CHELATING SOLUBLE IRON(II) FROM IRON GALL INK USING CALCIUM PHYTATE IN AGAR GEL

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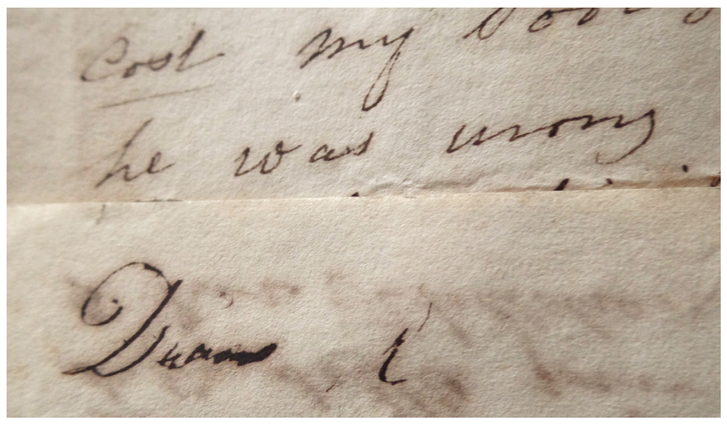


Sacrificial document with degraded ink.

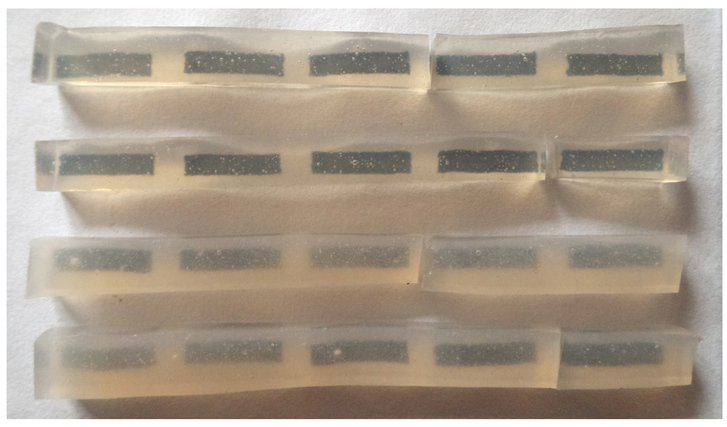
Introduction

Iron gall ink degradation is a common problem in manuscripts. It is made from iron and tannin, usually oak galls and ferrous sulphate, which react to form the black ink compound. Historic recipes often contain excess iron, which can catalyze oxidative radical chain reactions that damage cellulose. Paper becomes weak and brittle, and can disintegrate entirely. High humidity transports water-soluble ferrous ions to damage new areas, which makes treatment difficult.

A common treatment uses phytate, an antioxidant in plants, to chelate excess iron and prevent them from reacting. However, the phytate treatment must be used aqueously.

Disbinding and washing a book is extremely invasive and difficult to justify.

Agar gels may be a solution. Their rigid network structure allows controlled application of phytate without leaving agar residue. These experiments focus on chelating iron as tested using bathophenanthroline iron(II) indicator paper. Gels without phytate were used as a control.



Gels on sample during treatment.

Recipes

Gelatin-alum size (Kolar et al., 2005)
2.3 g gelatin type B
0.26 g alum
100 mL tap water

Ink (Neevel, 1995)
0.785 g gum arabic
1.05 g iron(II) sulfate heptahydrate
1.23 g tannic acid (95%)
Deionized water to 25 mL

Concentrated phytate (Reißland and de Groot, 1999)
1 mL water
0.23 g of 40% phytic acid
0.04 g calcium carbonate.

References

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., Strlic, 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.

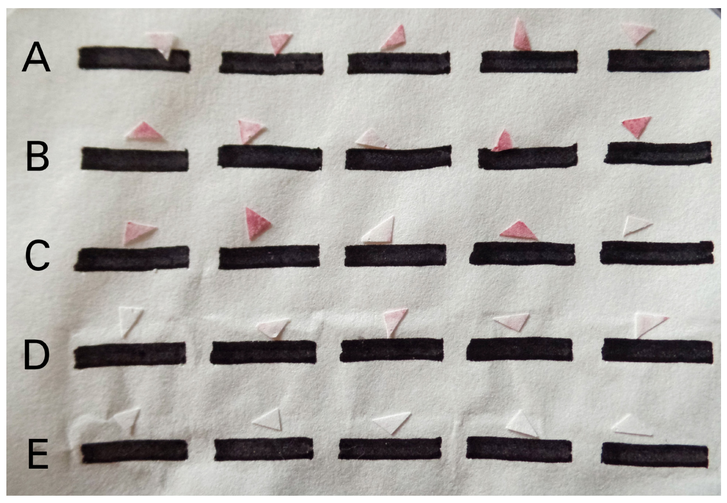
Neevel, J.G. 2001. '(Im)possibilities of the phytate treatment', in Postprints from the Iron Gall Ink Meeting. Newcastle: University of Northumbria, 125–34.

Neevel, H., Reissland, B., Scheper, K. and Fleischer, S. 2007. 'Preparation of calcium phytate', The Iron Gall Ink Website. Ljubljana: Instituut Collectie Nederland.

Methodology

Solutions of concentrated calcium phytate were introduced to agar (5% w/v) before casting.

The concentration of phytate with the volume of water in the gel was calculated to be proportional to the standard 0.116% treatment in a bath. The pH of the concentrated phytate was increased to 7 with ammonium hydroxide.
The standard treatment is applied in two baths, chelation and deacidification, but this version used one step.
Samples of new material used model ink applied to lightly sized Whatman filter paper, and historic samples used early 19th-century letters on thin, lightly sized rag paper.
The samples were treated on a sheet of Perspex with a felt and light weight on top of the gels. The samples were dried between felts before testing with iron(II) indicator paper.
Tests on treatment duration in small areas used 5- and 10- minute exposures to gels with and without phytate, and larger areas used 10 minute exposure to a phytate-loaded gel.



