A Complex Problem: Elucidation of Iron Gall Ink Chemistry Through Collaborative Research

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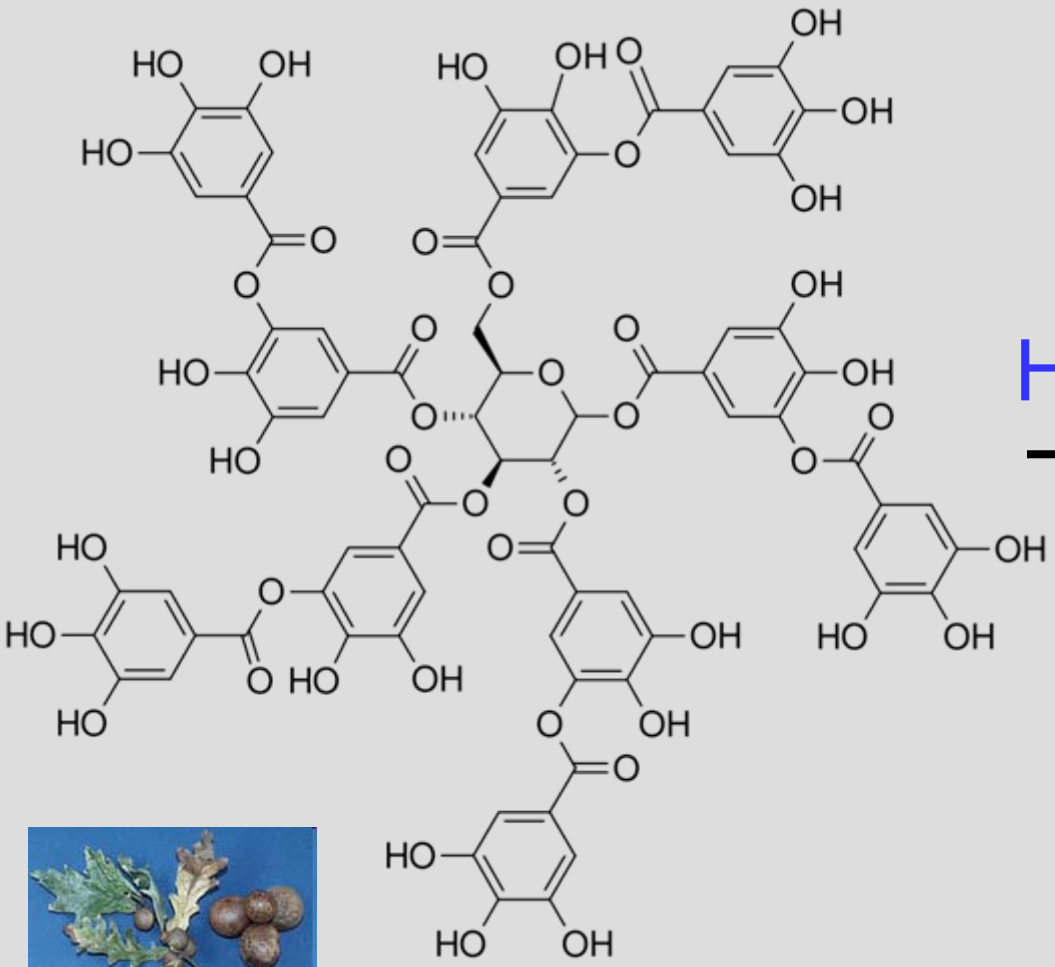
What is iron gall ink?
Why do we care?

Ink chemistry…

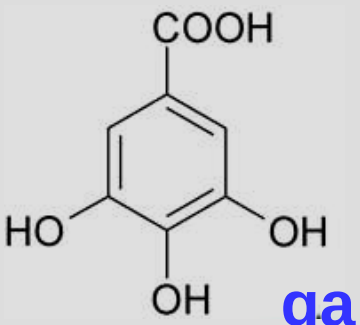


gall nut extract (tannins)

