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Iron-gall inks: a review of their degradation mechanisms and conservation treatments

Maria João Melo[1,2*], Vanessa Otero[1], Paula Nabais[1,2], Natércia Teixeira[3], Fernando Pina[1], Conceição Casanova[1,2], Sara Fragoso[1,4] and Sílvia O. Sequeira[1,5*]

Abstract

Iron-gall inks are an essential element of our written cultural heritage that is at risk of a total loss due to degradation. This degradation leads to the loss of the support, particularly the cellulose-based support. Intending to stabilize it, we have come a long way from the nineteenth-century cellulose nitrate laminations to the relatively recent phytate treatments; nevertheless, less invasive treatments are needed. To pave the way for developing safer and more sustainable treatments, tailored as much as possible to the object, this paper reviews the conservation treatments and the advances that have taken place over the last decade in our understanding of the degradation mechanisms of iron-gall inks, based on a careful selection of references to support a concise microreview. This discussion is based on the currently accepted models based on the Fe^{3+}-gallate and the identification of degradation products for iron-gall inks observed in heritage objects, including manuscripts dating from the fourteenth to seventeenth centuries and drawings from the fifteenth to nineteenth centuries. The degradation promoted by iron-gall inks induces scission of cellulose through acid catalysis and/or redox reactions. The causes of these acid-base and redox reactions are also assessed. Finally, we detail the state-of-the-art conservation treatments used to mitigate iron gall ink deterioration, covering treatments from the late nineteenth century to the beginning of the twentieth century, followed by the presentation of current phytate treatments and new postphytate treatments.

Keywords: Iron-gall inks, Polyphenols, Degradation mechanisms, Conservation, Cultural heritage

Introduction

Iron-gall inks are an essential element of our written cultural heritage that is at risk of a total loss due to degradation. This degradation leads to the loss of the support, particularly when it is based on cellulose [1–5]. These inks were extensively used from medieval times to the twentieth century, when they became obsolete. Iron-gall inks were usually prepared by combining plant extracts such as *Quercus infectoria*, iron salts and gum arabic [2, 5, 6]. The ink obtained is perceived as black and is based on Fe^{3+}-complexes with phenolic compounds [5]; e.g., the colour coordinates of an Iberian medieval ink (Braga recipe) are $L^* = 19.5$, $a = 0.8$, $b^* = -3.9$ [5]. However, this black colour transforms into shades of brown over time, a phenomenon yet to be fully understood [7]. Until very recently, gallic acid was considered the main component of gallnut extracts, and consequently, iron-gallate complexes were assumed to be the main chromophores of iron-gall inks [8, 9]. Through the use of historically accurate reconstructions of Iberian inks and a multi-analytical approach, Melo and Teixeira et al. demonstrated that different manufacturing processes result in distinct iron-gall ink compositions and proved that the main components present can also be galloyl esters of glucose such as pentagalloylglucose and hexagalloylglucose [5, 10, 11], Fig. 1. This agrees with the results on Fe^{3+} coordination obtained by Lerf and Wagner using Mössbauer spectroscopy [12, 13]; these authors proved that Fe^{3+}-gallate

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*Correspondence: mjm@fct.unl.pt; silvia.sequeira@fct.unl.pt

[1] LAQV-REQUIMTE, Department of Conservation and Restoration, NOVA School of Sciences and Technology, Campus da Caparica, 2829-516 Caparica, Portugal
Full list of author information is available at the end of the article

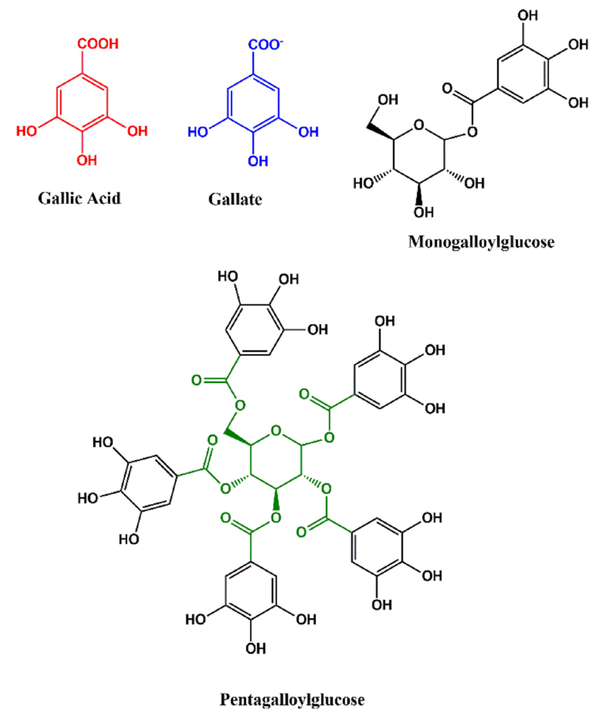


Fig. 1 Chemical structures of gallic acid, gallate, monogalloyl glucose and pentagalloyl glucose. In the first two, the main functional group is based on a carboxylic acid and the other on an ester. Phenolic OH groups are also important in the formation of the iron(II)-phenol complex. The galloyl esters of glucose can also be named gallotannins

complexes binding through the carboxylate group cannot be formed at the pH found in ink preparation, which is between 2 and 3. They propose that iron oxyhydroxides best represent the iron clusters and that these nanoparticles are "covered by a shell of polymerized oxidation products of the phenols" [13].

