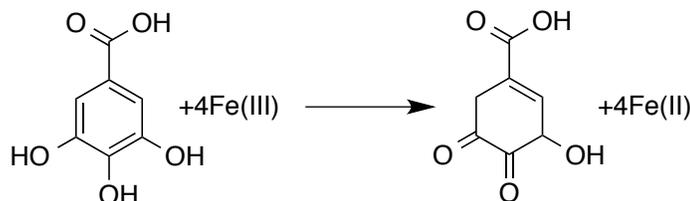


# Potentiometry, a tool for understanding the oxidation-reduction chemistry within iron gall ink documents

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*Oxidation-reduction, potentiometry, iron gall ink, document conservation*

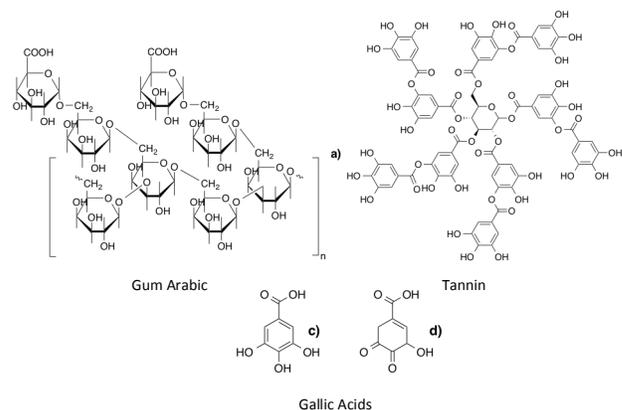
**ABSTRACT:** Iron gall ink contains multiple species that undergo oxidation-reduction reactions. While the exact mechanisms are unknown, potentiometry provides a means to measure the Fe(II)/Fe(III) ratio of iron gall inks upon their submersion in aqueous solutions. This study illuminates the reactions within iron gall ink, and in particular, demonstrates that the redox potential of solubilized inks is driven by the Fe(II)/Fe(III) redox couple and that one gallic acid molecule may reduce up to four Fe(III) cations. An understanding of this study draws upon oxidation-reduction chemistry and will be used to illustrate some of the possible Fe(II)-Fe(III) redox reactions and associated mechanisms.



## Introduction

Iron gall ink currently poses one of the largest and most important problems in art and cultural heritage conservation. Iron gall ink was one of the most prolifically used writing materials in western countries before the beginning of the Twentieth Century.<sup>1</sup> It can be found in documents ranging from medieval manuscripts, including the oldest most complete Bible in known existence, to the Declaration of Independence, and from Michelangelo's drawings, to Isaac Newton's notebooks, where he even included his own recipe for the ink. While iron gall inks' specific compositions differ between documents and depend on the original recipe used, conservators and scientists have determined the majority of these inks contain a mixture of vitriol, tannins, and a binder.<sup>1</sup> Vitriol is the archaic name of sulfuric acid. However, in traditional ink recipes, vitriol actually refers to a solution of Fe(II)SO<sub>4</sub>, that often also contained Fe(III) ions as well. Tannins contain polyphenolic acids that hydrolyze to gallic acid and other smaller molecules.<sup>2</sup> Gum Arabic is the most common binder in iron gall ink, and improves the ink's binding to the substrate, usually the paper support, and helps the pigment disperse uniformly within solution.<sup>3</sup>

While iron gall ink is one of the most common inks, it is also one of the most harmful ones, for it is a corrosive material. The problem iron gall ink poses is extensive. It is estimated that 60-70% of Da Vinci's works have been



**Figure 1.** The major organic species found in iron gall ink that contribute to its acidity: a) gum Arabic b) tannin c) gallic acid d) oxidized gallic acid.

degraded by iron gall ink corrosion.<sup>4</sup> The ink's degradation of paper may occur via several ways. For example, the tannins and iron species produce an acidic environment, which degrades the paper's cellulose through acid hydrolysis, while

any free Fe(III) ions can catalyze cellulose oxidation, which contributes to cellulose's de-polymerization and thus is also linked to paper degradation. Iron, in particular, can participate in a myriad of possible reactions including: Fenton-like reactions;<sup>3</sup> chelation with polyphenols and/or sugars; oxidation-reduction reaction with gallic acid;<sup>5</sup> oxidation induced by oxygen; and formation of hydroxy compounds. Due to ink's high reactivity, scientists have difficulty pinpointing the exact chemistry occurring within these papers. Unfortunately, while the specific chemistry remains challenging and obscure, the detrimental results of these reactions are clear and a growing problem in art conservation.

