Chelating soluble iron(II) from iron gall ink using calcium phytate in agar gel

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Introduction

Iron gall ink degradation is a common problem in manuscripts created up to the 20th century. Iron gall ink is made from a source of tannin and a source of iron, usually oak galls and ferrous sulphate, which react to form the characteristic blue-black ink compound. However, historic ink recipes often contain excess iron, which can catalyse oxidative radical chain reactions that break the long chains in the cellulose molecule. The paper becomes weak and brittle and can eventually disintegrate entirely. Ink degradation can be slowed by keeping the object in stable conditions. High or fluctuating relative humidity (RH) transports the water-soluble ferrous ions causing damage in new areas. The ink is often stable enough for the paper to be supported with Japanese tissue where treatment is deemed necessary, but in some cases more invasive treatment may be required.

The current most popular interventive treatment for iron gall ink degradation is the use of phytate, an antioxidant found in plants which chelates the excess ferrous ions and prevents them from participating in radical reactions. However, the phytate treatment is applied in an aqueous bath, which requires volumes to be disbound. Disbinding and washing a book is an extremely invasive treatment, which makes it difficult to justify even if it would prolong the life of the paper. Agar gels may be a solution to this problem. The rigid network structure of the agar gel can contain the phytate solution and allow a controlled application without leaving agar residue, reducing disruption to the structure of the object. The following experiments use an inexpensive and widely available food-grade agar, as it does not appear to produce different results from the purer laboratory-grade agarose when used in conservation applications (Cremonesi 2012).

This project investigates the use of agar gels to apply calcium phytate solution in situ to objects that cannot be immersed. The focus of the trials is on chelating iron as tested using bathophenanthroline iron(II) indicator paper. Gels without phytate are used as a control.

Methodology

Samples of Whatman No. 1 filter paper were immersed in a solution of gelatin-alum size as described in a study at the University of Ljubljana, Ljubljana, Slovenia, on the treatment of iron gall ink using phytate and chelators (Kolar et al. 2005). Ink was prepared according to the recipe in Neevel (1995), wherein the phytate treatment was proposed, using 0.785 g gum arabic, 1.05 g iron(II) sulphate heptahydrate, and 1.23 g tannic acid (95%), with distilled water added to bring the volume to 25 mL. The ink was applied using a 3 mm broad edge pen in rows of five 15 mm lines. The inked samples were left for three weeks at room temperature to allow the ink to oxidize.

Samples of historic material were taken from early 19th-century letters written on thin, soft lightly sized rag paper purchased from a local bookseller. Solutions of agar (5% w/v) were prepared using tap water which did not react with the iron(II) indicator paper. The solution was boiled and cast into Petri dishes to set. Five percent is a high concentration for an agar gel, and produces a coherent structure which can be easily removed from the paper's surface. A concentrated phytate solution was mixed with the agar before casting.

Concentrated phytate solutions were prepared with 1 mL water. The quantities of the ingredients were calculated to be proportional to the

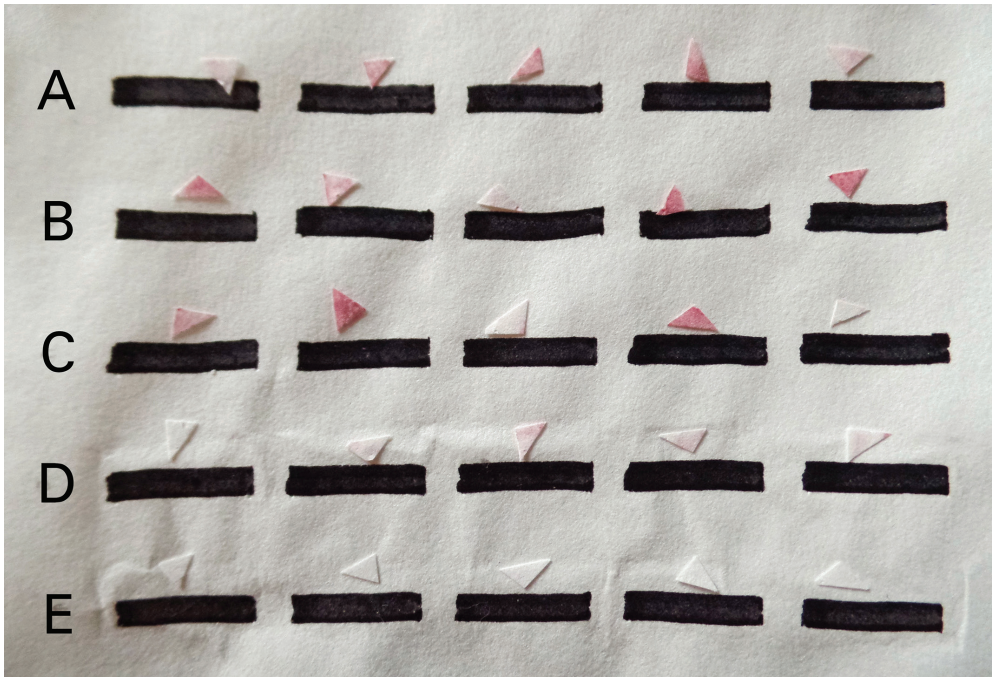

FIG. 1 Residual iron(II) concentration testing using bathophenanthroline iron(II) indicator paper on freshly inked Whatman filter paper samples.