Much research has been conducted on the causes of iron-gall ink corrosion, as well as on the efficacy of various conservation treatments to solve the problem in cultural heritage institutions caused by the so-called "iron-gall ink burn". This microreview will address the state-of-the-art research on the degradation of iron-gall inks and will present an important review of the conservation treatments used since the end of the nineteenth century.

Degradation mechanisms

This section will review the advances that have taken place over the past 10 years in understanding the degradation mechanisms of iron-gall inks. The reader is referred to the book "Iron-gall Inks". On manufacture, characterization, degradation and stabilization" published in 2006 for previous years [1]. We focus on the experimental models that have been applied in the field of cultural heritage to mimic the ageing of iron-gall inks, as well as on the studies of the degradation products found in historical artworks [3, 4, 14]. These experiments have usually been based on Fe^{3+}-gallates, and their reactivity was assessed indirectly by their impact on paper degradation. These chromophores were possibly first proposed in 1924 by Zetzsche et al. [13, 15].

The literature proposes that iron-gall inks can induce the scission of cellulose by acid catalysis and/or through redox reactions. Therefore, we will discuss the causes of these acid-base and redox reactions.

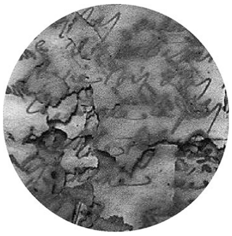
Reaction mechanisms based on the Fe^{3+}-gallate model

In this section, the main conclusions based on models using gallic acid as the phenolic counterpart will be reviewed. Using gallic acid to represent polyphenols extracted from galls assumes that "gall nut extracts are rich in gallic acid" [9]. An assumption broadly accepted in the field of cultural heritage that we have recently proven may not be the general rule [5, 6].

For the past 10 years, model systems have been based on the synthesis of Fe-gallates, obtained by adding Fe^{2+} sulfate to a gallic acid solution, and when a binder is used, it is gum arabic. In these inks, an excess of iron sulfate can be used, and in these cases, part of the Fe^{2+} binds to the phenolic compounds present in solution being converted into Fe^{3+}, and another part is "free" to react [16]. Fe^{3+} is strongly complexed by gallic acid or galloyl esters of glucose present in solution, Fig. 1. For this reason, "free" Fe^{2+} is assumed to play a crucial role in degradation phenomena [3].

Rouchon et al. studied the distribution of both Fe^{2+} and Fe^{3+} in reference compounds, showing a heterogeneous distribution of the ink components in a cellulose fibre due to the different binding affinities [3]. The studies were carried out on an ink-impregnated linen fibre prepared in cross-sections of 15 µm · 5 µm · 80 nm to be transparent to X-rays. The fibre was studied by synchrotron techniques, namely XANES, and the authors concluded: "Altogether, the present study evidences that the different components of the iron-gall ink do not behave the same way during ink penetration within paper fibres. In the absence of gum arabic, ink migrates into the fibre and Fe(III) gallate precipitates during this migration. However, gallic acid and Fe(III) gallate precipitates penetrate less through the fibres compared to soluble Fe(II). The addition of gum arabic significantly increases the viscosity of the ink, thus preventing the penetration of most of its components. Importantly, with or without gum arabic, low amounts of soluble Fe(II) appear to impregnate the linen fibres fully" [3].

Table 1 Summary of the main results obtained in [14] for the analysis of two historic inks

Sample M03 (18th c.)	Sample C04 (18th c.)
	
Large brown halos; paper was very fragile but could be manipulated	Degradation of the cellulose in the inked areas led to paper crumbling
≈90% Fe^{2+} [§]	≈90% Fe^{3+} [§]
≈90% Fe^{2+} and ≈10% Fe^{3+} [#]	≈100% Fe^{2+} [#]

[§] Mössbauer analysis in dried residues containing inked and non-inked areas

[#] Calibration curve measured Fe^{2+}/Fe^{3+} ratio in solution, measured in an electrochemical cell

This critical information shows that the uncomplexed Fe^{2+} penetrates deeply into the cellulose fibre when used in excess. In contrast, the dispersion of the black chromophore in gum arabic remains on the surface. "The main consequence of this heterogeneity is the lack of uniform distribution of degradation" [17]. This heterogeneous distribution means that there are areas of paper in relatively good condition and others very fragile; so, when we take in our hands a paper in these conditions, by the parts in "good condition", we can "tear" the most degraded. The open question that deserves to be explored concerns the lifetime of Fe^{2+} in paper since, in solution, it would have reacted readily [18].