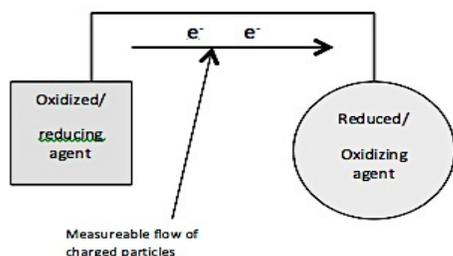
Because this ink is found in such a large number of historic and artistic documents and can be so harmful, the current goal in conservation is to minimize its damage. The accepted treatment of iron gall ink documents is to wash them in water for varying lengths of time, as this can partially dissolve any excess Fe compounds. However, washing may also lead to the migration of iron and sulfur, which can cause a haloing effect around the ink. While washing is generally accepted as the standard treatment, the chemical effects of this aqueous treatment are not well understood.

The article, "Determination of the Fe(II)/Fe(III) Ratio in Iron Gall Inks by Potentiometry: A Preliminary Study," aims to understand the behavior of iron species during these aqueous treatments by conducting potentiometric experiments. The study hypothesizes that due to the imbalance between Fe(II) and Fe(III) ions within these inks, submerging them in water will promote oxidation-reduction chemistry. The key questions this study attempts to address are: what is the ratio of Fe(II)/Fe(III) as determined through measurements of the redox potential of a solution made from 'iron gall ink'; and how does the ratio determined by the electrochemical cell compare to results of Mossbauer spectroscopy performed on dried ink residues and two sample ancient manuscripts.

## Data

### Potentiometry and electrochemistry:

The experiments within this paper focus on oxidation-reduction chemistry and its study through potentiometry. Oxidation-reduction (redox) reactions involve the transfer of electrons within aqueous solutions, and are characterized by a change in the oxidation state of one or more reactants due to the loss or gain of electrons<sup>6</sup>. A redox reaction includes an oxidized half, which loses electrons and is also called the reducing agent, and a reduced half, which gains electrons and is also called the oxidizing agent<sup>6</sup> (Fig. 2). Because redox reactions involve a transfer of electrons from one source to another, redox reactions may be observed and analyzed by measuring this flow of charged particles.



**Figure 2.** The general system of a redox reaction in which electrons flow from left to right.

**Table 1.** Possible chemical equilibria within solubilized iron gall ink and corresponding constants.

| Equilibria  | Log K  |
|---|--------|
| $\text{FeSO}_4^0 \leftrightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$                                 | -2.25  |
| $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$                    | 9.5    |
| $\text{FeSO}_4^+ \leftrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-}$                                 | -3.92  |
| $\text{Fe}(\text{SO}_4)_2^- \leftrightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-}$                     | -5.42  |
| $\text{FeOH}^{2+} + \text{H}^+ \leftrightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$                 | 2.19   |
| $\text{Fe}(\text{OH})_2^+ + 2\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$       | 5.67   |
| $\text{Fe}(\text{OH})_3^0 + 3\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$       | 13.6   |
| $\text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+ \leftrightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$ | 2.95   |
| $\text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+ \leftrightarrow 3\text{Fe}^{3+} + 4\text{H}_2\text{O}$ | 6.3    |
| $\text{HSO}_4^- \leftrightarrow \text{SO}_4^{2-} + \text{H}^+$                                      | -1.987 |

Electrochemical cells are used to measure this current and the potential difference between electrodes caused by the system's distance from equilibrium. Potentiometry is an analytic method that measures the difference in potential between two electrodes in an electrochemical cell with a high impedance voltmeter in order to determine the concentrations of the species in solution. Nernst's law (eq. 1) may be used to theoretically predict this voltage/potential difference based on the equilibrium constant of the dissolved species, the distance of the system from equilibrium, and the standard cell potential at a specified temperature ( $E^\circ$ ).

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln(K_{\text{eq}}) \quad (1)$$

In this study the cell potential is due almost exclusively to the redox reaction of iron. The possible reactions are presented in Table 1.