$Fe(II)SO_4$

+

H_2O



gallic acid

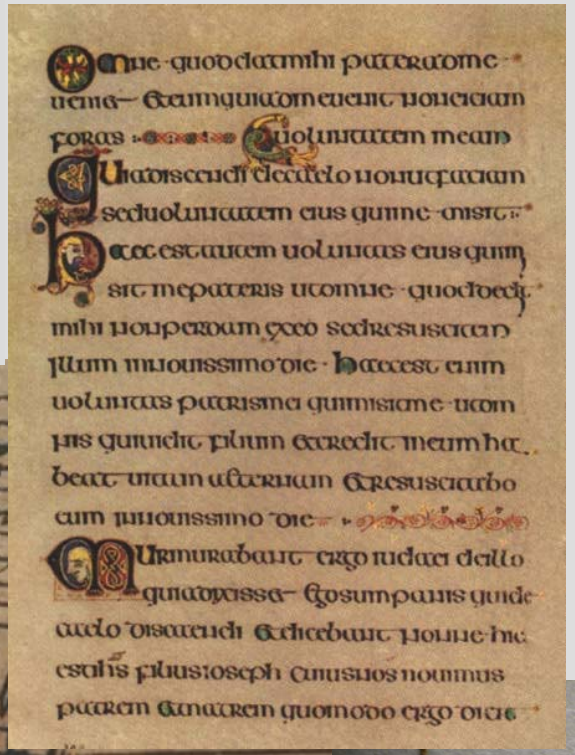
Insoluble, blue-black Fe(III) gallate *complex*

Final Ink Mixture

- Fe gallate *complex(es)*
- *Gum* (arabic): suspension agent or emulsifier
- Additional *colorants*, e.g., indigo or logwood
- *Additives*, e.g., wine, $KAl(SO_4)_2$ or $CaCO_3$
- *Contaminants*, e.g., trace metals such as Cu, Co, Mn, Ni, and Zn