The same group, led by Rouchon, proposed that iron acts as a catalyst for cellulose chain scission in a mechanism partially based on acid hydrolysis through intermediates that lower the activation energy [9]. Experiments were carried out on filter paper impregnated with Fe^{2+} and Fe^{2+} in the presence of gallic acid solutions, the latter leading to the formation of a gallate-Fe^{3+} complex. These papers were thermally aged (temperature range 20–90 °C.) and cellulose depolymerization was monitored by calculating the activation energies: $E_a = 95.3$ kJ mol^{-1} for the gallate-Fe^{3+} complex and $E_a = 98.6$ kJ mol^{-1} for the Fe^{2+}-impregnated sample. These similar values for the activation energies are somewhat unexpected and deserve further investigation.

Degradation products for iron-gall inks observed in heritage objects

In another publication by Refait et al., two samples of paper from the eighteenth century heavily damaged by iron-gall-inks were studied, as shown in Table 1 [14]. In the sample in which ink degradation led to paper crumbling, Fe^{3+} was the main species detected by Mössbauer analysis in the dry residue. On the other hand, in the sample in which large brown halos were observed (paper was very fragile but could be manipulated), Fe^{2+} was the main species in the dry residue. However, when samples were extracted in water, the Fe^{2+} to Fe^{3+} ratio, calculated by potentiometric methods using a calibration curve, shows that the main species detected in solution was Fe^{2+}. This observation can be explained considering the high complexation constant of Fe^{3+} with phenolic compounds. However, it is intriguing to see Fe^{2+} as the main species in one of the ink samples, although at the moment, we cannot explain this or the different patterns of paper degradation observed. Another interesting observation made in this electrochemical study of iron ions in the presence of gallic acid is the following: the solutions of Fe^{2+} and gallic acid were light blue and tended to darken over time; Fe^{3+} and gallic acid were initially dark blue but rapidly turned green [14]. One of the authors' main conclusions of this study is that "acidity values for some manuscripts in apparently good condition are not far from those obtained for degraded manuscripts. The results indicate that in some partially degraded manuscripts, the coexistence of acid areas and areas with an alkaline reserve which do not participate in the neutralization process is possible".

In a recent publication by Lerf et al., three historical documents were studied by Mössbauer spectroscopy [20]: two damaged documents from a library in Granada (Chancery MS and Latin MS) and a book handwritten in German from the eighteenth century. In the Chancery MS it was possible to identify Fe^{2+}-oxalate, possibly as $FeC_2O_4{\cdot}2H_2O$, and basic iron sulfates of the jarosite type, $(H_3O)Fe_3(SO_4)_2(OH)_6$. The formation of oxalate can be a consequence of binding media degradation [21, 22] or, as also suggested by Lerf et al., of the degradation of cellulose. As pointed out by these authors, Fe^{2+}-oxalates were previously detected in ancient documents [23, 24]. It should also be noted that it was possible to prove that iron gallate complexes (Fe^{2+} or Fe^{3+}) were not present in the inks [20].

Iron sulfates were also proposed by La Camera as degradation products by examining iron gall ink crystals in drawings dating from fifteenth to nineteenth-century Europe in the collection of the Department of Prints, Drawings, and Photographs of the Museum of Fine Arts Boston and selected additional collections [25]. XRF showed that iron was the only major element present within the ink, and very similar infrared spectra were obtained for each sample. It was concluded that "analysis of specific drawings indicated the

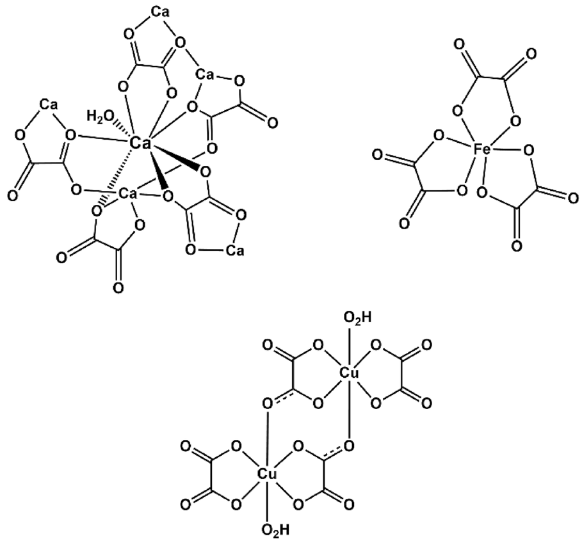


Fig. 2 Chemical structures for the following metal oxalates, described by Ferrer and Sistach: Ca^{2+}, Cu^{2+} and Fe^{3+} oxalates [4] (Structures adapted from [19])

predominance of iron sulphates within the crystals, though further analytical work is necessary for precise identification" [25].