Another example of a redox reaction is Fenton-like reactions that catalyze cellulose oxidation. The Fenton chemistry describes the oxidation of organic substrates by a combination of Fe (II) and  $\text{H}_2\text{O}_2$ . The proposed mechanism of these reactions includes the formation of a hydroxyl radical, as shown below (eq. 2), and uses an inner-sphere electron-transfer mechanism.<sup>7,2</sup>



There is evidence that these reactions occur within iron gall ink; in particular, cellulose's catalyzed oxidation is especially harmful to paper strength.

### Experimental setup and results:

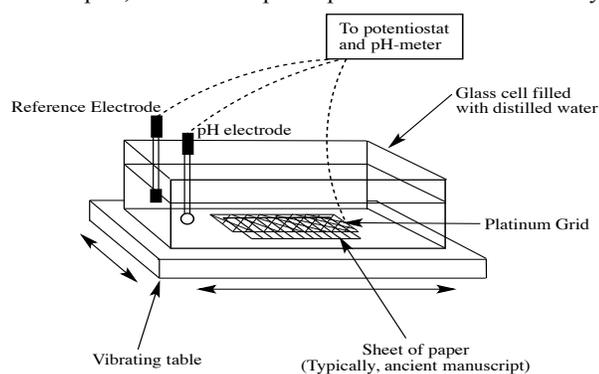
All three experiments in this study draw on redox chemistry; in particular, the two main experiments measure the potential produced by solubilized iron gall inks or their chemical approximation. The study's primary experiment attempts to recreate the chemical environment of a submerged iron gall ink document within an electrochemical cell.

An electrochemical cell (Fig.3) was designed to approximate the species in solution during the washing of an iron gall ink document. A glass container was filled with distilled water and placed on a vibrating table, in order to facilitate the movement of dissolved species. The redox electrode was a platinum grid placed above the iron gall ink document. While a mercury/mercurous sulphate electrode was used as the reference electrode in the potentiometer, the measurements and final results were converted into terms of a

**Table 2. Composition, concentrations, activities and pH of Fe(II)-Fe(III) Solutions**

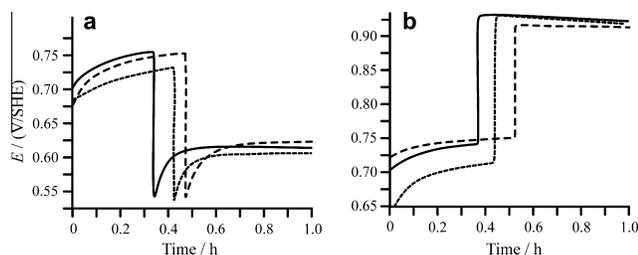
| Solutions              | Concentrations (mol L <sup>-1</sup> ) |                         | Computed activities            |                                | Measured pH |
|------------------------|---------------------------------------|-------------------------|--------------------------------|--------------------------------|-------------|
|                        | Fe (II)                               | Fe(III)                 | Fe <sub>aq</sub> <sup>2+</sup> | Fe <sub>aq</sub> <sup>3+</sup> |             |
| 99% Fe(II)-1% Fe(III)  | 4.66 x 10 <sup>-3</sup>               | 4.77 x 10 <sup>-3</sup> | 2.3 x 10 <sup>-3</sup>         | 6.3 x 10 <sup>-3</sup>         | 3.9         |
| 75% Fe(II)-25% Fe(III) | 3.52 x 10 <sup>-3</sup>               | 1.18 x 10 <sup>-3</sup> | 1.7 x 10 <sup>-3</sup>         | 2.5 x 10 <sup>-3</sup>         | 3.1         |
| 60% Fe(II)-50% Fe(III) | 3.52 x 10 <sup>-3</sup>               | 2.35 x 10 <sup>-3</sup> | 1.6 x 10 <sup>-3</sup>         | 5.2 x 10 <sup>-3</sup>         | 2.9         |
| 50% Fe(II)-50% Fe(III) | 2.35 x 10 <sup>-3</sup>               | 2.35 x 10 <sup>-3</sup> | 1.2 x 10 <sup>-3</sup>         | 6.0 x 10 <sup>-3</sup>         | 2.9         |
| 33% Fe(II)-67% Fe(III) | 2.35 x 10 <sup>-3</sup>               | 4.70 x 10 <sup>-3</sup> | 1.0 x 10 <sup>-3</sup>         | 1.1 x 10 <sup>-3</sup>         | 2.8         |
| 25% Fe(II)-75% Fe(III) | 1.18 x 10 <sup>-3</sup>               | 3.53 x 10 <sup>-3</sup> | 5.9 x 10 <sup>-3</sup>         | 1.0 x 10 <sup>-3</sup>         | 2.8         |
| 14% Fe(II)-86% Fe(III) | 1.18 x 10 <sup>-3</sup>               | 7.05 x 10 <sup>-3</sup> | 5.1 x 10 <sup>-3</sup>         | 1.6 x 10 <sup>-3</sup>         | 2.8         |
| 1% Fe(II)-99% Fe(III)  | 4.70 x 10 <sup>-3</sup>               | 4.66 x 10 <sup>-3</sup> | 2.4 x 10 <sup>-3</sup>         | 1.4 x 10 <sup>-3</sup>         | 2.8         |

