Modification toward Instability and Damage to Papers of Iron Gall Inks

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Abstract

Iron gall ink is one of the most critical types of ink in the western world, which has been applied for about 5400 years. Albeit its outstanding contribution to preserving human civilization treasure, it jams fountain pens and causes "ink burn" phenomena; thus, its recipes need to be modified. This study includes a brief history of iron gall inks, with central components and other additives in ancient and modern recipes, also their production processes. Additionally, this study reviewed the structures and stability of particles, especially metal-polyphenolic complexes, and the destruction of iron gall inks. Based on earlier research, this study compared Fe^{2+} ion and Fe^{3+} ion, studied effective ligands and the best solution conditions for the ligands, and proposed various ways to modify iron gall inks. Upon this analysis, this study suggested some outlook for the future study of the modification of iron gall inks.

Introduction

Iron gall ink, mainly consisting of macromolecular 1:1 complexes of iron ions and gallic acid (Wunderlich et al., 1991), is one of the essential inks in the history of western civilization (Teixeira et al., 2021). From around 3400 years ago, ancient Egyptians started using a mixture similar to the later iron gall inks (Festa et al., 2019). People widely used these inks until the 20th century, when they found new inks substituting most functions. Despite it becoming obsolete, iron gall inks are still known as the best kind of ink against water and time, having extremely dark and clear colours others seldom present. As long as the paper remains, it can be one of the most stable types of ink against wash and blur, so that the iron

gall inks earned themselves a credit for preserving many important manuscripts with high historical value, such as Thomas Jefferson's original draft of the Declaration of Independence (Fig.1.a), Abraham Lincoln's first draft of the Emancipation Proclamation (Fig.1.b), and Beethoven's original scores (Fig.1.c) (Ponce et al., 2016).

However, the persistent iron gall inks can catalyse the like-Fenton reaction and acid-catalysed hydrolysis of the paper containing it (Wagner & Bulska, 2002). Thus, they are also the arch-criminal of destroying many significant hand-written materials (Fig.1.d) (Zaccaron et al., 2019).

Figure 1. Hand-written materials of iron gall inks a) original draft of the Declaration of Independence; b) Abraham Lincoln's first draft of the Emancipation Proclamation; c) Beethoven's original scores; d) a manuscript with "ink burnt" phenomena which were caused by the high acidity of iron gal ink

Contributable works done by modern scientists mentioned various practical solutions for preserving archives endangered by iron gall inks. Though few of them pay interest in modifying iron gall inks' recipes for hand-writing or printing, these studies have given this study plenty of inspiration for some chemicals added to ancient recipes. New additives such as Tetrabutylammonium bromide, chloride, and dodecyl trimethylammonium bromide beneficial to the paper base are suggested for

the developed recipes. This study provides suggestions for the hand-written materials to be preserved against moisture and time, which is very important for future historians and people in need of knowledge in these papers. Based on this reason, the following study and suggestion of the possible solution to improve the recipes of iron gall inks can be very significant.

In this study, the recipes collected are mainly distinguished into two categories: ancient recipes (created before the 20th century) and modern recipes (created in and after the 20th century). These categories can give a better insight into how to imply modern science of chemistry to use chemicals from nature, analyse structures of complexes, and provide suggestions for modifying recipes in a much more reasonable and convenient way.

Components of Ancient Recipes
Central components and their ratio: a majority of ancient recipes contain three central components: ferrous sulphate (a.k.a. green vitriol, copperas, Verdigris) (Fig.2.a), Arabic gum (Fig.2.b), and galls (especially from Aleppo, need to be crushed simply or into powder) (Fig.2.c) (Kaminari et al., 2018). Without other additives, using water alone as the solvent, the ratio of ferrous sulphate: gum: gall in mass (later referred to as FS:G:G), would lay approximately between 1:1:1 to 1:1:2. However, neither the ratio between water and these components is predictable, nor their production procedure, except for galls need to be crushed simply. Come to those in the 19th century, the ratio jumped to between 1:1:2 to 1:1:4, but other features in production never changed (Table S1).

