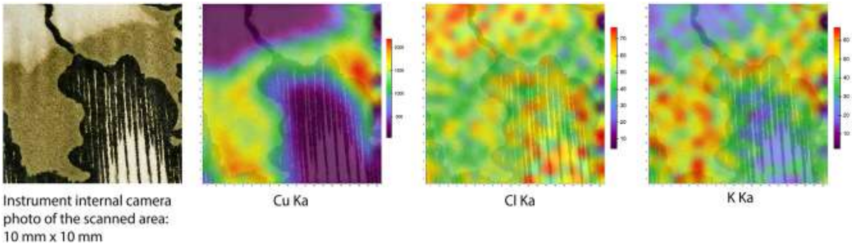

Figure 4: XRF scan on the map *Italia* in Atlas 393686-E KAR 2, with elemental distributions of copper (Cu), chlorine (Cl), and potassium (K).

brown transfer areas on adjacent maps in the atlas confirms the ability of copper ions to migrate to surrounding pages.

Combining XRF, FORS (data not shown in this context), and visual comparison, the following palette could be described for maps in the atlases 393686-E KAR 2, 393952-E KAR 2 and FKB 273-5:

– Green: copper containing pigment (possibly verdigris)
– Blue: azurite, indigo
– Red: vermilion, red ochre
– Yellow: organic colourant (not identified)
– Pink: scale insect dye
– Violet: azurite, scale insect dye

For washes on territories and colouration of borders, green copper-based pigments, azurite as well as yellow and pink colourants were used. City outlines were defined with vermilion. The palette corresponds to recent findings on coloured Western maps (Enzel et al. 2021; Pereira et al. 2024).

3.3 Optical Microscopy

The fibre morphology was studied with a polarised light microscope (Zeiss Axiolab 5 KMAT) at 100× magnification in transmitted light and with crossed polarisation filters. Fibres from new paper handmade with flax and hemp fibres (Gangolf Ulbricht), naturally aged rag paper and uncoloured paper from the folded upper corner of the map *Arabia* (393686 – E KAR 3) were compared with fragments of degraded copper green colouration on paper from the maps *Italia* and *Picentia* (393686 – E KAR 2). The fibres from the margin of the copper print are shorter than those of new rag paper (Figure 5 upper image). On the historical uncoloured paper, broad fibres, degraded fibre walls and split ends can be observed (Figure 5, middle image). In comparison with uncoloured papers, the fibres from the historical fragments of brown copper-degraded areas are extremely short and deteriorated (Figure 5, lower image). The fibre morphology illustrates the brittleness and fragility of the paper degraded by copper pigments.

3.4 Scanning Electron Microscopy (SEM)

The same sample set as mentioned above was studied by SEM at USTEM of TU Wien. Images of the samples' surfaces and cross-sections (see Appendix B) confirm that the cellulose fibres with degraded copper green have changed the most in comparison

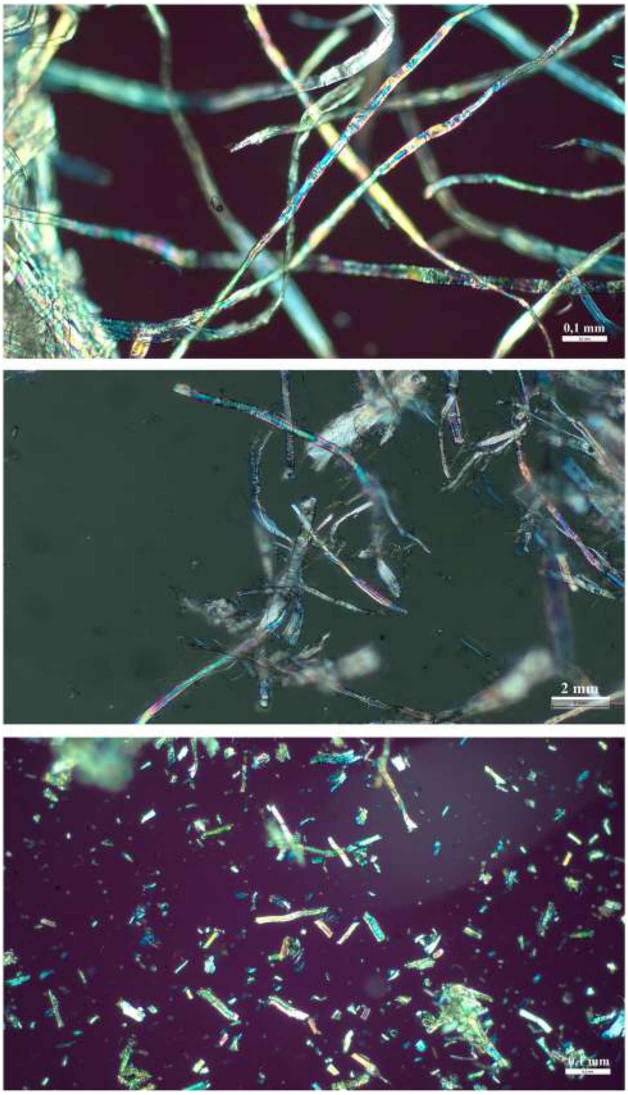

Figure 5: Flax and hemp fibres of new hand-made paper (upper image), fibres from uncoloured paper from a folded upper corner of the map *Arabia*, Atlas 393686-E KAR 3 (middle image) and degraded fibres from a fragment with corroded green colour of the map *Italia,* Atlas 393686-E KAR 2 (lower image) at 100× magnification in transmitted light and with crossed polarisation filters.

with historical and new uncoloured paper (Figure 6). In cross-sections, fibres have collapsed. On the surface and in cross-sections, broken cellulose fibres are visible

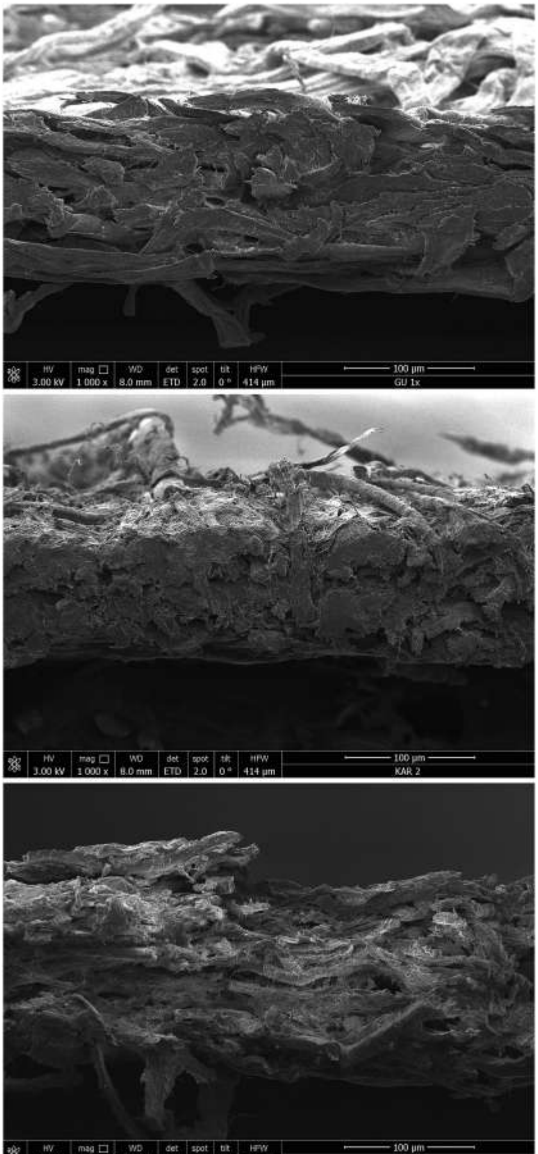

Figure 6: SEM images of paper cross-sections at 1,000×, upper image: new hand-made rag paper, middle image: uncoloured paper from the folded upper corner of the map *Arabia* (393686-E KAR 3), lower image: paper with degraded copper green colour from the map *Italia* (393686-E KAR 2).

(Figure 6, lower image). In comparison, the fibres from the uncoloured paper margin show less collapsed fibre-cores and more intact fibre structures (Figure 6, middle image). In the cross-section of the new handmade paper, the fibre-cores are distinguishable and the fibre structure is the least altered (Figure 6, upper image).

3.5 Cellulose Analysis with Carbonyl Group Labelling Followed by Gel Permeation Chromatography (GPC)

Samples from the map *Picentia* (KAR 393686-E KAR 2), both uncoloured paper from the margin and fragments with degraded copper green were analysed with GPC coupled with light scattering and fluorescence labelling for carbonyl groups to determine the molar mass distribution and the content of carbonyl groups. The average molar mass of the paper sample from the margin is 94.5 kDa which corresponds to degraded historical rag paper (Henniges et al. 2009). The paper sample with copper green has a Mw of 38.3 kDa which can be considered extremely fragile and close to the level-off degree of polymerisation of rag paper (Figure 7). When cellulose is degraded, this includes hydrolysis and oxidation, its molar mass, i.e., degree of polymerization, drops fast at first and then reaches a nearly constant plateau. That plateau value is called the level-off DP (LODP). Physically, the LODP can be viewed as the limiting chain length that remains after the more degradation-susceptible amorphous regions have been cleaved. A LODP of native cellulose is in the range of 200–300, i.e., ~ 30–50 kDa (Battista and Smith 1962).