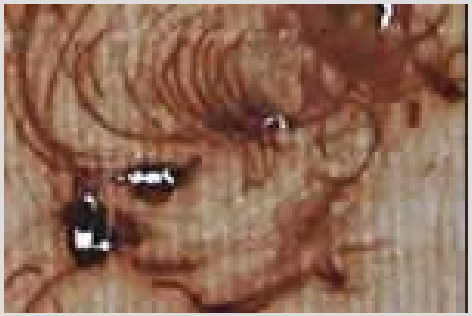
The Preservation Problem

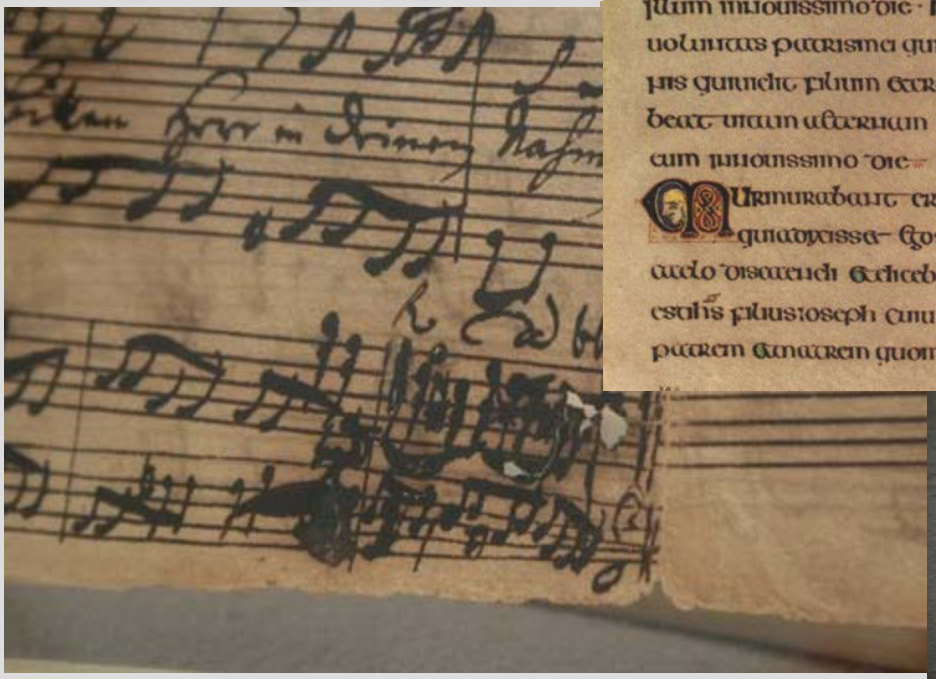
Dead Sea scrolls



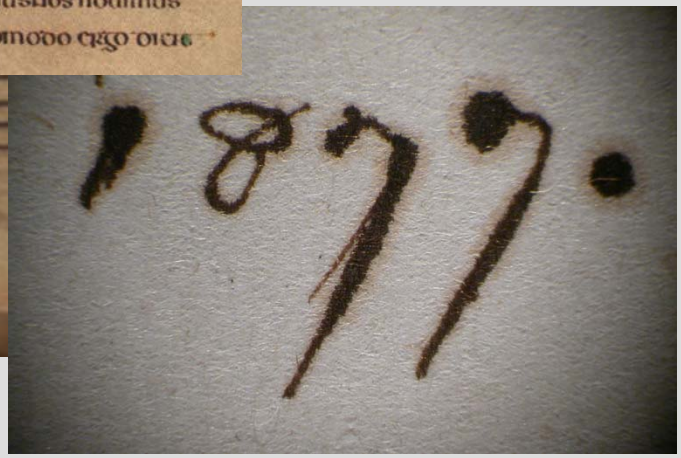
Book of Kells

Guercino drawing

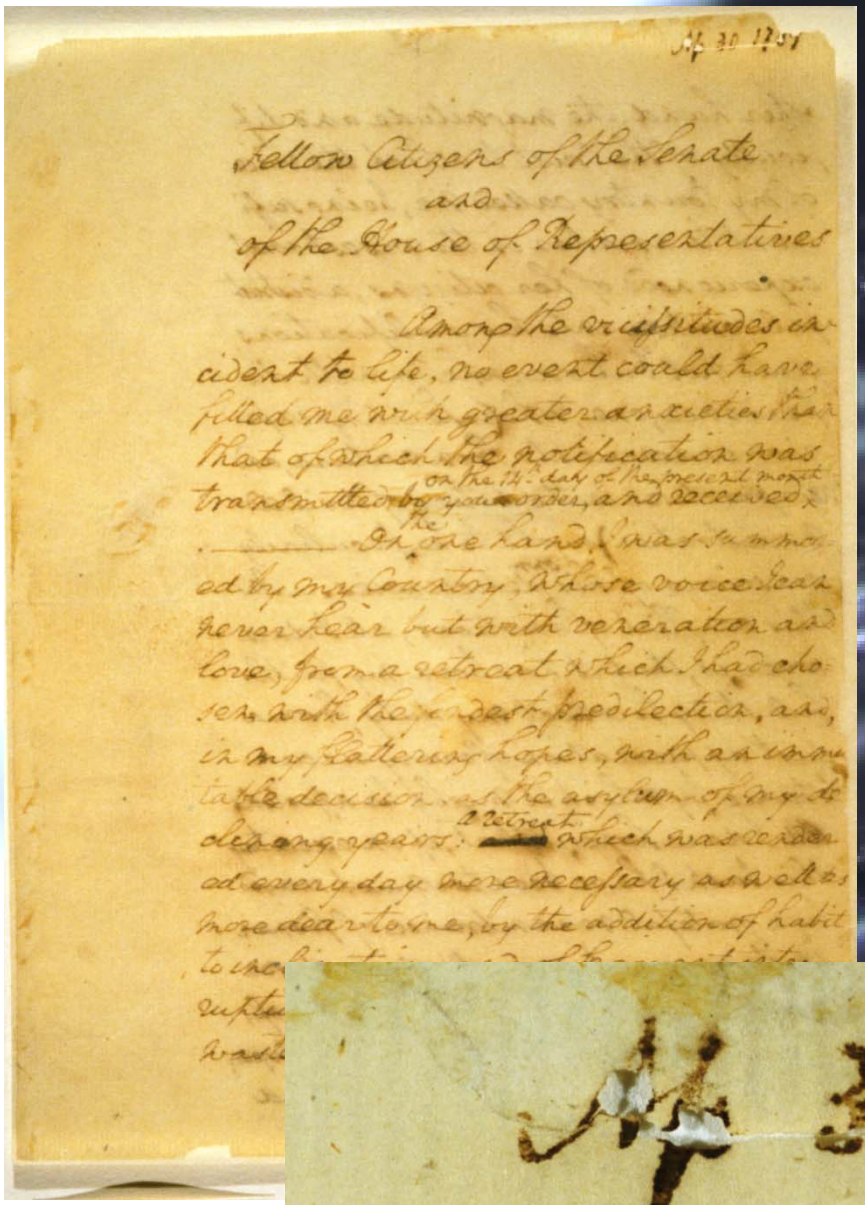




Bach manuscript

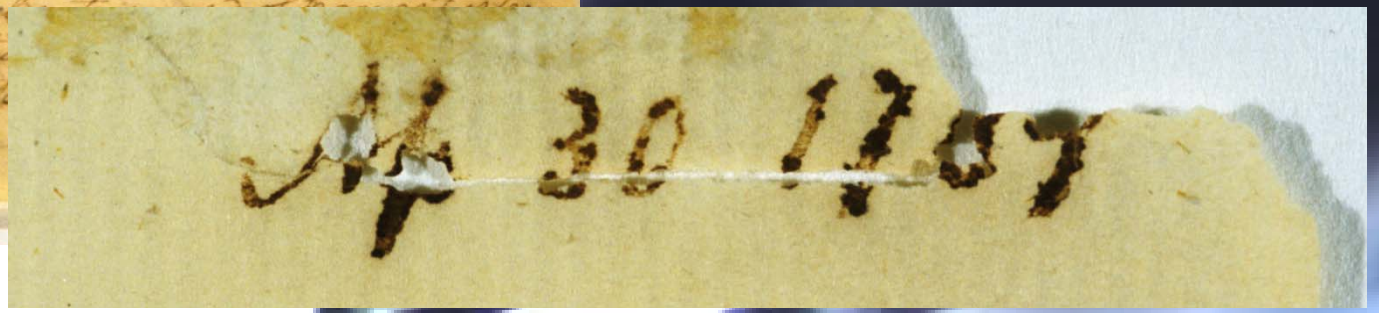


19th C document



iron gall ink “corrosion”:

degradation of paper substrate from interaction with the ink



George Washington’s First Inaugural Address, Library of Congress Collection

Iron Gall Ink (IGI)-induced degradation

- Changes in paper chemical properties
  - migration of ions into paper (Fe, S, Cu)
  - lowering in cellulose degree of polymerization
  - presence of paper degradation products
  - acidic pH
- Change in paper physical properties
  - yellowing
  - embrittlement overall and locally
  - Loss of strength and flexibility
  - water resistance changes around ink lines

IGI-induced degradation

- Change in ink properties
  - fading
  - darkening
  - embrittlement and cracking
  - acidic pH
  - solubility
- Fluorescent haloes at early stages
- Visual spreading of ink line

Previous studies – last 30 years…

- Different Fe(III) gallate molecular structures separately proposed by Krekel and Wunderlich (1990s); both have 1:1 Fe:GA
- Important advances through EU research
- Many empirical and treatment evaluation studies in the conservation literature
- Food Industry, Biochemistry, Corrosion literature contains much relevant information about Fe-polyphenol chemistry

IGI-induced degradation

- Vast majority of conservation studies center on cellulose degradation, not ink
- *Known*: most inks have low pH (H_2SO_4 product)→ acid hydrolysis
- *Known*: Fe(II) ions catalyze cellulose oxidation
- *Unknown*: why some artifacts remain stable