An important contribution to the knowledge of the degradation products of iron-gall-inks was made by Ferrer and Sistach based on their characterization of sediments found on the surface of writing inks in manuscripts dated between the fourteenth and seventeenth centuries [4]. The authors clearly show that these sediments are probably degradation products of the writing inks. Fifteen samples were studied by infrared spectroscopy, mainly using microFTIR. The pH of the ink's surface was measured with a surface electrode. Samples were described in terms of ink corrosion (ic) as follows: no ic, little ic, medium ic and strong ic. 47% were considered to have little or no ink corrosion, and 33% were considered to have medium or strong ink corrosion. Other samples were described as water damaged. pH values gave a precise indication of the degree of corrosion, with pH values of 3.5 attributed to strong ink corrosion, 3.8–4.1 to medium and higher pH values, and 4.2–5.8 to little or none. Calcium, copper and Fe^{2+} oxalates were identified in samples with higher pH values and low degradation, Fig. 2.

On the other hand, magnesium and Fe^{3+} oxalates were detected in severely degraded inks. In addition to oxalates, an iron basic sulfate was identified in five samples, and a good match with amarantite ($FeSO_4OH{\cdot}3H_2O$) was found; in two of these samples, little ink corrosion was observed, but in the other three strong ink corrosion was present. Another iron sulfate, $(NH_4)2Fe(SO_4)_2{\cdot}6H_2O$, was observed in the sediment of a seventeenth-century ink, in which copper oxalate was also present. This is an interesting finding as it indicates the use of ammonium salts in the recipe to prepare the iron-gall-ink.

The authors also discuss the correlation between degradation products and ink corrosion: "Generally speaking, calcium, copper and iron (II) oxalates are found in inks with pH above 5, with little ink corrosion and black sediments on the ink lines. Iron (III) potassium oxalate has been analysed in samples, and other authors detected these types of iron (II) oxalates at a pH of approximately 4" [20, 23, 24].

The introduction by Ferrer and Sistach mentions that the hydrolysis of cellulose in paper can result "from sulfuric acid, which is produced during the formation of the iron-gall ink complex". Given the lack of experimental evidence of the presence of H_2SO_4 in the ink formulation and that iron-gall inks have pH values above 1, it is not expected to find this very strong acid in solution but rather sulfate ions [9]. Nevertheless, this assumption that sulfuric acid is considered a product has been generally accepted in the field of cultural heritage [17, 26]. A possible explanation for the very acidic pH can be found by looking at Fe^{3+}. Part of the Fe^{2+} added to the solution can be converted to Fe^{3+}, which is a strong Lewis acid with $pKa_1 = 2.2$ and $pK_{a2} = 3.5$ [27]. These p*K*as are a consequence of the hydrolysis of Fe^{3+} in water, which results in the formation of oxo-hydroxo species [27]. The first p*K*a could explain the pH of approximately 2 measured in reproductions of medieval paints [5].

Conservation treatments

Iron-gall ink corrosion

From the first International Conference for Preservation and Conservation Access of Antique Manuscripts (i.e. Internationale Konferenz zur Erhaltung uns Ausbesserung alter Handschriften) in 1898 at St. Gallen, until the Ink Corrosion Conference—IIC in 2019 at Krems, and the development of several projects in recent decades (e.g., InkCor, 2002–2005), a great deal of effort was made and continues to be made in terms of the study of the efficacy of various conservation treatments to solve the cultural heritage institutions' problem caused by the so-called "iron-gall ink burn" [28].

An early treatment approach was mainly directed toward recovering the strength of the paper support. From the late nineteenth century to the early twentieth century several consolidation materials and methods were applied, from traditional lining and lamination (sandwich-like method) procedures with adhesive and thin papers or chiffon-silk to new synthetic materials, such as the commercial product Zapon, a cellulose nitrate [29–31]. The latter was first used for waterproofing of geographic maps by the German army, but due to its flammability, in 1909, the Royal Materials Testing Office/Berlin (e.g., Königliches Materialprüfungsamt Berlin) recommended the use of a safer product, Cellit, a cellulose acetate (possibly with a degree of substitution (DS) of 2.2–2.6, considering it is soluble in acetone) [30, 31].

In the mid-twentieth century, cellulose acetate and poly(vinyl chloride) films were used for the consolidation of deteriorated documents. At the time, the bookbinder/conservator William Barrow, collaborator of the well-known Library of Congress, recognized acid hydrolysis as one of the main causes of paper deterioration and corrosion increase of iron-gall ink, when present. Therefore, he developed a two-step method (immersion in a saturated calcium hydroxide bath, followed by a calcium bicarbonate bath) plus his lamination method that involves the application of cellulose acetate and a tissue paper, on both sides of the document, to avoid a plasticised appearance [29, 32]. The result was a rather heavier, stiff, and uncharacteristic flat paper sheet document, but quite alkaline.