The carbonyl group content of the paper is 65 µmol/g and of the paper with copper green 140.0 µmol/g. To better illustrate these numbers, we can say that every 66th anhydroglucose unit (AGU) is oxidised and bears a keto group in presence of copper but only every 154th AGU in case of no copper contact. In the sample with

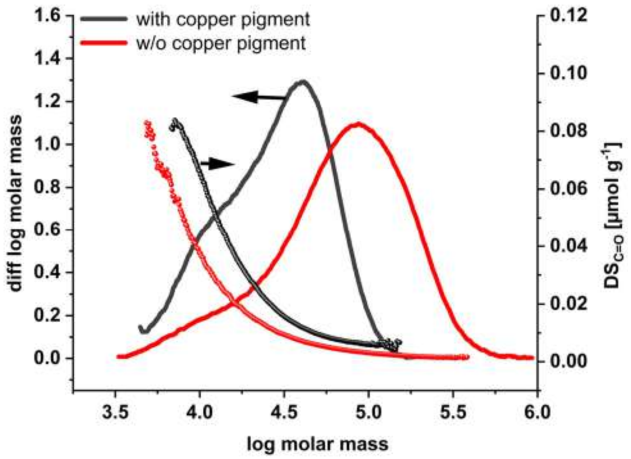

Figure 7: Molar mass distribution and distribution of carbonyl groups of samples from the map *Picentia* (393686-E KAR 2) with copper (black) and without copper pigment (red).

copper contact, approximately 95 μmol/g correspond to keto groups along the cellulose chain and about 45 μmol/g to reducing end groups (Sulaeva et al. 2024a, 2024b).

The rag paper of the map is aged. The paper with copper green is extremely oxidised. This confirms the visual assessment and the observed fragility of the paper. The results of the material characterization – the extreme decrease in molar mass, the high carbonyl group content, and the collapsed fibre structures observed by SEM – provided the analytical basis for the subsequent decision-making process and the design of the ageing experiments with test specimens. In particular, the GPC data from the historical samples served as a benchmark against which the artificially aged test specimens could be evaluated.

4 Decision Making Process

For our two-year project, we selected nine atlases with coloured maps (see Appendix A). The green colours were in the afore mentioned categories IV to V (Table 1). Due to the poor condition, access to the atlases was restricted or not possible for readers. When turning the pages, there was a high risk of causing tears and losses, especially in areas close to the gutter. Some folded maps could no longer be opened. The aim of the conservation treatment was to stabilise the condition, to prevent further damage, and to enable limited access.

In our decision making process we considered the results of a previous research project on copper based green pigments on paper at the Austrian National Library (Hofmann et al. 2015) which showed that the complexing agent BTA and the antioxidant TBAB (Malešič et al. 2020) can stabilise test specimens of copper-green pigments on paper in accelerated aging experiments (Ahn et al. 2015). In a following conservation project, areas with degraded copper-green pigments of coloured prints in books and of maps in an atlas were treated locally with 3 % BTA in ethanol applied to the verso by brush (Hofmann et al. 2016). Tears and brittle paper were reinforced with precoated Japanese tissue papers. The copper-green corrosion appears to be stable after one decade of natural ageing. There is no new physical damage in brittle areas. The treatment has not resulted in obvious colour changes. The books can be handled and consulted with due care.

With the objective to test treatment options for copper-green pigments in coloured maps in atlases, Hannemann (2023) prepared pre-aged samples of verdigris on paper and treated them with BTA and TBAB individually or combined, including BTA- and TBAB-loaded precoated Japanese tissues in collaboration with the Conservation Department of the Austrian National Library (Hannemann 2023). After accelerated ageing, verdigris samples treated with BTA and TBAB showed both visually and haptically a positive effect; however, no chemical analysis of these papers is available.

Therefore, we considered treating degraded copper green (category IV to V) on the maps with BTA and to reinforce mechanical damage with TBAB-loaded precoated Japanese tissue papers. To support the decision making, a new series of experiments was conducted. A limited number of test specimens was chemically analysed.

5 Ageing Experiments with Test Specimens

Based on the decision to apply BTA and TBAB as treatment options (see Section 4), test specimens were prepared to evaluate these treatments under conditions matching the observations in the atlases. Two ageing series were conducted: the first to identify the paper and colour recipe most closely resembling the degradation observed on 17th century maps, and the second to assess the effectiveness of the selected treatments.

In preliminary tests for the choice of treatment at the Austrian National Library, 10 year naturally aged samples with verdigris (Kremer Pigments) in gum Arabic (powder, Kremer Pigments) from the previous project (Hofmann et al. 2015) and pieces of Whatman No. 1 were treated with 3 % BTA (VWR) in isopropanol and with 1 % TBAB (VWR) in isopropanol. SEM images showed that the solutions penetrated the paper fibre network uniformly and did not change the surface morphology (images not shown in this publication). On the naturally aged samples with verdigris, line scans with energy dispersive X-ray analysis (EDX) did not detect higher copper concentrations outside the coloured area on samples taken from treated areas, in comparison with samples taken from untreated areas. This means that the applied solutions did not lead to the migration of copper ions.

Based on our previous experiments (Hofmann et al. 2015; Ahn et al. 2015), Hannemann's master thesis (2023), the condition survey, and the study of historical sources, we aimed to prepare test specimens that match the appearance of green washes on maps. To gain a sense of the practical aspects of the colouration process and the materials involved, several variations of the application of alum in different concentrations as well as colour recipes were recreated in preliminary tests. Painters' manuals, which describe the colouration of prints, mention the use of alum, the preparation of verdigris solutions, and the addition of vinegar to verdigris (Lindenbergh 1742; Salmon 1685). In contrast to our previous test specimens (Hofmann et al. 2015), we applied verdigris as wash without gum Arabic.

In a first ageing series we investigated the influence of alum and vinegar on both the green colour and on the condition of the paper. Verdigris (Kremer Pigments)

Table 3: 1st ageing series.

		Description
	1st ageing series	
	Paper	
	Paper made from “recycled” rag paper	60 g/m^2, unsized, handmade by Gangolf Ulbricht, recycled rag paper from 1848
	Paper from flax and hemp fibres	80 g/m^2, unsized, handmade by Gangolf Ulbricht
	Printing paper “Somerset”, cotton fibres	300 g/m^2, sized, from St. Cuthberts Paper Mill
	Preparation of the paper	
	None	No preparation
	Alum water	Alum solution (10 %), two layers applied by brush
	Size of alum water and gelatine	Alum solution (10 %) mixed with gelatine (1 %) (1:1), two layers applied by brush
	Colour recipe (name references author of historical source/painter’s manual)	
A	Salmon	Colour wash made from verdigris in vinegar
B	Lindenbergh recipe 1	Colour wash made from verdigris with tartrate in vinegar
C	Lindenbergh recipe 2	Colour wash made from verdigris with tartrate in water
	Accelerated ageing	10 days at 70 °C and 55 % RH

washes, with and without vinegar, were applied to three papers, with and without alum (Table 3).

Following a visual evaluation of the aged specimens, the coloured papers which most resembled areas degraded by verdigris in atlases were selected for a second series. The treatment options with the complexing agent BTA and the antioxidant TBAB were applied for further evaluation in the context of coloured maps in atlases. The treatments were also tested in combination. Reinforcements with precoated Japanese papers were included as a necessary treatment on brittle and torn paper (Hofmann et al. 2016). Interleave papers impregnated with TBAB were investigated as an option for folded maps (Table 4). Pre-aged specimens were treated with BTA, TBAB, a combination of the two, reinforcement with precoated Japanese paper, and with interleave papers. References and treated specimens were post-aged (Table 4). The samples were evaluated visually, by colour measurement and selected samples by fibre morphology and cellulose analysis.

5.1 Test Specimens’ Preparation and First Ageing Series

For better comparison, two types of handmade rag paper that had been used in the previous project (Hofmann et al. 2015) and in Hannemann’s master thesis (2023) were

Table 4: 2nd ageing series.