- *Unknown*: how to accurately predict which inks are “corrosive” or water sensitive
- *Unknown*: why current treatments do not permanently fix problem

Solutions: treatment strategies...

Main treatment strategies entail de-acidification and detection and removal of “excess, free” Fe(II)

- water or solvent washing
- de-acidifying baths
- alkaline reserves
- antioxidants:

→ is goal to remove Fe(II) more effectively or to leave reservoir for Fe scavenging?

Status quo: common assumptions in the conservation field

- Krekel's proposed Fe gallate complex formation reaction is correct (and Wunderlich's is wrong)
- Balanced vs. unbalanced inks: *excess* Fe(II) ions, along with acidity, are the major causes of IGI-induced degradation
- Treatments currently used do not affect the stability of the Fe(III) complex
- Antioxidant treatments with phytate salts are generally effective at retarding IGI-induced degradation

New directions: collaborative research

Lecture 1 **New Insights into the Chemistry and Structure of Iron Gall Ink**

Dr. Aldo A. Ponce, Visiting Scientist, Library of Congress;
Dr. Karen J. Gaskell, University of Maryland-College Park;
Dr. Lynn B. Brostoff, PRTD, Library of Congress

Lecture 2 **Iron Gall Ink Corrosion of Historic Documents Probed by X-ray Photoelectron Spectroscopy**

Dr. Karen J. Gaskell, Department of Chemistry and Biochemistry, University of Maryland - College Park;
Dr. Aldo A. Ponce, Visiting Scientist, Library of Congress;
Dr. Lynn B. Brostoff, PRTD, Library of Congress

Lecture 3 **Two Dimensional EPR Imaging of Mixed Oxidation States in Iron Gall Ink Containing Papers: Towards a Treatment Evaluation Methodology**

Prof. Richard C. Wolbers, Art Conservation Department, University of Delaware; Dr. Anthony F. Lagalante, Department of Chemistry, Villanova University

Questions and Comments