Already in the nineteenth century, the use of the ‘ammonia collodion process’ was recommended, which involved the application of ammonia vapours, followed by mechanical stabilization with collodion [31]. Collodion is a cellulose nitrate solution in ethanol and ethyl ether [33]. The invention is attributed to Schönbein, who mixed the two solvents in a 50:50 ratio. Reilly proposed a DS of 2 for cellulose nitrate in collodion [33]. Again, applying the highly flammable cellulose nitrate with shrinkage and low penetration problems was intended [31]; adding that long-term stabilizing was not achieved with ammonia neutralization [34]. In the mid-twentieth century, Barrow established an alkaline treatment prior to lamination as a regular procedure, namely, to treat ink-corroded documents. Due to the high pH of treated documents and ink colour changes observed in the mid-1960s, Barrow suggested the use of a single bath of saturated magnesium bicarbonate, known as the “Barrow One-Step” [29, 35].

After Barrow’s achievements, several authors followed the idea of iron-gall ink document stabilization through deacidification.

Minogue was one of the first to mention washing with distilled water as a possible treatment [36]. Nevertheless, Peter Waters established washing with water as a regular step for iron-gall ink corroded documents. Waters became a main figure in the field after his role in the 1966 flood of Arno in Florence and was invited in the 1970s to coordinate the conservation services at the Library of Congress [32]. At the Library of Congress, he set up as current praxis an immersion bath in warm water for acid removal, followed by an immersion bath in diluted calcium or magnesium bicarbonate for paper buffering [37]. The type of water used was not described, but currently, it can be deionized or “purified” tap water obtained using an activated carbon filter. The diluted calcium or magnesium bicarbonate solutions aimed to avoid “gripping” (deposition of a thin whitish layer causing a rough surface, mostly visible in dark areas), a phenomenon already described by Brannahl as the main drawback for inked documents [38].

Waters also recommended the use of newly available materials (e.g., “heat-set mending tissue”) to be applied as much as possible locally, only on the damaged affected areas of the documents; and the substitution of the complete lamination by polyester film encapsulation, providing physical support for the weaker documents [37].

The ink discolouration problem, namely after alkaline treatments, plus the risk of iron spreading during aqueous treatments, also promoted different studies.

Nonaqueous methods for treating manuscripts were also investigated early on, namely that of barium hydroxide dissolved in methanol. According to Baynes-Cope (1969), folding endurance tests indicated the method’s safety, and pH measurements before and after treatment showed that this method was effective; however, he also recognized that when insufficient buffer was deposited, the acidity would return [39]. In the mid-1970s the use of methylmagnesium carbonate, patented by George Kelly, was also seen as a possibility for water-soluble iron-gall inks. A study on its efficacy proves that both methods, spraying and immersion, leave the considered adequate alkaline reserve (approximately 1%, which can be measured as described in [40]). Nevertheless, the solvent’s fast evaporation rate left an uneven deposit [41].

In the 1980s, Hey assumed that the main cause of degradation was the presence of sulfuric acid and ferric oxides in the ink and considered that, whenever possible, washing should be a mandatory first step. In her research, she compared four different solutions for deacidification: 4% sodium borate; 1/2 saturated calcium hydroxide; magnesium bicarbonate and methylmagnesium carbonate dissolved in methanol and Freon. She concluded that sodium borate was unsuitable and that the best performance was of calcium and magnesium baths. She also suggested that the higher the ratio of calcium or magnesium carbonate to iron, the greater the protection conferred to cellulose [36].

“Simmering” or “boiling” water treatments for iron-gall ink-containing manuscripts were also seen as a possible solution and have been used for over 40 years. Carried out in the Conservation-Restoration Laboratory of the Vatican Library in the 1970s, the treatment was used in a few other European laboratories (e.g., Poland, Austria) and was later adopted by American [42] and Canadian scientists and conservators [43, 44]. It was confirmed that high levels of the destructive iron (II) ions (Fe^{2+}) could be removed from the paper into the simmering wash water and that the concentration of possibly redeposited Fe^{2+} in other areas of the support was negligible (below the limit of detection by the analytical methodology used) [42]. However, on the other hand, the long-term effects of filler and size loss are a concern, plus the fact that this method is not yet completely proven to be safe on rather weak and fragile papers [44].

It is also worth mentioning that some authors were especially concerned with the regeneration of texts by applying chemical compounds that can later damage both the ink and support, adding to the complexity of the deterioration process of iron-gall ink documents [45, 46].

Searching for proper treatment was still ongoing in the 1990s, namely, in the field of deacidification/alkalinization. A work comparing the effect of fully aqueous and ethanol-diluted solutions of magnesium bicarbonate on six iron-gall ink documents dating from the eighteenth and nineteenth centuries was developed. Test results suggested that the addition of ethanol preserves the visual appearance of aged iron-gall inks, while both fully aqueous treatments (of 100% and 25% saturated magnesium bicarbonate) both caused loss of intensity and colour change in the ink of four of the six documents [47].