		Description
	2nd ageing series	
	Paper	
	Paper from flax and hemp fibres	80 g/m^2, not sized, hand-made by Gangolf Ulbricht
	Preparation of the paper	
	None	No preparation
	Alum water	Alum solution (10 %), two layers applied with brush
	Size of alum water and gelatine	Alum solution (10 %) mixed with gelatine (1 %) (1:1), two layers applied with brush
	Colour recipe	
B	Lindenbergh recipe 1	Colour wash made from verdigris with tartrate in vinegar
	Pre-ageing	
	Set with pre-ageing	5 days, 50 °C, 55 % RH
	Set without pre-ageing	
	Treatment of the aged test specimen	
	none	Test sample with one of the preparation variations and one of the colour recipes left without treatment as reference
	BTA (3 %)	Solution of benzotriazole 3 % in isopropanol applied by brush on verso
	BTA (3 %) and reinforcement	Solution of benzotriazole 3 % in isopropanol, Japanese paper KR4C (4 g/m^2), coated with 2.5 % Klucel GF PH in 1 % TBAB in water
	TBAB (1 %)	Solution of tetrabutylammonium bromide (1 %) in isopropanol applied by brush on verso
	Interleaf with TBAB (1 %)	28 g/m^2, cotton tissue paper, Klug, impregnated with 1 % TBAB in water, inserted between the folded test-specimen
	Reinforcement (version with gelatine)	Japanese paper KR4C, coated with 2.5 % gelatine (gelatine No. 1, from GMW)
	Post-ageing	
	Post ageing of both sets	10 days, 70 °C, 55 % RH

chosen for the preparation of test specimens. To compare and visualize colour changes on a white paper, a modern printmaking paper was added to the first ageing series (Table 3). On the coloured prints in the atlases, we could hardly detect pigment grains. Therefore, we assume that verdigris was applied as a solution that penetrates the paper fibres more easily than a pigment in a binder. This assumption is supported by historical colour recipes, which describe the application of verdigris as a liquid preparation rather than a bound pigment. Colour recipes from the painters' manuals of Lindenbergh (1742) and Salmon (1685) were selected because they specifically mention the colouration of maps, their texts originate from the time of the atlases, and in the case of Lindenbergh, are also geographically close to the production site of the maps in Amsterdam. For the sizing of the papers, it was decided to leave one set of test specimen unsized, a second set was treated with a 10 % alum (potassium aluminium sulphate, Kremer Pigments) solution, which was applied by brush two times, and a third set was sized with a mixture of 1 % gelatine (Photographic gelatine, GMW) and 10 % alum.

Of the colour recipes for verdigis the following were chosen (Table 3):

Salmon (Salmon 1685), p. 205: "Fine Verdigrise, dissolved in Rhenish wine or Vinegar, makes a transparent Green inclining to blew."

7 g verdigris (Kremer Pigments) were added to 50 mL white wine vinegar (7 %, food quality). After 30 min the coloured liquid was decanted and used as a wash.

Lindenbergh (Lindenbergh 1742), recipe 1, pp. 38–9: "Men neemt Spaensch Grien van 't beste ('t welk men ligt aan zyn coleur kennen sal, wyl die de allergroenste is) en wryft dat sterk ende lang met witten Wyn asyn en een weinig wyn steens, daar na laaten zy het door een doek gaan, en gebruiken het selve."

7 g Verdigris (Kremer Pigments) and 1.7 g tartrate (mono potassium tartrate, Kremer Pigments) were mixed and ground with 50 mL white wine vinegar (7 %, food quality) in a mortar. The resulting liquid was sieved through nylon stockings.

Lindenbergh, recipe 2, pp. 38–9:

7 g verdigris (Kremer Pigments) and 1.7 g tartrate (mono potassium tartrate, Kremer Pigments) were mixed, 50 mL water was added. After 4 h the mixture was heated to 100 °C on a magnetic stirrer. The solution was cooled and left over night. The next day the liquid was sieved through nylon stockings.

The verdigris solutions were applied to strips of paper, 30 mm × 100 mm. The paper was pre-wetted with a synthetic brush and after a short drying time, the liquid colour was applied with a water-colour brush (DaVinci Cosmotop-Mix) on one half of the paper strip (50 mm). To imitate border colouration, the verdigris pigment particles, which were obtained from steeping or straining the liquid, were mixed with gum Arabic (20 g in 100 mL water, Kremer Pigments), and a line was drawn on the test specimen. It should be noted that even though the colours were applied from the same solutions, there is a noticeable visual difference in the saturation of the applied colour on the paper. The interpretation of this observation is still ongoing. After drying, the coloured papers were humidified and flattened between non-woven polyester and blotting paper under weights. To imitate the situation in an atlas, the test specimens were folded in the middle and put between two pieces of museum board (Canson 1.8 mm). The boards were held together with strips of Japanese paper and wheat starch paste.

The packages of test specimens between board were aged in glass bottles (Duran) in a Memmert drying oven (Memmert UN55) at 70 °C for 10 days. In the glass bottles, the relative humidity was adjusted with silica gel (ProSorb beads from Long Life for Art) preconditioned to 55 % RH.

5.2 Visual Evaluation of First Ageing Series and Colour Measurements

After 10 days of ageing at 70 °C and 55 % RH the colour of all samples changed. The papers with alum and the colours that contain vinegar turned brown and most resemble the appearance of degraded verdigris in the atlases (Figure 8). The strip with verdigris and gum Arabic, which should imitate the border colouration, darkened to brownish and almost black shades, a change that we did not observe on the maps. Haptically, the aged paper specimens with verdigris seem less flexible and more brittle.

On the unsized papers and the modern cotton paper, the blue-turquoise colour turned green. The preparation of the second recipe from Lindenbergh, conducted without vinegar, results in a colour shift from blue turquoise to green turquoise (images not shown). The application of alum solutions alone and with the addition of vinegar in the preparation of verdigris washes caused a brown colour change that resembles the discolouration observed on 17th century maps.

For the second ageing series, the 80 g hemp-flax paper and the first Lindenbergh recipe with vinegar were selected because the aged test specimens match the observed degradation. The objective was to evaluate the considered treatments with BTA and TBAB on mock-ups resembling the originals.

5.3 Second Ageing Series

Test specimens were prepared from the 80 g/m^2 hemp-flax paper (Gangolf Ulbricht), see Table 4. For the first sample set, the paper was left unsized, for the second set a 10 % alum solution was applied by brush two times. The third set was sized with a solution of 2 % gelatine (Photographic gelatine, 250 g Bloom, GMW) and 10 % alum (Kremer Pigments) in the ratio 1:1. Verdigris (Kremer Pigments) was prepared according to the first recipe by Lindenbergh, which contains vinegar and tartrate (see chapter 4.1). The colour was applied as a wash, as described in the first series. One set of test specimens was pre-aged for 5 days at 50 °C in glass bottles with silica gel

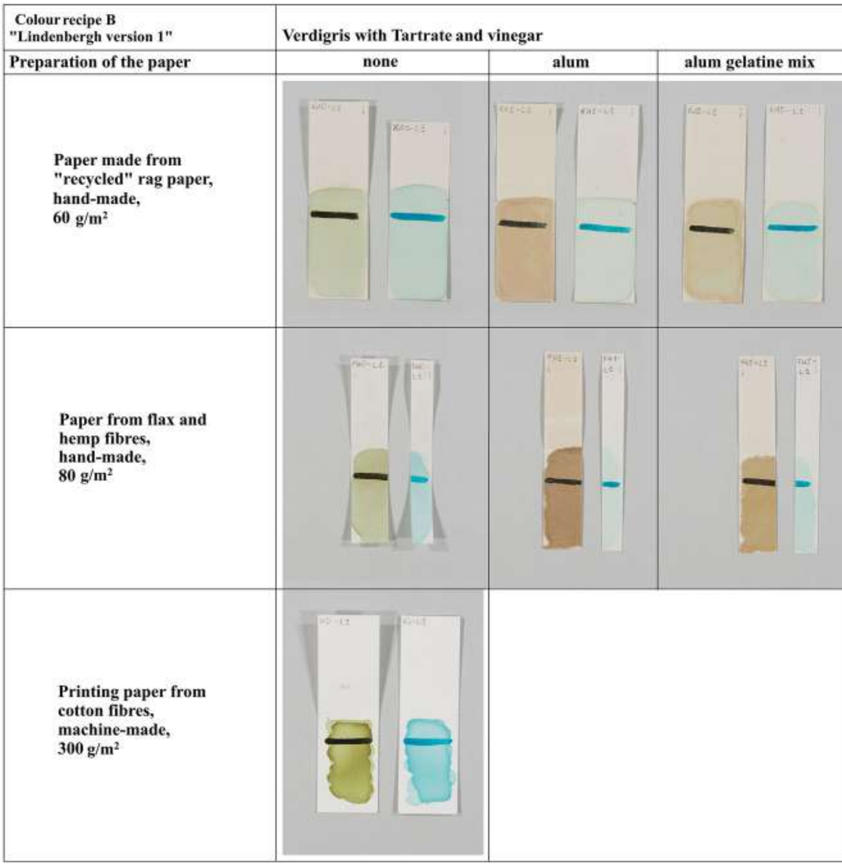

Figure 8: Test specimens of the first ageing sequence: recipe of Lindenbergh 1 with verdigris, tartrate, and white wine vinegar on three different papers with no pre-treatment; with 10 % alum and with 10 % alum plus 1 % gelatine; the line (pigment with gum Arabic) was meant to imitate a border line: right unaged specimens, left aged specimens (10 days, 70 °C, 55 % RH).