standard hydrogen electrode (SHE) ( $E_{SHE} = E_{MSE} + .0651V$ ). The mercury/mercurous sulphate electrode was used as the reference electrode because it is less reactive than its hydrogen counterpart, and will not participate in the redox chemistry.

**Figure 3.** Electrochemical cell designed to analyze iron gall ink.

Various solutions of Fe(III)/Fe(II) were prepared and the Fe ions' activities were computed for the different solutions based upon the potential vs. time curves recorded by a potentiostat. Results are shown in Table 2.<sup>3</sup>

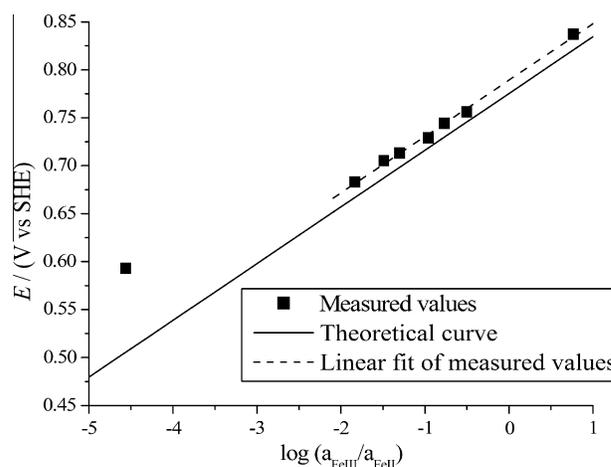
Besides providing the activities of the different iron solutions, the first experiment also demonstrated that these measurements could be conducted in open-air conditions, and that the possible oxidizing action of O<sub>2</sub> with Fe(II)<sup>2</sup> did not have to be considered. To control for the possible oxidizing action of O<sub>2</sub>, the redox potential of various Fe(II) and/or Fe(III) was taken over time (Fig. 4).

**Figure 4.**<sup>3</sup> Potential versus time curves measured over time as Fe(II) sulphate (a) or Fe(III) sulphate (b) was added to distilled water. Carried out in electrochemical cell as described by Fig. 1.

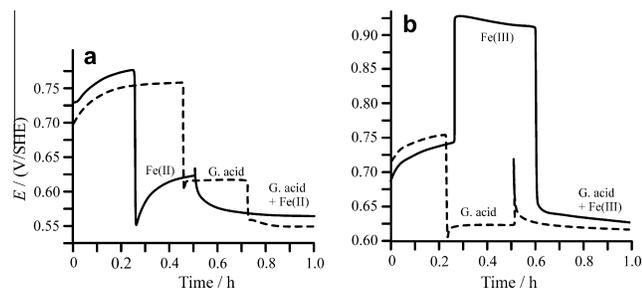
Addition of Fe(II) produced an immediate decrease in potential to .54±0.01 V/SHE (Voltage/Standard Hydrogen Electrode). However, after falling the redox potential then increased before stabilizing at .61 ±0.01 V/SHE; this increase could be attributed to the partial oxidation of Fe(II) by the dissolved oxygen. Similarly, addition of Fe(III) produced an immediate increase in potential, to .93±0.01 V/SHE and again stabilization was seen with this curve, but in this case there was no decrease before the curve stabilized, since there was no reaction with O<sub>2</sub>. Results showed that the effect caused by the oxidizing action of O<sub>2</sub> was only a significant problem when Fe(II) concentration was extremely high, which is not the chemical condition of iron gall ink. Thus conducting this experiment under air should not cause significant error in the data, and provides an accurate account iron species redox system.