Since 1997, a nonaqueous deacidification method composed of submicron-sized particles of magnesium oxide dispersed in perfluoroalkane has been applied to a selection of iron-gall ink manuscripts in the Library of Congress [29]. When sprayed, the particles become lodged in paper and it is supposed that afterwards, they react with ambient moisture to form magnesium hydroxide. Further studies on this nonaqueous system revealed uniform spraying and an adequate alkaline reserve on the tested papers [48].

The phytate treatments

Han Neevel, a conservation scientist at the Netherlands Institute for Cultural Heritage, proposed in 1995 an innovative aqueous iron-chelating treatment based on the premise that excess Fe^{2+} was mainly responsible for ink corrosion on paper [16]: the application of *myo*-inositol hexakisphosphate salts (phytates), which are naturally occurring antioxidants that would inactivate the iron ions responsible for cellulose oxidation [49]. Phytic acid (*myo*-inositol hexakisphosphate) forms complexes with a variety of divalent and trivalent cations, Fig. 3. The antioxidant action of phytic acid is based on its ability to coordinate all sites of Fe^{2+} and Fe^{3+} [50], Fig. 3. Phytate also offers protection against oxidation by diminishing the concentration of *free* Fe^{2+} as it lowers the redox potential of the Fe^{3+}/Fe^{2+} couple [51].

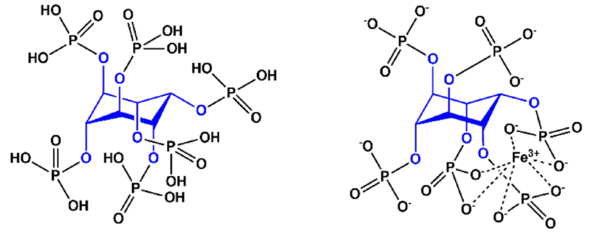


Fig. 3 Molecular structure of phytic acid (*right)* and of mono ferric-phytate at pH 6–7 (*left*), in which the six Fe^{3+} coordination sites are bound to phytate (Adapted from [50])

Myo-inositol hexakisphosphate forms high-affinity complexes, 1:1 stoichiometry, with Fe^{2+} and Fe^{3+} (as with many other transition metal ions), and the stability constants are pH-dependent [51]. Bearing in mind that during the conservation procedure of the iron-gall ink, the pH is kept in the range of 5–5.8, the species in solution will possibly be: for Fe^{2+}, $[Fe(H_6L)]^{4-}$ and $[Fe(H_5L)]^{5-}$ with $\log K = 5.95$ and 7.7 respectively; for Fe^{3+}, the only complex should be $[FeH_3L]^{6-}$, $\log K = 18.20$. On the other hand, in solution, gallate-Fe^{3+} constants are $\log K = 14$ [52].

These stability constants are measured in solution and refer to soluble species. However, the brown pigments found in aged iron-gall inks can be insoluble, particularly those based on Fe^{3+}. Thus, a first complexation with iron ions not complexed with gallotannins is expected, but considering that phytate salts can complex both Fe^{3+} and Fe^{2+}, it will always be important to carry out preliminary tests to assess the safety of this type of treatment.

Calcium phytate (CaPhy) treatment is usually composed of these primary steps: wetting and washing of the paper; calcium phytate immersion, deacidification (neutralization and deposition of alkaline reserve) with calcium bicarbonate, application of gelatin sizing, mending any cracks and losses, and drying [53, 54], Fig. 4. For the aqueous washing step, instead of deionized water, the use of tap water of good quality or recalcified water is recommended to prevent removing original substances that are known to contribute to the chemical stability of paper, such as finely distributed calcium carbonate deposits [53, 54]. Gelatin is generally used as a resizing agent for iron gall inked documents rather than the other adhesives commonly used in paper conservation, due to its demonstrated ink corrosion protection effect [55].

Several studies have attested to the effectiveness of CaPhy treatment in preventing paper deterioration caused by iron-gall ink by comparing different properties of treated and untreated samples after artificial

Fig. 4 Calcium phytate main treatment steps: (1) humidification, gradual transition from a dry to a wet state to minimize dimensional tensions in the object; (2) washing in water, for removal of acids and soluble transition metal ions such as Fe^{2+} or Cu^{+}; (3) immersion in calcium phytate solution, complexation of Fe^{2+} and Fe^{3+} by phytate; (4) deacidification with calcium bicarbonate, neutralization of remaining acids and deposition of an alkaline reserve in the paper; (5) sizing with gelatine, increasing the mechanical strength of paper and adding a protective layer between the atmosphere and the surface of the ink; and (6) local mending to support areas with mechanical damages and prevent further losses

ageing, such as bursting strength; folding endurance; tensile strength; degree of cellulose polymerization; colour or whiteness; pH; alkaline reserve; or fluorescence labelling of carbonyl and carboxyl groups in combination with GPC-MALLS [56–59]. This treatment has been, at least partially, adopted by the international paper conservation community [60].