(ProSorb beads, Long Life for Art) preconditioned to 55 % RH. As described above, the samples were folded and aged between pieces of museum board (Canson 1.8 mm) to imitate the environment of a map in an atlas. After pre-aging, the blue-turquoise colour turned green with variations (not shown in this paper). Un-aged and pre-aged papers were subsequently treated with the following methods, except the reference sample (Table 4):

– Application of 3 % BTA (VWR) in isopropanol by brush from the verso

– Application of 3 % BTA in isopropanol, reinforcement with Japanese paper KR4C ($4 g/m^2$, Moriki Papers), coated with 2.5 % Klucel® GF PH (Deffner & Johann) in 1 % TBAB (VWR) in water.
– Application of 1 % TBAB in isopropanol by brush from the verso
– Interleaf paper ($28 g/m^2$, cotton tissue paper, Klug Conservation) impregnated with 1 % TBAB in water, inserted between the folded test-specimen.
– Reinforcement with Japanese paper KR4C, coated with 2.5 % gelatine (Photographic gelatine, 250 g Bloom, GMW)

The Japanese paper with gelatine coating was included to compare it with the Klucel®-coated paper. After treatment and drying, we observed no visual changes of the treated colour layer. The unaged and pre-aged test specimens were aged, again in packages of museum board, at 70 °C in glass bottles with silica gel (ProSorb beads) conditioned to 55 % RH for 10 days. One sample set was left unaged as reference as well as for long-term natural ageing.

5.4 Visual Assessment and Colour Measurement of Second Ageing Series

After 10 days of accelerated ageing, the visual appearance of the test specimens treated with BTA and TBAB, with and without pre-aging, was similar (Figure 9) with some variations. The green colour turned brown. The treatments had no obvious negative effect on the paper samples. After post-ageing, no significant visual difference was observed between specimens that had been treated prior to ageing and those that had been treated after an initial ageing step. The reinforcement with Klucel® G and KR4C remained unobtrusive. The Japanese paper adhered well to the rag paper. On the other hand, the reinforcement paper could be removed with a scalpel without visible residues which proved the retreatability of the mending. On the samples that were reinforced with a gelatine coated Japanese paper, the browning of the green colour looks like the untreated, aged reference except with some light-greenish spots. The gelatine reinforcement appeared glossy in some areas. Handling of the folded aged specimens showed that their flexibility is lower than that of the un-aged references. Folding and unfolding the aged specimens more than three times would have resulted in a tear.

The coloured area on all samples was measured with the X-rite spectrophotometer (Appendix B). The coloured areas appear darker after ageing (L^* values decreased by an average of 21.2) and the colours shifted towards red and yellow (a^* values increased by an average of 13.6 and b^* values by 10.4), see Tables 5a and b. The

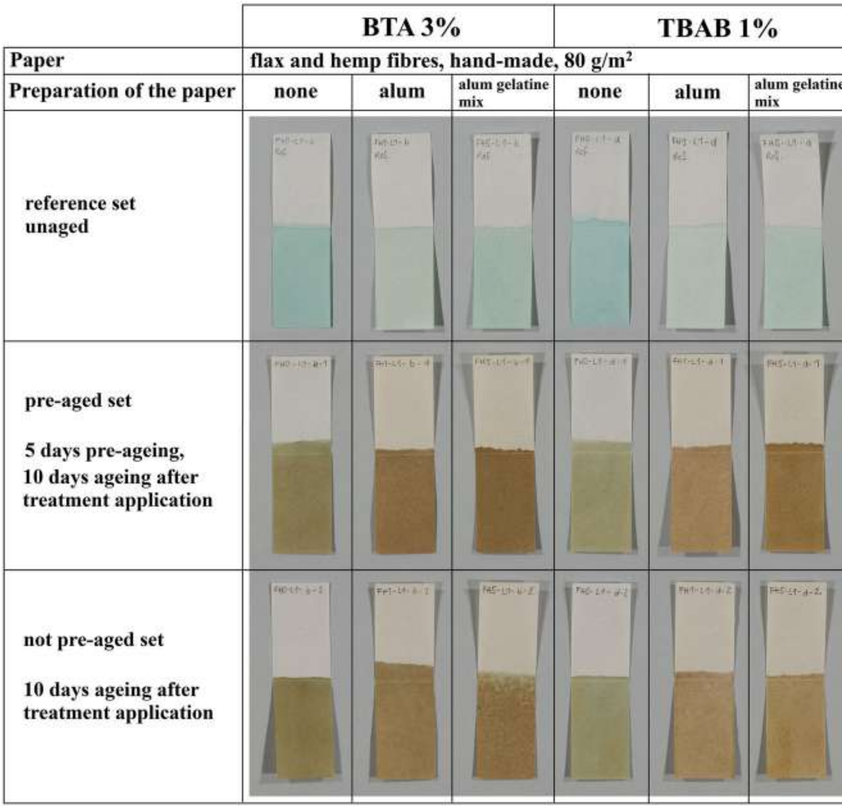

Figure 9: Test specimens of the second ageing sequence: recipe Lindenbergh 1 on 80 g hemp-flax paper of the test specimens treated with 3 % BTA and 1 % TBAB applied by brush on verso: unaged (above), 5 days pre-aged at 50 °C, 55 % RH, 10 days post-aged at 70 °C, 55 % RH (middle), without pre-aging, 10 days post-aged (below) at 70 °C, 55 % RH.

treatments did not cause significant colour changes after accelerated ageing in the dark in this limited experiment.

5.5 Fibre Morphology

The fibre morphology of selected samples with verdigris were compared in the light microscope (Zeiss Axiolab) at 100× magnification in transmitted light and with crossed polarisation filters (images not shown). The fibres of the untreated flax-hemp paper with alum-gelatine sizing and verdigris with vinegar and tartrate (FH1-L1-a-1) show significantly shorter fibres after 15 days of ageing compared with the un-aged

Table 5a: Measurements of Xrite spectrometer from the 2nd ageing series on test specimens made from flax and hemp fibres with a layer of 10 % alum solution. Paint layer contains verdigris, tartrate, and vinegar.

Test specimen (paper: flax and hemp fibres, preparation: layer of alum 10 %, colour: Verdigris, tartrate, vinegar) label and treatment	*L**	*a**	*b**
FH1-L1-a, untreated reference, unaged	88.49	−6.26	9.96
FH1-L1-a-1, untreated reference, aged (15 days)	**61.85**	**8.21**	**20.52**
FH1-L1-b, treated with BTA 3 % in isopropanol, unaged	84.7	−6.34	10.66
FH1-L1-b-1, treated with BTA 3 % in isopropanol, aged (5 days pre-ageing, 10 days post-ageing)	**67.68**	**3.90**	**19.90**
FH1-L1-c, treated with BTA 3 %, reinforced with Japanese paper (4 g/m^2) coated with 2.5 % Klucel GF PH in 1 % TBAB in water, unaged	84.57	−6.45	10.82
FH1-L1-c-1, treated with BTA 3 %, reinforced with Japanese paper (4 g/m^2) coated with 2.5 % Klucel GF PH in 1 % TBAB in water, aged (5 days pre-ageing, 10 days post-ageing)	**64.85**	**5.93**	**18.18**
FH1-L1-d, treated with TBAB 1 % in isopropanol, unaged	87.46	−7.28	11.07
FH1-L1-d-1, treated with TBAB 1 % in isopropanol, aged (5 days pre-ageing, 10 days post-ageing)	**70.13**	**4.44**	**20.33**
FH1-L1-e, interleaf paper (28 g/m^2, cotton tissue paper) impregnated with 1 % TBAB in water, inserted between folded test-specimen, unaged	88.35	−6.38	10.94
FH1-L1-e-1, interleaf paper (28 g/m^2, cotton tissue paper) impregnated with 1 % TBAB in water, inserted between the folded test-specimen, aged (5 days pre-ageing, 10 days post-ageing)	**64.66**	**7.66**	**19.99**

The bold values are the sample labellings (name and number).

reference (FH1-L1-a). The fibre morphology resembles the original samples from the maps *Italia* and *Picentia*, described above. The naturally aged historical samples are more degraded. During sample preparation, the coloured fibres from the maps decomposed into small particles. The fibres of pre-aged specimens that were treated with BTA (FH1.L1-b-1) and TBAB (FH1.L1-d) and post-aged are shorter than the unaged reference. Between short fibre particles, some longer fibres are visible in the microscope.

5.6 Cellulose Analysis with Carbonyl Group Labelling Followed by GPC

The following four test specimens were selected for cellulose analysis:

– Untreated reference, flax-hemp paper 80 g/m^2, alum-gelatine sizing, verdigris with vinegar and tartrate (Lindenbergh recipe 1), pre-aged 5 days (50 °C, 55 % RH), aged 10 days at 70 °C and 55 % RH (sample FH1-L1-a-1).

Table 5b: Measurements of Xrite spectrometer from the 2nd ageing series on test specimens made from flax and hemp fibres with a layer of 10 % alum mixed with 2 % gelatine. Paint layer contains verdigris, tartrate, and vinegar.