Row A: Untreated control
Row B: Agar without phytate 5 minutes
Row C: Agar without phytate 10 minutes
Row D: Agar with phytate 5 minutes
Row E: Agar with phytate 10 minutes

Results

Tests varying duration
New material: Agar gels with phytate were more effective. Very little iron(II) was detected after a 5-minute exposure (D), and after a 10-minute exposure (E) no iron(II) was detected. The sample was sprayed with a solution of bathophenanthroline several months later and only row E displayed no reaction. However, gels containing phytate caused cockling.
Historic material: Gels with phytate caused a greater decrease in iron(II), although the ink did not react as extensively so the range was less pronounced. However, the treatment created tidelines, making the treatment inappropriate for use on discolored objects.

Treating a full page of historic material
A 10-minute treatment with phytate-containing agar gel resulted in minimal detectable iron(II), but uneven wetting caused the paper to ripple. Cockling was reduced but not eliminated after drying under weight. Fragments of ink adhered to the gel exposing oxidised cellulose below. This sample may have been sized more heavily, causing the ink to remain on the surface.

Conclusion

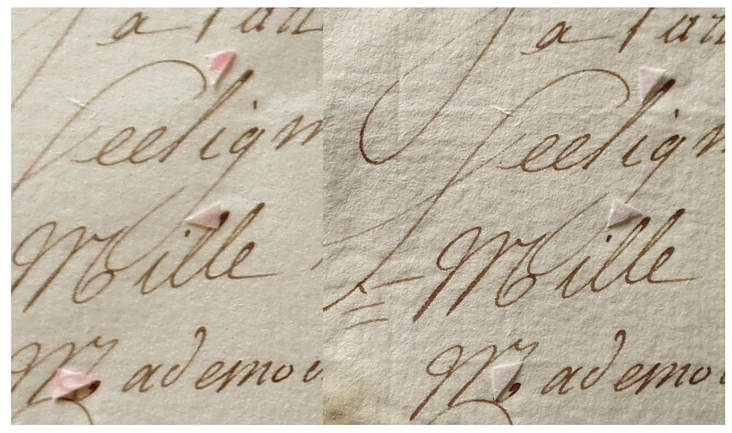
Agar with phytate appears to be successful in chelating iron in both historic material and samples prepared for the experiment.

A 10-minute application of phytate-loaded gel was most successful.

No reaction with iron(II) indicator paper was evident for new material, and reaction was eliminated or dramatically reduced in historic material. Agar without phytate reduced iron(II) levels to a lesser extent.

However, the treatment caused cockling, tidelines, and color change, making it inadvisable for practical use without further development.

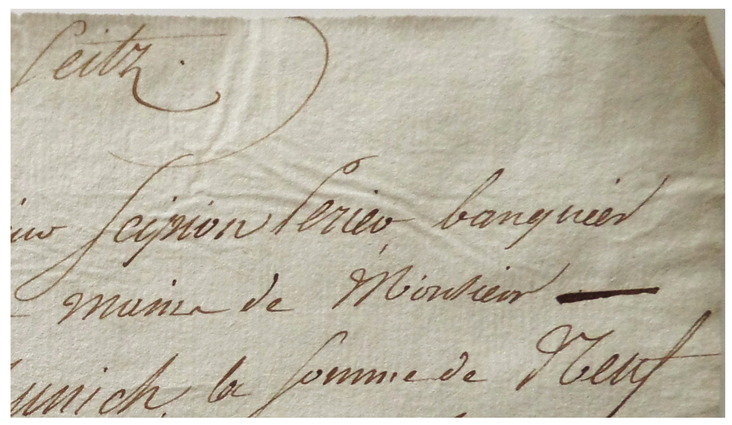
The cockling may be due to the amount of phytate being pushed into the paper, as well as differential wetting.



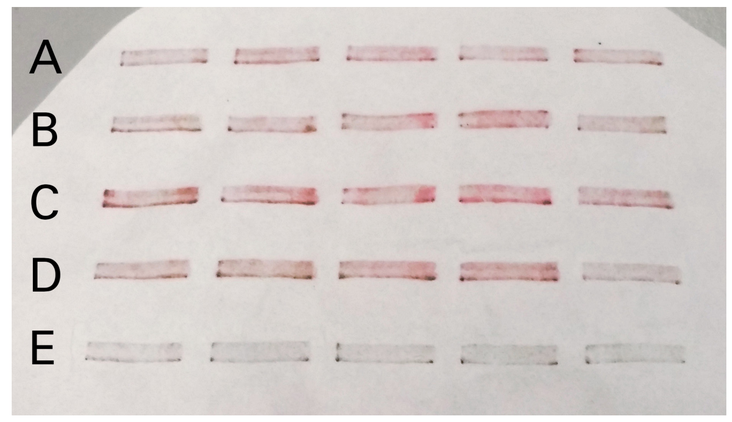
Historic sample before and after treatment.

Further research

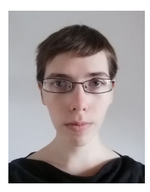
The concentration of phytate in the gel could be reduced, the agar could be cut into pellets to distribute the moisture more evenly, or a different gel could be used. This research is being continued at the National Archives, where better results were produced with gellan than agar.



Cockled areas after treating full page



Sprayed with bathophenanthroline solution
6 months after experiment



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