Additives and their influence on the ratio of

central components: besides ferrous sulphate, Arabic gum, and galls, to improve its functions, various kinds of other solvents, herbs, and chemicals were added to the recipes. For instance, wine (especially white wine) or alcohol can reduce polarity; glycerol and sucrose (also sugar, honey, syrup or molasses) can prolong drying time for the copying process (Kaminari et al., 2018); logwood （Fig.2.d） and indigo (Fig.2.e) can endarken the colour; pomegranate peel (Fig.2.f) and clove (Fig.2.g) can be used as natural aromatic and preservative; alum and silver nitrate can be used simply as preservatives; vinegar and sulphuric acid can be used as a stabilizer (Hidalgo et al., 2018). In the presence of wine or alcohol, the mixture would need to be heated slightly in the production, while the FS:G:G lays between 1-1.5:1:1-2.5 (Table S1). When logwood and indigo were added (incredibly fashionable in the 19th century), FS:G:G lays between in the range of 1:1-1.5:1-2 (Table S1).

Figure 2. Stocks of ancient recipes: a) green vitriol (ferrous sulphate) mine; b) Arabic gums; c) galls and crushed gall pieces being soaked in a bottle of rainwater; d) logwood; e) indigos; f) pomegranate peel; g) cloves

Production Processes of Ancient Recipes
Various time-consuming production procedures required by ancient recipes were usually designed reasonably. Crushing galls into pieces

(or sometimes into powder) and pre-boiling or fermenting gall nuts before mixing were several steps that need to be done in most of the recipes collected (Table S1). These treatments can enhance gallic acid formation through tannin hydrolysis and raise concentrations of gallic acid in the mixture, presumably leading to a more efficient iron complexation (Kaminari et al., 2018). The fermenting was usually done before boiling before the 15th century, turned to after a longer boiling at the end of the 16th century (Table S1).

In most recipes, the author asked either a one-day deposition or filtration through white linen cloth (sometimes even both) to remove solid content, such as residues of galls and impurities brought by ferrous sulphate (Table S1) due to no refinement were done before production. After completing the procedures above, a few recipes in the 19th century would ask for stirring (frequently) the mixture during deposition.

Components of Modern Recipes
Central components and their containment: when it came to the 20th century (i.e., modern society), as chemistry became much more developed, people started to add chemicals from factories directly instead of refining the chemicals needed from natural products during production. The three central components (ferrous sulphate, Arabic gum, and galls) changed to crystals of Fe^{2+} containing compounds, blue dye (mostly aniline blue), and gallic acid crystals (usually with tannic acid crystals) (Stratton et al., 1920), but Arabic gum lumps at the time were added only for printing inks (Stratton et al., 1920). Something noticeable is that inks containing gallic acid without tannic acid had a very low permanence when exposed to the weather (Ruppert, 1923).

Figure 3. Stocks of modern recipes: a) ferrous sulphate heptahydrate; b) ferric chloride; c) tannic acid; d) aniline blue

Instead of calculating ratios in mass, the statistics about the containment of element iron and hydrogen in every 100 ml of ink can show the composition of modern iron gall inks clearer. According to the US Bureau of Standards, the mass of iron in every 100 ml of writing ink must be between 0.29g and 0.35g, while the standard doubled for 100ml of printing ink (Stratton et al., 1920). Delocalized protons are provided by the gallic acid with tannic acid and stabilizing agents (mostly acidic) in the mixture. In the recipes collected in Table S2, on average, there is 0.0354 mole of protons per 100 ml, with a minimum of 0.0286 mole and a maximum of 0.0835 mole (Table S2).

Additives of Modern Recipes
For the stabilizing agents, the most widely used ones will be dilute hydrochloric acid, concentrated sulphuric acid, tartaric acid, and oxalate acid. According to J. W. McBain (1901), sulphuric acid tends to improve the stability of ferrous sulphate solutions, whereas hydrochloric acid has the opposite effect on solutions of ferrous chloride (Zimmerman, 1935). Chemists and manufacturers preferred Tartaric acid as a much cheaper chemical (Zimmerman, 1935). According to Zimmerman et al. (1935), oxalic acid will catalyst the destruction of paper fibres at a much higher rate than other stabilizing agents. Thus, though it

can reduce the corrosion of steel pens in iron gall inks by forming dense protection layers, the chemists welcome oxalic acid less (Briggs, 1936).