Test specimen (paper: flax and hemp fibres, preparation: layer of alum 10 % with gelatine 2 %, colour: Verdigris, tartrate, vinegar) label and treatment	*L**	*a**	*b**
FH1-L1-a, untreated reference, unaged	86.10	−11.24	8.65
FH1-L1-a-1, untreated reference, aged (15 days)	**63.86**	**5.77**	**21.92**
FH1-L1-b, treated with BTA 3 % in isopropanol, unaged	84.08	−9.63	10.12
FH1-L1-b-1, treated with BTA 3 % in isopropanol, aged (5 days pre-ageing, 10 days post-ageing)	**61.61**	**5.12**	**20.47**
FH1-L1-c, treated with BTA 3 %, reinforced with Japanese paper (4 g/m^2) coated with 2.5 % Klucel GF PH in 1 % TBAB in water, unaged	83.49	−8.27	10.10
FH1-L1-c-1, treated with BTA 3 %, reinforced with Japanese paper (4 g/m^2) coated with 2.5 % Klucel GF PH in 1 % TBAB in water, aged (5 days pre-ageing, 10 days post-ageing)	**62.46**	**4.13**	**20.67**
FH1-L1-d, treated with TBAB 1 % in isopropanol, unaged	86.53	−9.55	10.61
FH1-L1-d-1, treated with TBAB 1 % in isopropanol, aged (5 days pre-ageing, 10 days post-ageing)	**64.76**	**6.07**	**22.71**
FH1-L1-e, interleaf paper (28 g/m^2, cotton tissue paper) impregnated with 1 % TBAB in water, inserted between folded test-specimen, unaged	87.47	−8.85	9.94
FH1-L1-e-1, interleaf paper (28 g/m^2, cotton tissue paper) impregnated with 1 % TBAB in water, inserted between the folded test-specimen, aged (5 days pre-ageing, 10 days post-ageing)	**66.97**	**4.85**	**22.56**

The bold values are the sample labellings (name and number).

- As above, treated with 3 % BTA in isopropanol after pre-aging (sample FH1-L1-b-1)
- As above, plus reinforcement with Klucel® G in 1 % TBAB and KR4C (sample FH1-L1-c-1)
- As above, treated with 1 % TBAB in isopropanol after pre-aging (sample FH1-L1-d-1)
- The paper without copper green on the test specimens served as reference.

The average molecular weight distribution of the aged untreated reference with verdigris, 38 kDa, was comparable to the molar mass distribution of the sample from the copper degraded paper of map *Picentia*, Mw = 38.3 kDa. The carbonyl group content of the historical sample, 140 µmol/g on average was in the same range as the test specimen with 129 µmol/g. The aging resulted in a degree of cellulose degradation that is comparable to the naturally aged historical sample from an atlas (Figure 10).

The treatment of the pre-aged specimen did not result in significantly lower degradation of cellulose in the setting of the experiments. On the few selected

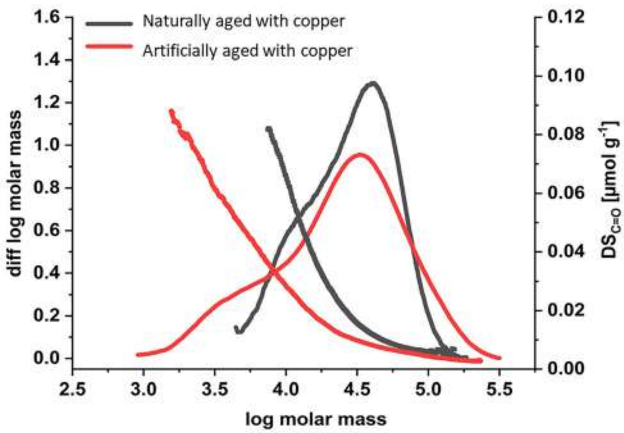

Figure 10: Molar mass distribution and distribution of carbonyl groups of samples from the map *Picentia*, atlas 393686-E KAR 2, with copper (black) and from an artificially aged sample with copper pigment, 10 days at 70 °C, 55 % RH (red).

samples, a tendency for higher molecular weight distribution and lower carbonyl group content can be observed. The combination of BTA and TBAB did not have negative effects on the molecular weight distribution nor the carbonyl group content

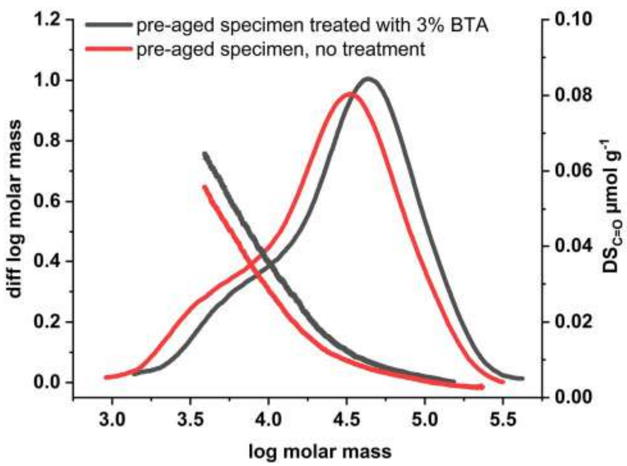

Figure 11: Molar mass distribution and distribution of carbonyl groups of artificially aged test specimens: untreated reference, FH5-L1-a-1, pre-aged for 5 days (50 °C, 55 % RH) and post-aged for 10 days (70 °C, 55 % RH) (red); FH5-L1-b-1: pre-aged for 5 days (50 °C, 55 % RH), treated with 3 % BTA, post-aged for 10 days (70 °C, 55 % RH), (black).

(Figure 11). We assume that on strongly degraded cellulose fibres, the detectable differences between treatments are low.

This ageing study with test specimens showed by visual observation and by cellulose analysis that the application of verdigris in diluted solutions, with the addition of vinegar on papers with alum, can change the colour from a green to a brown hue and degrade the cellulose fibres, similar to the deterioration observed on 17th century maps. Maps bound in atlases demonstrate that mechanical stress exacerbates the risk for physical damage of paper with verdigris. A new series of ageing experiments at higher relative humidity with test specimen with lower amounts of alum is planned.

6 Treatment of Nine Atlases: Applications, Observations, and Assessment

The result of the previous research project (Hofmann et al. 2015; Ahn et al. 2015) indicated that BTA can inhibit the activity of copper in green pigments on paper after accelerated ageing of test specimens. The risk of yellowing during light exposure that appeared during light ageing (Hofmann et al. 2016) seems neglectable as the colour has turned brown already and the books are stored closed in the dark. Due to the damage that has already occurred, the atlases will not be presented in exhibitions. In the experiments of Hannemann (2023) and our above-described studies, the application of BTA did not lead to negative changes of the test specimens after accelerated ageing in the dark. Based on these results and our current evaluation with test specimens adjusted to the observations in the atlases, we decided to apply BTA locally to copper green colouration in categories IV to V (see Table 1) in the nine selected atlases. The aim was to prevent further degradation and migration of copper ions within the book.

We decided to apply a 3 % solution of BTA in isopropanol with an acrylic brush one time to the verso of browned colouration in accordance with the above-described experiments on test specimens. On the verso the treatment could be better limited to areas with dark brown strikethrough (see Table 1). In the research project (Hofmann et al. 2015), the 3 % solution complexed copper ions more effectively than lower concentrations. BTA was dissolved in isopropanol to achieve good penetration and to avoid tide lines. With brushes it was possible to apply the solution precisely on the coloured territory or border (Figure 12). The treatment was carried out in a fume hood with safety equipment. During treatment, non-woven polyester was inserted between the maps on which the solution was applied. The effect of the BTA treatment on the complexation of copper ions was monitored with copper indicator papers. On a few selected spots, copper indicator papers were applied before and one day after treatment. The orange colour change of the indicator paper, which indicates the amount of unbound copper ions, was significantly lower than before the application of BTA (see Section 3.1).

It was decided that brown, brittle areas on the maps with tears and those parts at risk of breaking must be reinforced to prevent further damage and loss. The observation of previous treatments in the atlases (see Section 2) confirmed that reinforcements with low moisture and low tension remain stable and do not endanger the brittle paper. Accelerated ageing experiments in the previous (Hofmann et al. 2015) and this project as well as positive experiences with precoated Japanese tissue papers (Pataki 2009) since 2012 prompted the decision to use Japanese paper coated with Klucel® G 2.5 %. Klucel® G was chosen because it can be

Figure 12: Application of a 3 % BTA solution by brush on brown discolouration on the verso of a map.

activated with ethanol, thereby introducing less moisture than activating a gelatine coating with water. The observed adhesive strength of Klucel® G 2.5 % seemed sufficient on the brittle paper. The condition survey has shown that strong adhesives can cause new damage on copper corroded paper (see Section 2). To avoid possible negative effects of adhesive mixtures, e.g., different ageing properties, pure Klucel® G was used. Klucel® GF PH in food and pharmaceutical quality (Steger et al. 2022) was dissolved in water, because it is easier to apply the aqueous solution on a self-prepared silicon mat. The silicon form was taken from the surface of matted glass, which results in a mat adhesive layer on the coated paper. It was decided to prepare Klucel® GF PH in a 1 % solution of TBAB. If BTA is consumed in reactions with copper ions, the antioxidant TBAB could possibly offer additional long-term protection according to research by Malešič (Malešič et al. 2020, 2025). The experiments by Hannemann (2023) and those conducted in the described project did not indicate negative effects of a combined treatment with BTA and TBAB. The toned Japanese tissue paper KR4C (4 g/m^2) supplied by the company Moriki was chosen because it is thin but of sufficient strength to secure the brittle rag paper and to bridge tears. The toned paper appears unobtrusive on the browned copper green. The adhesive layer was activated indirectly with a mixture of ethanol–water 5:1 utilising a polyester needle felt (Filtraloom, GMW) and blotting paper (Hofmann et al. 2016). The polyester needle felt was immersed in ethanol. Two layers of blotting paper were subsequently put on the felt soaked in ethanol–water (5:1). For activation, one strip of pre-coated paper was positioned with the adhesive layer on the blotting paper humidified with ethanol–water. The water component prevents the activated adhesive layer from drying too quickly during handling.