amount of water used to make the gel to ensure that the resulting solution would have the same concentration of phytate as the traditional 0.116% bath (Neevel et al. 2007). To produce an 80 mL solution of agar, the concentrated phytate solution was prepared using 1 mL water with 0.23 g of 40% phytic acid and 0.04 g calcium carbonate.

The pH of the phytate solution was increased to 7 with ammonium hydroxide. The resulting gels were approximately pH 7. Phytate treatment usually involves a bath at a lower pH followed by a deacidification bath because the solubility of calcium phytate decreases sharply above approximately pH 5.6 (Neevel 2001). Although the undissolved phytate may have a reduced ability to chelate iron, a preliminary experiment showed no perceptible difference in efficacy between gels containing phytate at pH 7 and phytate below pH 5.6. Because the object would not be exposed to an acidic solution, it would not need to be deacidified, and a one-step process would not expose it to as much moisture.

For tests on treatment duration, 5- and 10-minute exposures were used, employing gels with and without phytate. In trials treating a single line, 5 × 20 mm gels were applied to the samples. To mimic treating a larger area such as an entire page of a book, a gel containing phytate was applied to a 12 × 20 cm letter for 10 minutes. The sample papers were treated on a sheet of Perspex, with a felt and a light weight on top of the gels. After treatment, the samples were dried between felts and under a light weight for 20 minutes before testing for residual iron(II) concentration. Bathophenanthroline iron(II) indicator paper was prepared according to Jacobi et al. (2011) by dipping Whatman filter paper in a 0.116% w/v solution of bathophenanthroline in ethanol. Each row on the Whatman paper sample was tested in five locations. On historic material, five areas with high ink concentration were chosen for testing.

Effectiveness relative to treatment duration

The results of iron(II) concentration testing on material prepared for the experiment shown in Fig. 1 indicate that agar gels with phytate were more effective than those without. After a 10-minute exposure (E), iron(II) was no longer detected by this method, and its concentration was greatly reduced after a 5-minute treatment with the phytate-loaded gel (D). Areas of ink exposed to agar gels without phytate also showed a detectable reduction of iron(II) (B and C). However, gels with phytate demonstrated a reduction in the residual iron(II) at a faster rate, indicating that chelation in situ is more effective than treatment with a water gel. Gels containing phytate caused noticeable cockling of the paper, which did not improve after drying under

weight. This cockling may make the treatment inappropriate for localized use. It is unclear why gels without phytate did not cause cockling to the same extent.

Effectiveness relative to treatment duration on historic material

An agar gel with phytate was most effective in reducing the amount of soluble iron in the historic sample. An agar gel without phytate also produced a significant decrease in soluble iron. The ink on the historic sample did not react with the iron(II) indicator paper as extensively as the ink used on the contemporary mock-ups, so the range of reaction was less pronounced. There was no evident cockling of the paper after treatment, but the treatment created tidelines around treated areas as soluble discoloured material reached the edge of the area wetted by the gel. Much like the cockling in the previous experiment, these effects make the treatment inadvisable for use on discolored objects.

Treating a full page of historic material

After a 10-minute treatment with a phytate-containing agar gel, there was very little detectable soluble iron(II) on the historic sample shown in Fig. 2. However, uneven wetting caused the paper to ripple. The lower areas of the page were not treated as thoroughly and produced a slight reaction with iron(II) indicator paper, shown in the uppermost test area. The cockling was reduced, but not eliminated, after pressing the page between felts to dry. The gel absorbed discoloured degradation products in both experiments on historic material. In the full-page experiment, fragments of ink also adhered to the gel, exposing the oxidized cellulose below. The sample used in this experiment may have been sized more heavily, causing the ink to remain on the surface rather than sinking into the paper.