The experimental potentials were also compared to theoretically expected results (Fig. 5) as calculated with Nernst's law. Nernst's law predicts the following relationship:

$E_{redox} = .789 + 0.058 \log(a_{Fe^{III}}/a_{Fe^{II}})$ . As shown in Fig. 5 the measured and potential curves are within experimental error.

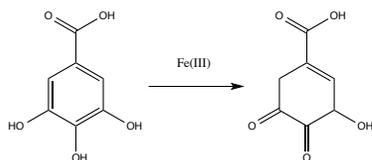
**Figure 5.**<sup>3</sup> Compares the measured potential of the cell versus the activity ratio of  $a_{Fe^{III}}/a_{Fe^{II}}$ , and compares the experimental results with the relationship predicted from Nernst's law.

Other results show that gallic acid acts as a reducing agent, and one gallic acid molecule readily reduced two Fe(III) ions and could reduce up to four (Fig. 6). The proposed mechanism for this reaction involves the oxidation of two adjacent –OH groups linked to the aromatic cycle (Fig. 7).



**Figure 6.**<sup>3</sup> Potential vs. time curves obtained when adding solutions of gallic acid and a solution of Fe(II) sulphate (a) or Fe(III) sulphate (b) to distilled water. In one case the Fe sulphate solution was added first, in the other case it followed the addition of gallic acid.

This reaction causes a distinct color change in the different solutions. Solutions with Fe(II) species and gallic acid were light blue and then darkened as the reaction progressed. The solutions with Fe(III) species and gallic acid were originally dark blue but quickly turned green.<sup>3</sup> These observed color shifts reveal the presence of several reactions. These reactions are particularly important to consider in the conservation of inks because they will alter the color of the ink over time.



**Figure 7.** Proposed oxidation of gallic acid by Fe(III).

Finally, results of the potentiometric experiments also show that species associated with gum Arabic react with the Fe ions, and reduce the Fe(III) to some degree as well.

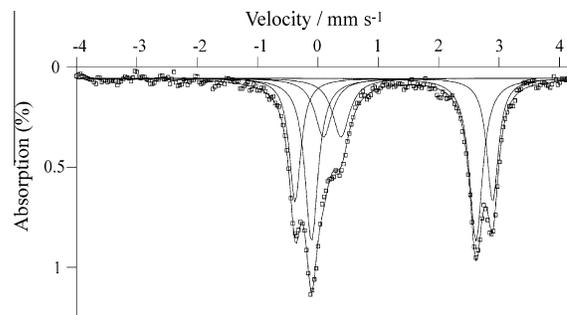
#### *The application Mossbauer spectroscopy to determine Fe(II)/Fe(III) ratios:*

During the second part of the study, Mossbauer spectroscopy (Fig. 8) was conducted to determine the percentage of Fe(III) species left in various dried ink residues. These experiments were conducted in order to determine a baseline approximation of the Fe(II)/Fe(III) ratio in new inks. The fresh ink residues were prepared only from Fe(III) sulphate and gallic acid (and excluded other components found in iron gall ink such as gum Arabic) but were left for 14 days to approximate the waiting time described in original recipes for iron gall ink.<sup>8</sup> After dehydration, the remaining residue was ground for analysis.

The peaks in the Mossbauer spectrum revealed the presence of Fe(II) and Fe(III), and the remaining ratio was consistent with what was expected if every gallic acid molecule reduced four Fe(III). As Table 3 illustrates the ratio of relative areas of Fe(III)/Fe(II) is approximately 1:4.

#### *Manuscript analysis:*

Two French manuscripts that showed extensive and irreparable damage due to iron gall ink corrosion were used for the third and final part of the study. The experimental procedures conducted on synthesized ink samples were applied to actual documents in order to both characterize the inks and verify the realistic application of these procedures within art conservation.