As a further precaution, we inserted 90 g/m^2 museum paper with alkaline reserve (Klug Conservation) between the folded layers of maps. The paper was impregnated with a 1 % aqueous solution of TBAB as a barrier preventing the migration of copper ions. The paper of some folded maps in the atlases is so brittle that the maps can no longer be opened without the risk of damage. These maps were not treated. The stabilisation effort was limited to inserting an impregnated interleave paper.

The treatment of the nine atlases consisted of the following steps:

- Dry cleaning of book covers and book block edges
- Dry cleaning of the maps
- Local application of 3 % BTA in isopropanol on browned copper green (categories IV–V, see Table 1)
- Reinforcement of endangered browned copper green and tears with precoated Japanese paper
- Mending of tears and infills with Japanese paper in the margin areas of the maps

- Inserts of museum paper (90 g/m^2) impregnated with 1 % TBAB between folded maps
- Conservation of leather and paper bindings if necessary
- Archival dust jackets for the book covers

The application of BTA was restricted to areas of discolouration of a dark brown hue on the verso of the pages, indicative of physical impairment or mechanical stress when the pages are turned. When the solution was brushed on, the paper did not deform. We did not observe changes in texture or colour.

After the application of BTA, dark brown areas on recto and verso, and those with existing tears and losses, were reinforced on the verso with the precoated KR4C Japanese tissue paper (Figure 13). On losses and on tears close to the gutter that opened, it was necessary to adhere the tissue paper also on the recto of the map (Figure 14). We tried to limit mending on the recto as much as possible.

The maps in the first volume of Atlas 393686-E KAR 1, *Nova Totius Geographica Telluris Projectio*, Amsterdam 1708, were in the worst condition due to the tight binding and the thickness of the guards. 122 of 149 maps were damaged and had to be treated as described above. The tight binding and the strong mechanical stress on the paper in the gutter when turning the pages promoted tears and breaks in the brittle paper (see Figure 2). Volume one illustrates the influence of stress on the condition of degraded green colouration.

In Atlas Alb. Geb. 129 the green colouration on all 39 maps had turned dark brown, which promoted the decision to insert interleave papers. The small number

Figure 13: Reinforcement of tears close to the gutter with precoated Japanese tissue paper on the verso of the map *Status ecclesiasticus* in Atlas 393686-E KAR 2.

Figure 14: Reinforcement of tears close to the gutter with precoated Japanese tissue paper on the recto of the map *Status ecclesiasticus* in Atlas 393686-E KAR 2.

of maps and the binding structure impeded the use of the described 90 g/m^2 museum paper. A thinner paper (28 g/m^2), also impregnated with 1 % TBAB in water, was necessary to limit the gain of height in the body of the book; it was interleaved between the maps to prevent transfer of copper ions and further oxidation. In Atlas Alb. Geb. 129, the distribution of TBAB in the adhesive layer was monitored with an XRF-scan in an area of 10 mm × 10 mm by marking the element bromine. Bromine appeared to be evenly distributed in the adhesive layer of the tissue paper.

7 Conclusions

The assessment of 163 atlases with coloured maps from the 17th century offered the opportunity to study the condition of green colouration that contains copper. It showed a great variety of ageing phenomena. In most atlases, the green colours have changed to brownish-green or brown hues. In a minority of about 9 % of the atlases, the discoloured paper is degraded by the activity of copper compounds to a point that handling posed a risk.

In the two-year conservation project, nine atlases from this high-risk group have been conserved based on results from previous and ongoing research. Degraded, browned areas were locally treated on the verso with the complexing agent BTA to prevent further deterioration and the migration of copper ions to adjacent pages. Breaks, tears, and losses in the maps were stabilised with precoated Japanese tissue papers including the antioxidant TBAB in the adhesive layer. The addition of TBAB could potentially introduce additional long-term protection of endangered areas as supported by previous research. On folded maps and in areas in the gutter, stabilisation was limited by the difficult access to the degraded paper. After treatment, maps in poor condition stay fragile and must be handled with greatest care. Access to atlases with folded and very deteriorated maps remains limited.

After conservation treatment, no adverse effects like colour change or migration of copper ions have been observed so far. Yearly controls of the treated atlases are planned. Storage under controlled conditions offers the opportunity for long-term monitoring, which will include visual observation of treated areas, tests with copper indicator papers, and colour measurements.

Acknowledgments: We thank Jan Mokre, Director of the Map Department, and Elisabeth Zeilinger, curator of the Map Department, for accompanying the project with their advice and expertise. Bernhard Tuider, head of the Department of Planned Languages, translated the recipes of Lindenbergh from Old Netherlandish into German. Cheryl Porter kindly revised the English manuscript. The Friends of the Austrian National Library generously supported the project with a donation.

Appendices

Appendix A: List of Atlases:

Alb. geb. 42 (2)

Atlas nouveau with maps by Alexis Hubert Jaillot and Nicolas Sanson. Paris: Pierre Mortier, sine anno, around 1704.

Intaglio prints of different size, size of atlas: 753 mm × 625 mm × 100 mm.

Alb. geb. 51

Atlas minor with maps by Nicolaes Visscher. Amsterdam: N. Visscher, sine anno, after 1702.

188 maps including folded maps, intaglio print, size of maps: 530 mm × 610 mm.

Alb. geb. 129

Caart-Boeck van alle de Dorpen, en Polders gelegen Inden Lande van Oost-, ende West- Voorne, Mitsgaders Over-Flacqueê …; maps by A. Steyaart, sine loco, 1701.

Title page und 32 maps, copper print and etching, size of maps: 530 mm × 720 mm.

FKB 272-20 (I)

Collective atlas with maps by Danckerts, Janssonius, Schenk, Valk and others; sine loco, sine anno.

73 maps, intaglio prints; maps of different size including folded maps, size atlas: 522 mm × 380 mm × 70 mm.

FKB 273-5

Atlas Maior: cum Privilegio Potentissimorum D. D. Ordinum Hollandiae et Westfrisiae; with maps by Visscher, Allard, Homann, de Wit, Schenk, Ram, Delisle and Jaillot. Amsterdam: Frederick de Wit, sine anno, between 1688 and 1715.

224 maps, intaglio prints, size of maps: 530 mm × 618 mm, 21 larger folded maps.

393686-E KAR 1

Harmonia Macrocosmica Seu Atlas Universalis Et Novus, with maps by Andreas Cellarius, and Nova Totius Geographica Telluris Projectio with maps by Gerard Valk, volume 1, Amsterdam: Gerardus Valk, sine anno, around 1708.

149 maps (29 maps from Harmonia Macrocosmica), intaglio prints, size of maps: 530 mm × 620 mm

393686-E KAR 2

Nova Totius Geographica Telluris Projectio with maps by Gerard Valk, volume 2. Amsterdam: Gerardus Valk, sine anno, around 1708.

201 maps, intaglio prints, size of maps: 531 mm × 622 mm.

393686-E KAR 3

Nova Totius Geographica Telluris Projectio with maps by Gerard Valk, volume 3. Amsterdam: Gerardus Valk, sine anno, around 1708.

114 maps, intaglio prints, size of maps: 532 mm × 621 mm

393952-E KAR 2

Atlas Nouveau, contenant Toutes les parties du Monde … Pres. à M. le Dauphin Par … Hubert Jaillot, maps by Nicolas Sanson le père. Amsterdam: Mortier, sine anno.
88 maps, intaglio prints, size of maps: 1000 mm × 630 mm

Appendix B: Methods

Colour Measurement

Colour measurements were taken with the Xrite eXact Advanced spectrophotometer with a 2 mm diameter measurement surface at D50/2°. Three measurements were averaged. The results were processed with the CIE L^*a^*b colour space, CIE ΔE^* (1976), and with UV–Visible remission spectra. In the CIE $L^*a^*b^*$ colour space, lightness value, L^* defines black at 0 and white at 100. The a^* axis is relative to the green–red opponent colours, with negative values toward green and positive values toward red. The b^* axis represents the blue–yellow opponents, with negative numbers toward blue and positive toward yellow.