Variants of the CaPhy treatment have been proposed, such as the use of magnesium phytate (MgPhy) instead of calcium [61], Fig. 3. MgPhy prevented paper deterioration similarly to CaPhy, while having the advantage over CaPh of not requiring the use of toxic ammonia to adjust the pH of the phytate solution [61]. Other myo-inositol derivatives, such as myo-inositol 1,2,3-tris(dihydrogen phosphate) and myo-inositol 1,2,3,5-tetrakis(dihydrogen phosphate) were investigated as they could be derivatized to give less polar compounds and constitute a nonaqueous alternative to CaPhy or MgPhy [62].

Dilution of CaPhy in ethanol could also be an alternative for documents with water-soluble inks, but the higher the dilution is, the lower the treatment efficacy, manifested by a decreased mechanical resistance in the treated paper [63]. Völkel and colleagues [64] tested the addition of fibrillated nanocellulose into the different steps of the CaPhy treatment and proved its potential as a mechanical stabilizer of iron-gall ink-damaged paper. This addition would eliminate the need for subsequent local mending.

CaPhy treatment, however, introduces a new chemical into the paper (calcium phytate precipitate), which can be visible on the surface of the paper as a white powder. Although this superficial deposit can be removed by brushing, this operation is not advisable on paper severely deteriorated by iron-gall ink. One of the major limitations of this treatment is the poor solubility of phytate in nonaqueous media, hampering its application in water-sensitive items. As an aqueous treatment, it has the additional shortcoming that only unbound volumes are eligible for it. Additionally, the multiple immersion steps required [53] imply significant mechanical stress of such damaged papers [65], in addition to ink colour alteration [56], and a significant modification of the paper/ink composition [66].

Pos-phytate treatments

To overcome the drawbacks of CaPhy treatment, several alternatives have been proposed. Jana Kolar and colleagues, proposed for the first time the use of halides as antioxidants to stabilize iron gall inked paper [57]. An aqueous solution of tetrabutylammonium bromide, a peroxide decomposer, was shown to prevent cellulose depolymerization to a higher extent than CaPhy [57]. Malesic et al. continued testing this class of compounds using a nonaqueous solvent: dichloromethane [67]. Tetrabutylammonium chloride, bromide and dodecyltrimethylammonium bromide exhibited the strongest stabilization effect and were the first nonaqueous alternatives to CaPhy [67]. Later, Kolar and her research team tested alkylimidazolium bromides in a less toxic organic solvent: ethanol [68]. 1-Ethyl-3-methylimidazolium bromide and 1-butyl-2,3-dimethyl-imidazolium bromide, in combination with alkali magnesium ethoxide in ethanolic solution, had a higher stabilization effect on iron gall inked paper when compared with the previously tested tetraalkylammonium bromides, CaPhy or MgPhy, while causing no significant colour alteration on the treated ink [68]. Data on the toxicity and environmental impact of these imidazolium-based ionic liquids are quite limited, though [69].

Rouchon et al. [70] also tested the use of halides to treat iron gall ink-damaged papers, but in this case, using them as salts (NaCl, NaBr, $CaBr_2$) and compressing the iron gall inked documents between two interleaves charged with the active compound. However, for the migration of the active compounds from the interleaves to the documents to occur, high relative humidity conditions (above 80%) for several days are required, and these conditions may additionally induce the migration of iron and acidic compounds out of the ink line and across the paper.

Kolar and colleagues demonstrated that the transition metal content of historical iron-gall inks varies greatly, and due to its superior catalytic activity, it is copper, not iron, the main oxidation catalyser on paper containing copper-rich iron-gall inks [57].

To address this problem, Zaccaron et al. compared CaPhy treatment with a new method using glucose as a reducing sugar, which based on the Fehling reaction, would selectively remove free copper ions by precipitating them as an insoluble cuprous oxide in the treatment bath [71]. However, this glucose treatment caused severe hydrolytic and oxidative degradation with remarkable yellowing on the paper and is not a viable conservation option. Moreover, the authors concluded that CaPhy treatment was still very effective and safe even for iron-gall inks with a high percentage of Cu ions.

Piero Baglioni's group, which specializes in nanotechnology, has also studied stabilization treatments for iron gall inks, including copper-containing ink. They compared the effect of two nonaqueous deacidification solutions: magnesium hydroxide nanoparticles dispersed in isopropanol and a commercial Bookkeeper solution [72]. The pH of paper deacidified with the nanoparticles was maintained at approximately pH 7 to reduce the rate of cellulose oxidation, since the catalytic activity of iron and copper ions is minimal when the pH is approximately neutral [73]. Both magnesium hydroxide and Bookkeeper treatments partially prevented cellulose depolymerization caused by iron gall ink with artificial ageing. The nanoparticles performed slightly better while having the advantage of not using fluorinated solvents [72]. How the final pH of treated paper was controlled to be near 7 is not clear, and this is a crucial step due to the influence of pH on the efficacy and safety of the treatment. Sequeira et al. showed in a previous study that when using calcium hydroxide nanoparticles, the final pH of treated papers will depend not only on the concentration of applied nanoparticles but also on the initial pH of the paper itself [74].