Conclusion

Agar with phytate appears to be successful in chelating iron on both historic material and the samples prepared for these experiments. A 10-minute application of the gel was sufficient to ensure that no detectable iron(II) remained in new material after the treatment, and to eliminate or dramatically reduce the iron(II) in the historic material. Agar gels without phytate also demonstrated the same effect but to a lesser extent, indicating that some of the success of gels with phytate is due to the agar itself. Some

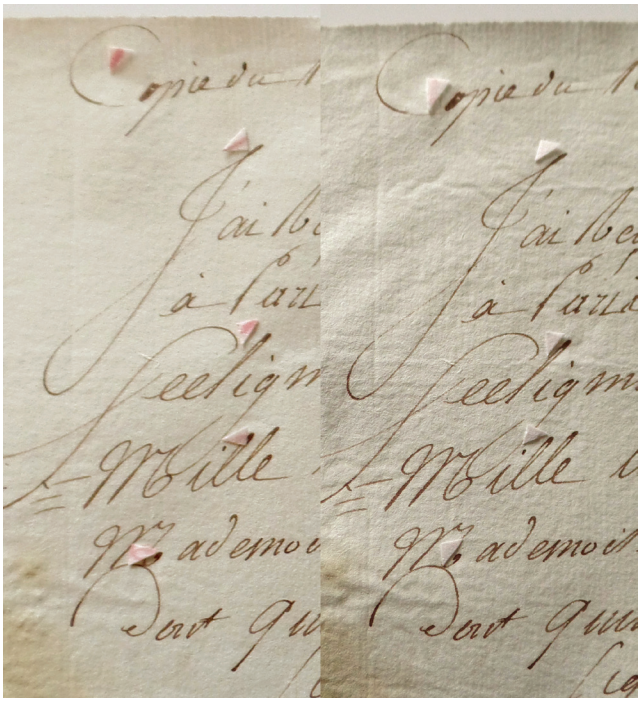

FIG. 2 Historic sample before and after phytate-containing agar gel treatment, showing cockling.

cockling was evident when using agar gels with phytate on the samples produced for the experiments and when treating larger areas of historic material. No cockling was evident when treating small areas of the historic sample, but the treatment caused tidelines and colour change.

Using gels to apply the phytate treatment may prove to be a simple, inexpensive and effective method of treating iron gall ink degradation without immersion. Any conservator using a phytate treatment can easily apply it in a gel. Unfortunately, the treatment is inadvisable due to the cockling and tidelines demonstrated in these experiments, and requires further practical development.

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References

Cremonesi, P. 2012. 'Rigid gels and enzyme cleaning', in M.F. Mecklenburg, A.E. Charola and R.J. Koestler (eds), *Cleaning 2010: New Insights into the Cleaning of Paintings*. Washington, DC: Smithsonian Institution Scholarly Press, 179–83.

Jacobi, E., Reißland, B., Phan Tan Luu, C., van Velzen, B. and Ligterink, F. 2011. 'Rendering the invisible visible', *Journal of Paper Conservation* 12: 25–33.

Kolar, J., Šala, M., Strlič, M. and Šelih, V.S. 2005. 'Stabilisation of paper containing iron-gall ink with current aqueous processes', *Restaurator* 26(3): 181–89.

Neevel, J.G. 1995. 'The development of a new conservation treatment for ink corrosion, based on the natural anti-oxidant phytate', in M.S. Koch and J. Palm (eds), *Preprints of the 8th Congress of IADA, Tubingen, 19–23 September 1999*, 93–100.

Neevel, J.G. 2001. '(Im)possibilities of the phytate treatment', in *Postprints from the Iron Gall Ink Meeting*. Newcastle: University of Northumbria, 125–34.

Neevel, H., Reissland, B., Scheper, K. and Fleischer, S. 2007. 'Preparation of calcium phytate', *The Iron Gall Ink Website.* Ljubljana: Instituut Collectie Nederland. Available at: http:// inkcorrosion.org/images/file/pdf 9_preparation of calcium phytate_ok.pdf (accessed 27 May 2017).

Abstract

Iron gall ink degradation is a familiar problem in manuscripts. Most historic ink recipes contain excess iron, which catalyzes oxidative degradation in the paper. Ink degradation on paper is commonly treated by immersion in a phytate solution to chelate iron. This is not always feasible, as in the case of bound books, where disbinding and immersion would be an unacceptably interventive treatment.

This project investigates the use of rigid aqueous agar gels containing phytate solution to treat iron gall ink degradation in-situ.

A 5% w/v agar gel in deionized water and 5% w/v agar gel containing calcium phytate were applied to new and historic ink samples on paper. The iron content was tested using bathophenanthroline filter paper which turns magenta in the presence of iron(II).

In a trial to determine the time necessary to treat the ink, a 10 minute application of agar with phytate produced a negative result during iron(II) testing on material prepared for the experiment, and dramatically improved reaction on historic samples. Agar without phytate also displayed improvement to some extent.

There were, however, serious problems with cockling, tidelines, and color change. The gels removed degradation products, which caused color change and tidelines as discolored material moved through the area wetted by the gel. In some cases these problems prevent the treatment from being appropriate for practical use without further development. If the treatment is refined, any conservation lab should be able to apply it using widely available and inexpensive food-grade agar.