XRF

XRF scanning was performed with a portable instrument Type Elio (Bruker). The XRF instrument is equipped with a Rh X-ray tube and an SSD detector, providing approx. 1 mm^2 X-ray spot size. The XRF measuring head is mounted on a tripod with a motorised scanning stage (x and y axis, each 10 cm) and can therefore be easily positioned in relation to the object. To adjust the focus of the X-ray beam on the object`s surface (intersection of the primary X-ray beam and the detector axis), a two laser pointer positioning system in the instrument was used. For our investigations, the analysed map was positioned horizontally, thus the primary X-ray beam hit the analysed map surface vertically. Measuring parameters used for the XRF scan were 40 kV and 100 μA tube current. The size of the scanned area on the selected map was 1 cm × 1 cm. Total XRF scanning time was 399 s. For the evaluation, the Elio internal software Version 1.6.0.57 was used.

FORS

For the FORS measurements an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source were used, connected with fibre optic cables to an FCR-7UV200-

2-1, 5 × 100 probe. The probe contained six emitting fibers and one fiber collecting the reflected light. The incident and detecting angles were 45° from the surface normal, in order not to include specular reflectance. The overall operational range of the device (combination of lamp + detector) was 375–1,100 nm. Depending on the features of the monochromator (slit width 50 μm, grating of UA type with 300 lines/mm) and of the detector (2,048 pixels), the best spectral resolution was 2.4 nm calculated as FWHM. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98 % or more in the spectral range investigated. The investigated area on the sample had an estimated 1 mm diameter. The probe was held by hand and in all measurements the distance between probe and sample was kept constant to 0 mm; however, considering the angle at which the probe is held (approx. 45°), the contact area with the sample was negligible. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1 s for each spectrum. The whole system was managed by means of AvaSoft v. 8 dedicated software, running under Windows 11™.

SEM/EDX

EDX analysis and imaging of samples were made using a FEI Quanta 250F FEGSEM at USTEM, TU Wien. Imaging was made using an acceleration voltage of 3 kV at spot size 2.0 in high vacuum at a range of magnifications. This low voltage was used to preserve the sensitive structures of the historical paper and to minimize the penetration depth (to approx. 0.05–0.1 μm) to optimize image quality. To achieve a conductive surface, the samples were sputter-coated with 4 nm of AuPd 60:40 using a Quorum Q150T S. EDX areas and line scans were performed at 20 kV and spot size 3.5 using an EDAX-Ametek Octane Elite 55 SDD system and EDAX TEAM™ software. Elemental quantification was made using the ZAF method to show the distribution and concentration of constituent elements. The cross-sections of paper could not be embedded without changing the fiber morphology. They were cut with a fresh scalpel blade and mounted with tape on the stub.

Cellulose Analysis with Carbonyl Group Labelling Followed by GPC

Fluorescence labelling of cellulose carbonyl groups. The carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide (CCOA) approach for selective labelling of cellulosic carbonyl groups was implemented (Potthast et al. 2003). In short, 5–15 mg of cellulose sample was disintegrated in a mixer with 100 ml of DI water and added to a CCOA label solution in zinc acetate buffer for seven days at 40 °C on a shaker. The labelled samples were washed with water to remove excess label followed by a washing step with ethanol and placed overnight in a vial with pure *N,N*-dimethylacetamide (DMAc, VWR, Austria) for a solvent exchange step. After that 2 ml DMAc/LiCl (9 % w/v) were added for dissolution. After dissolution the samples were diluted with neat DMAc and filtered through a 0.45 µm PTFE filter prior to injection in the GPC system.

GPC analysis. The molar mass distribution and profiles of oxidized functionalities were acquired on the following GPC system: Four serial Waters Ultrastyragel columns (20 µm, 7.5 × 300 mm, Waters, Austria), multi-angle laser light scattering detector (Wyatt Dawn DSP; Wyatt Technology, Santa Barbara, US) with a diode laser (λ_0 = 488 nm), fluorescence detector (TSP FL2000; Thermo Separation Products, USA) and a refractive index detector (Shodex RI-71, Showa Denko K.K., Kawasaki, Japan). A mobile phase of DMAc/LiCl (0.9 % w/v) was applied. The injection volume was 100 µL and the system was operated at a flow rate of 1.0 ml/min. Data analysis was performed using Chromeleon 4, Astra 4.73, and GRAMS/32 software packages. The amount of reducing end groups (REGs) was estimated as $1/M_n$ (where M_n is number-average molar mass) assuming low error in M_n determination and no conversion of REGs to the acid stage (Potthast et al. 2008). The experimental uncertainties were taken from a previous study that evaluated the same substrate for relative standard deviations (RSD) of M_n (6.9 %), M_w (3.5 %), and M_z (3.9 %) values (Sulaeva et al. 2024a, 2024b). The RSD value for C=O values (2.88 %) was taken from Potthast et al. (2002).

References

Ahn, K., C. Hofmann, M. Horsky, and A. Potthast. 2015. "How Copper Corrosion Can Be Retarded – New Ways Investigating a Chronic Problem for Cellulose in Paper." *Carbohydrate Polymers* 134: 136–43.

Banik, G., and J. Ponahlo. 1982. "Some Aspects of Degradation Phenomena of Paper Caused by Green Copper-Containing Pigments." *The Paper Conservator* 7 (1): 3–7.

Battista, O. A., and P. A. Smith. 1962. "Microcrystalline Cellulose." *Industrial & Engineering Chemistry* 54 (9): 20–29.

Boltz von Ruffach, V. 1913. *Iluminierbuch – Wie man allerlei Farben bereiten, mischen und auftragen soll; Allen jungen angehenden Malern und Illuministen nützlich und förderlich. IV. Sammlung maltechnischer Schriften*, 74–76. München: Georg D. W. Callwey.

Brostoff, L. B., and C. Connelly Ryan. 2020. "Tracing the Alteration of Verdigris Pigment Through Combined Raman Spectroscopy and X-Ray Diffraction, Part I." *Restaurator* 41: 3–30.

Brostoff, L. B., S. Albro, J. Bertonaschi, and E. Spaulding. 2011. "The Relationship between Inherent Material Evidence in Cultural Heritage and Preservation Treatment Planning: Solving the Ptolemy Puzzle, Part II." *The Book and Paper Group Annual* 30: 29–33.

Brostoff, L. B., C. Connelly Ryan, and I. Black. 2020. "Tracing the Alteration of Verdigris Pigment Through Combined Raman Spectroscopy and X-Ray Diffraction, Part II: Natural Ageing." *Restaurator* 41: 177–203.