Later, this same research group developed a combined deacidification and strengthening treatment consisting of hydroalcoholic gelatine solutions (ethanol or isopropanol) mixed with $Ca(OH)_2$ nanoparticles called GeolNan, which could increase the resistance of cellulose to hydrolysis and oxidation induced by iron gall ink [75]. According to the authors, this achievement is mainly due to the nanoparticles, even if gelatin itself partially hampers the depolymerization of cellulose, probably slowing down the oxidation reaction by reducing ion mobility or complexing metal ions. A previous study on the effects of nonaqueous deacidification with $Ca(OH)_2$ nanoparticles on iron gall inked paper also revealed that the nanoparticles alone may diminish the depolymerization of cellulose under artificial aging, although to a lesser extent than aqueous $Ca(OH)_2$ saturated solutions [74].

Due to the high alkalinity of calcium hydroxide nanoparticles in the presence of moisture [76], special caution should be taken to control the pH when treating heavily oxidized cellulose, such as iron gall ink corroded paper, owing to the higher risk of alkaline degradation.

Conclusions and future perspectives

Twenty years after the prophetic article by Strlič and Kolar [77], significant advances have been made in our understanding of the degradation mechanisms of iron-gall inks and their support. However, it is still not possible to propose a complete vision covering the core of this phenomenon's complexity. This vision will have to encompass several types of degradation mechanisms, possibly competing with each other. Additionally, a dialogue must be established between this chemical understanding and the gathered knowledge on conservation treatments to develop safe and sustainable treatments tailored as much as possible to the object. Thus, 20 years later, the challenge launched by Strlič and Kolar awaits an answer:

"Treatment optimisation and testing should be founded on a sound choice of models and comprehensive photo- and thermal-accelerated ageing experiments, which are both time and work intensive, so their development should be encouraged. Many conservation procedures, even those which are regularly used, e.g. (mass) deacidification, are in need of such optimisation" [77].

For the first time, this microreview brings together both sides of a long endeavour, conservation science and conservation treatments. We have come a long way from the nineteenth-century cellulose nitrate laminations into the relatively recent treatments with phytates or nonaqueous halide antioxidants; nevertheless, less invasive and more ecological treatments are still needed. Ultimately, it should be considered that any conservation treatment can potentially alter the original composition of iron gall ink irreversibly, hampering the chance to link an ink to a specific provenance. Hence, direct treatment should always be the last resource to preserve these documents.

In the future, it will be important to discuss what will be most relevant in terms of strategy for the preservation of iron-gall inks in historical documents.

Several questions remain open: Do we need to define specific methodologies for solving specific problems such as eliminating “free” Fe^{2+}, or do we need to look for eco-friendly strategies that can act in the prevention of oxidation reactions? For example, based on the successful applications of amino acids such as cysteine to inhibit corrosion in metals such as iron and copper, these eco-friendly inhibitors could be tested on degraded references of iron-gall inks [78–84]; see also Additional file 1.

In addition, considering the role of chlorine ions in the oxidation of iron, which leads to a continuous and very difficult to stabilize corrosion process in metal objects [85], could chlorine ions also act as degradation agents if present in iron-gall inks or their support? As such, would it promote the reduction of Fe^{3+} to Fe^{2+} and a continuous chain of radical-based reactions based on chlorine radicals? Therefore, should we look for the presence of chlorine ions and try to understand their role in the degradation of iron-gall inks?

Abbreviations

CaPhy: Calcium phytate; microFTIR: Micro-Fourier Transform Infrared Spectroscopy; XANES: X-ray absorption near-edge structure; XRF: X-ray fluorescence.

Supplementary Information

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Additional file 1. Cysteine-based interventions to protect metals from corrosion.

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Author contributions

MJM and VO coordinated the review of the degradation mechanisms, with the collaboration of PN, NT and FP. SS and CC coordinated the review of the conservation treatments; CC was responsible for Iron-gall ink corrosion and SS for the phytate and pos-phytate treatments. SF was responsible for the cysteine-based interventions to preserve metals from corrosion. All authors contributed to the conclusions, revision and approval of the article’s final version. All authors read and approved the final manuscript.

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Availability of data and materials

Not applicable.

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

[1]LAQV-REQUIMTE, Department of Conservation and Restoration, NOVA School of Sciences and Technology, Campus da Caparica, 2829-516 Caparica, Portugal. [2]Instituto de Estudos Medievais Universidade NOVA de Lisboa, Avenida de Berna 26-C, 1069-061 Lisboa, Portugal. [3]LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal. [4]CENIMAT/i3N-Centre for Materials Research, NOVA School of Sciences and Technology, Campus da Caparica, 2829-516 Caparica, Portugal. [5]VICARTE, Department of Conservation and Restoration, NOVA School of Sciences and Technology, Campus da Caparica, 2829-516 Caparica, Portugal.

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