**Figure 8.**<sup>3</sup> Mossbauer spectrum of air-dried compound resulting from a mixture of Fe(III) sulphate and gallic acid solutions after 2 weeks of aging at 60° C.

The manuscripts were analyzed using: Mossbauer spectroscopy at room temperature; proton-Induced X-ray Emission to determine the elemental composition of the manuscripts; and gas chromatography to determine if gallic acid was present in the ink. These studies showed that both inks had very low gallic acid content.

**Table 3.** Mossbauer analysis of air-dried compounds resulting from a mixture of Fe(III) sulphate and gallic acid solutions.

| CS (mm s <sup>-1</sup> ) | Δ (mm s <sup>-1</sup> ) | FWHM (mm s <sup>-1</sup> ) | RA (%) | Fe oxidation no. | Compound                |
|--------------------------|-------------------------|----------------------------|--------|------------------|-------------------------|
| 1.279(9)                 | 2.73(9)                 | 0.262(6)                   | 47     | +2               | Szomolnokite            |
| 1.28(1)                  | 3.28(1)                 | 0.231(6)                   | 31     | +2               | Melanterite or rozenite |
| 0.25(3)                  | 0.29(3)                 | 0.34(2)                    | 22     | +3               | Fe(III) Sulphate        |

CS=center shift with respect to metallic α-iron at room temperature; Δ=quadruple splitting; RA=relative area; FWHM=full widths at half maximum.

The manuscripts were then washed for 30 minutes and the baths' redox potentials were measured. Both manuscripts showed similar potential vs. time curves. Mossbauer analysis showed that one manuscript contained high concentrations of Fe(II), while the other Fe(III).<sup>3</sup> Ultimately the results from this third experiment were not conclusive, and further research is required to examine the applications of potentiometry on document analysis and the inner chemistry of historic inks.

#### **Conclusion**

Overall, the experimental results support the study's conclusions that the Fe(II)-Fe(III) system dominates the redox chemistry within solubilized iron gall ink. In particular, a comparison of the potential of a solution of gallic acid and Fe(III) versus Fe(II) reveals the reducing power of gallic acid. However, one point that remains unclear is the effect of the timed addition used in these experiments. Within different potentiometric trials either the gum Arabic or gallic acid was added first and then the iron sulfate, or alternatively the iron

sulphate was dissolved first. During the aqueous treatments of manuscripts all the species should enter the solution within the same time frame. Thus the reasoning behind the timed addition is unclear. This stepwise procedure would be useful if one species solubilizes at a radically faster rate, but varying solubility rates were not demonstrated nor presented in the background. A follow up experiment is needed to measure the different rates of dissolution. Clarification of this result and supporting studies are particularly important because experiments such as those conducted by Rouchon et al.<sup>9</sup> show that an increase of Fe(II) ions directly contributes to the degradation of paper through Fenton-like reactions. Further studies of the determining factors behind the Fe(II)/Fe(III) ratio would also be invaluable to studies such as those conducted by Kumari et al. on the nano-assemblies of iron in ink and their geometries and magnetic properties.<sup>10</sup>

Though this study leaves future work to be conducted on actual documents, as the examination of the manuscripts was inconclusive, potentiometry shows promise. Even at this stage, this study has implications for art conservation treatments. Fe(II) is a known major contributor to paper degradation. This study's demonstration that Fe(III) reduces to Fe(II) in the presence of both water and gallic acid, suggests that treatment should focus on the removal of both these species.

Furthermore, this study provides important evidence that, washing iron gall ink documents may not be the best method for removing these iron ions. Aqueous treatments may even cause future damage, for if iron ions remain after the washing, this treatment is likely to increase the concentration of Fe(II) within the ink and surrounding paper. A study by Strlic et al. proposes that gallic acid consumption in Fenton-type systems slows at pH 6-8. Washing documents in a slightly alkaline solution may thus help slow the reduction of Fe(III) and mitigate this negative effect. Overall, however, this potentiometry study raises questions about standard conservation practices. Alternative, non-aqueous treatments, such as the halide inserts proposed by Rouchon et al.,<sup>5</sup> should be explored further.

Ultimately, this study contributes valuable information to the study of iron gall inks. Perhaps most importantly, the results illustrated that potentiometric experiments could be used to further evaluate the chemistry of inks and determine how best to preserve these documents.

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