Brückle, I. 1992. “Aspects of the Use of Alum in Historical Papermaking.” In *Conference Papers Manchester 1992*, edited by S. Fairbrass, 201–6. Gainsborough: G. W. Belton Limited.
Eastaugh, N., V. Walsh, T. Chaplin, and R. Siddall. 2004. *Pigment Compendium, A Dictionary of Historical Pigments*. Oxford: Elsevier Butterworth-Heinemann.
Enzel, K., O. Hahn, S. Knödel, J. Schlüter, M. Edney, D. Lange, et al. 2021. *Farbe trifft Landkarte / Colour meets map: Katalog zur gleichnamigen Ausstellung im MARKK Hamburg*, Vol. 16. Manuscript Cultures. Hamburg: Centre for the Study of Manuscript Cultures.
Gautier, H. 1708. *L’art de laver ou la nouvelle manière de peindre sur le papier suivant le coloris des desseins qu’on envoie à la cour*. Brüssel: Francois Foppens.
Hannemann, E. 2023. *Der Farbveränderung entgegenwirken. Anwendungsmöglichkeiten und Applikationstechniken von Benzotriazol und Tetrabutylammoniumbromid auf kupferfraßgeschädigtem Papier*. Masterarbeit, Stuttgart: Staatliche Akademie der Bildenden Künste Stuttgart.
Henniges, U., K. Schröter, and A. Potthast. 2005. *Tapeten und Kupferfraß*. Berlin: Berliner Wissenschaftsverlag.
Henniges, U., M. Schwanninger, and A. Potthast. 2009. “Non-Destructive Determination of Cellulose Functional Groups and Molecular Weight in Pulp Hand Sheets and Historic Papers by NIR-PLS-R.” *Carbohydrate Polymers* 76 (3): 374–80.
Hofmann, C., A. Hartl, K. Ahn, I. Faerber, U. Henniges, and A. Potthast. 2015. “Studies on the Conservation of Verdigris on Paper.” *Restaurator* 36: 147–82.
Hofmann, C., A. Hartl, K. Ahn, K. Druceikaite, U. Henniges, and A. Potthast. 2016. “Stabilization of Verdigris: Application of Research in Conservation Practice.” *Journal of Paper Conservation* 17 (3–4): 88–99.
Hulthe, P. 1970. “A Bathocuproine Reagent-Paper for the Rapid Semi-Quantitative Determination of Copper in the 1 to 70 p.p.m. Range.” *Analyst* 95 (1129): 351–55.
Jordan, P. 1531. *Artliche Künste Mancherlei Weise Dinnten Vnd Aller Hand Farben Zůbereyten. Auch Goldt Vnd Silber Sampt Allen Metallen, Auß Der Fedder Zů Schreyben* …. Mainz: Peter Jordan.
Kolbe, G. 2004. “Gelatine in Historical Paper Production and as Inhibiting Agent for Iron-Gall Ink Corrosion on Paper.” *Restaurator* 25: 26–39.
Lespinasse, L.-N. 1801. *Traité du lavis des plans, appliqué principalement aux reconnaissances militaires*. Paris: Magimel.
Lindenbergh, J. F. 1742. *Die nieuwe Verligter, op een beknopte en duidelyke wyze vertoonende de making en bereiding van alle Stof-en Sap-Verwen; (etc.)*. Rotterdam: Losel.
Malešič, J., J. Kolar, M. Denac, and B. Kolar Bačnik. 2020. “Stabilisation Treatments for Paper with Green Copper Pigment Verdigris.” *Restaurator* 41: 231–51.
Malešič, J., K. Retko, M. Finšgar, and I. Kralj Cigić. 2025. “Stabilization of Verdigris Pigment on Paper: Evaluation of Antioxidants Under Mild Accelerated Degradation Conditions.” *ChemPlusChem* 90 (5). https://doi.org/10.1002/cplu.202400670.
Malešič, J. 2025. “Evaluation of In-Situ Methods for Identifying Copper Ions in Paper-Based Objects.” In *International Iron Gall Ink Meeting 2025*. Caparica, Portugal: IADA.
Neunteufel, E. April 2024. Personal Communication. Drosendorf, 27: Grafik-Werkstatt Neunteufel Kreilinger.
Pahl, A. E. 2022. *Charakterisierung des Alterungsprozesses von Kupferfraß auf Papier*. Köln: Fakultät für Kulturwissenschaften der Technischen Hochschule Köln. Master’s Thesis.
Pataki, A. 2009. “Remoistenable Tissue Preparation and Its Practical Aspects.” *Restaurator. International Journal for the Preservation of Library and Archival Material* 30: 51–69.
Pereira, P., L. Neil Johnston, R. Mitchell, and A. Margey. 2024. “The Materiality of the Early Modern Maps of Ireland at The National Archives: Bridging History of Cartography and Heritage Science.” In *Maps and*

Colours, A Complex Relationship. Mapping the Past 3, edited by D. Lange, and B. van der Linde. Boston: Brill.
Petersen, D.-E. 2020. “Die Behandlung der Papiere in der Druckerei und der Buchbinderei im 18. und 19. Jahrhundert.” *Restauro* (3): 28–37.
Potthast, A., U. Henniges, and G. Banik. 2008. “Iron Gall Ink-Induced Corrosion of Cellulose: Aging, Degradation and Stabilization. Part 1: Model Paper Studies.” *Cellulose* 15 (6): 849–59.
Potthast, A., J. Röhrling, T. Rosenau, T. Lange, G. Ebner, H. Sixta, and P. Kosma. 2002. “A Novel Method for the Determination of Carbonyl Groups in Cellulosics by Fluorescence Labeling. 1. Method Development.” *Biomacromolecules* 3 (5): 959–68.
Potthast, A., J. Röhrling, T. Rosenau, A. Borgards, H. Sixta, and P. Kosma. 2003. “A Novel Method for the Determination of Carbonyl Groups in Cellulosics by Fluorescence Labeling. 3. Monitoring Oxidative Processes.” *Biomacromolecules* 4 (3): 743–9.
Salmon, W. 1685. *Polygraphice: Or the Arts of Drawing, Engraving, Etching, Limning, Painting, Washing, Varnishing, Gilding, Colouring, Dying, Beautifying and Perfuming*. London: T. Passinger and T. Sawbridge.
Steger, S., G. Eggert, W. Horn, and C. Krekel. 2022. “Are Cellulose Ethers Safe for the Conservation of Artwork? New Insights in Their VOC Activity by Means of Oddy Testing.” *Heritage Science* 10 (53). https://doi.org/10.1186/s40494-022-00688-4.
Stijnman, A. 2012. *Engraving and Etching 1400 - 2000: A History of the Development of Manual Intaglio Printmaking Processes*. London: Archetype Publications.
Sulaeva, I., D. Budischowsky, J. Rahikainen, K. Marjamaa, F. G. Støpamo, H. Khaliliyan, et al. 2024a. “A Novel Approach to Analyze the Impact of Lytic Polysaccharide Monooxygenases (LPMOs) on Cellulosic Fibres.” *Carbohydrate Polymers* 328: 121696.
Sulaeva, I., F. Gjerstad, F. Støpamo, I. Melikhov. et al. 2024b. “Beyond the Surface: A Methodological Exploration of Enzyme Impact Along the Cellulose Fiber Cross-Section.” *Biomacromolecules* 25 (5): 3076–86.
Theophilus. 1999. *Theophilus Presbyter und das mittelalterliche Kunsthandwerk: Gesamtausgabe der Schrift ‘De diversis artibus’*, Vol. 1, edited by E. Brephol, 75–8. Köln: Böhlau.
Thompson, D. V. 2018. *The Materials and Techniques of Medieval Painting*, 163–74. New York: Dover Publications.
Tsai, F.-W. 1992. “16th and 17th Century Dutch Painted Atlases: Some Paper and Pigment Problems.” In *Conference Papers Manchester 1992*, edited by S. Fairbrass, 19–23. Gainsborough: G. W. Belton.
van der Linde, B. 2020. “Von den angewandten Farben zur funktionalen Kolorierungsmethode – Zur Entwicklung der Kolorierungsformen von Verlagslandkarten in der Zeit des späten 16. bis frühen 19. Jahrhunderts.” *MEMO-quer 1*. https://doi.org/10.25536/2020q001.

Material Sources

1 H-Benzotriazol for synthesis Sigma-Aldrich® (Product-Nr.: 8.22315.0100), VWR International, https://at.vwr.com/store/.
Tetra-n-butylammoniumbromid for synthesis (Product-Nr.: 8.188.390.250), VWR International, https://at.vwr.com/store/.
Isopropanol: 2-Propanol, technical (Product-Nr.: ACRO444250050), VWR, https://at.vwr.com/store/.
Ethanol 96 %, AustrAlco, Österreichische Agrar-Alkohol Handels GesmbH, https://www.australco.at/.
Japanese Paper KR4C Kozu cream (4 g/m^2; Kozo fibres) by Moriki Paper https://www.morikipaper.co.jp/en/, available at Römerturm (Product-Nr. 88801396).

Museum paper light white BB (90 g/m^2; with alkaline buffer; Product-No.: 015090/1), Klug-Conservation, https://www.klug-conservation.de/.

Silk tissue paper (28 g/m^2; with alkaline buffer, Product-No. 0103), Klug-Conservation, https://www.klug-conservation.de/.

Klucel® GF Pharm Powder (Product-Nr.: 2440120), Deffner & Johann, https://deffner-johann.de/.

Potash Alum (potassium aluminum sulfate; Product-Nr.: 64100), Kremer Pigmente GmbH & Co KG, https://www.kremer-pigmente.com/.

Gelatine: Photographic gelatine type Restoration 1, 250 g Bloom (Product-Nr.: 40321), GMW Gabi Kleindorfer, https://gmw-shop.de/en/.

Tartrate powder (Mono potassium tartrate, Product-Nr.: 64170), Kremer Pigmente GmbH & Co KG, https://www.kremer-pigmente.com/.

Vinegar: *Billa* Weißweinessig (7 % acid), white wine vinegar from grapes, produced and bottled in Modena, Billa, https://shop.billa.at/produkte/billa-weissweinessig-00243043.

Verdigris, synthetic (synth.; 44450), Kremer Pigmente GmbH & Co KG, https://www.kremer-pigmente.com/.

Gum Arabic, powder (63330), Kremer Pigmente GmbH & Co KG, https://www.kremer-pigmente.com/.

„Recycled“ rag paper (from 1848 from the collection of the Department of Conservation), 60 g/m^2, not sized, hand made by Gangolf Ulbricht, https://papiergangolfulbricht.com/.

Paper from flax and hemp fibres, 80 g/m^2, not sized hand made by Gangolf Ulbricht, https://papiergangolfulbricht.com/.

Printing paper Somerset, St. Cuthbert Paper Mill, https://www.stcuthbertsmill.com/st-cuthberts-mill-stockists/.

Museum board, Conservation Backing Boards, by Canson (1.8 mm), https://en.canson.com/.

Universal Oven Memmert UN50 plus, Academy of Fine Arts Vienna, https://www.memmert.com/de/produkte/waerme-trockenschraenke/universalschrank.

ProSorb Beads, Long Life for Art, https://llfa.eu/prosorb-beads.html.

Glass Bottles: Duran borosilicate glass bottle with screw cap, 250 ml; Product-Nr.: 215–8402, VWR International.