Production Processes of Modern Recipes
Though the variety of chemicals required increased in the 20th century, production procedures became much shorter and more straightforward. The chemicals were usually added into the warm water of 60 degrees Celsius in a sequence of tannic acid with gallic acid, ferrous/ferric-containing chemicals, dye (filtrated into the mixture), and carbolic acid as a preservative. Then the production can be finished after a dozen times of inversion in a sealed container (Stratton et al., 1920).

Structures of Particles Within Iron Gall Inks
Scientists also researched the complex ions formed by iron ions in iron gall inks, which can be very helpful to this study. Previous studies showed that most coordination compounds of iron involve ions in oxidation state II or III, which primarily prefer octahedral structures (Fig.6.a), so up to three bidentate ligands can bind a single iron ion (Wunderlich et al., 1991). Thus, six dents can be distributed into different combinations of bidentate ligands (gallic acid molecules) and monodentate ligands (water molecules).
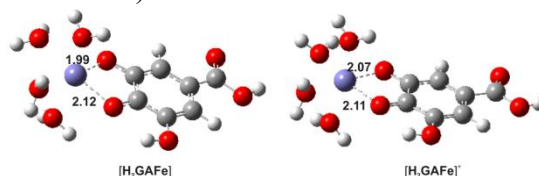
Figure 5. Optimized geometries of the most stable octahedral 1:1 complexes of Fe^{2+} (left) and Fe^{3+} (right) ions with H_2GA^{2-} gallic acid protonation species (bond distances are given in Å) (Frešer et al., 2021)

It is widely accepted that the particle is a

macromolecular 1:1 complex of iron ions and gallic acid (Wunderlich, Weber, & Bergerhoff, 1991), adverse to the existence of continuous debate on the specific structure.

The most widely accepted two structures are from Krekel et al. (1999) and Ponce et al. (2016).
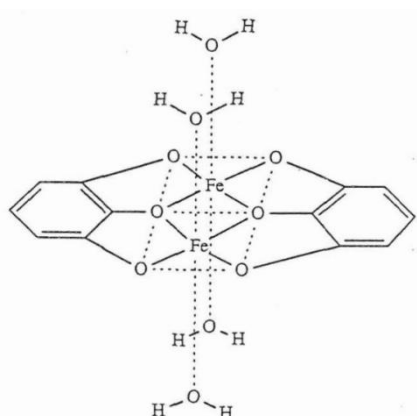

Figure 5. Structure of the Fe^{3+} octahedral pyrogallin complex $(Fe_2(C_6O_3H_3)_2 \cdot 4H_2O)$ proposed by Krekel et al. (1999)
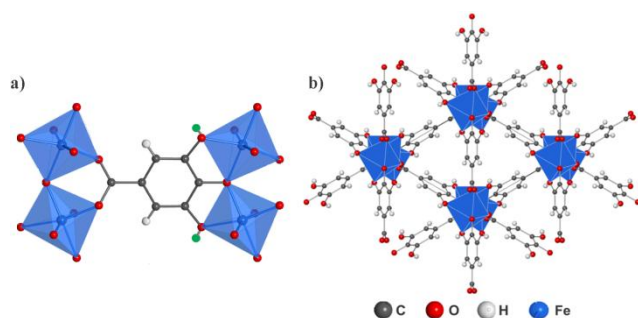
Figure 6. a) Ball-and-stick rendering of $Fe(C_7O_5H_3) \cdot 3.22H_2O$ complex showing coordination of the gallate ligand. The meta-hydrogen atoms (green) are 50% occupied. b) Framework structure viewed down the c axis. The water molecules in the channels have been omitted for clarity (Ponce et al., 2016)
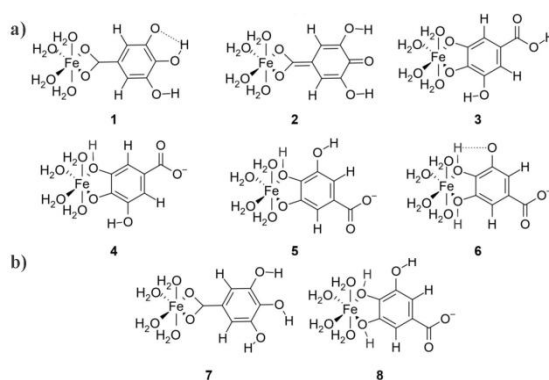

Figure 7. Chemical structures of all proposed coordination complexes between iron ions and gallic acid anion a) or monoanion b), which were considered in the DFT calculations. The numbering below the coordination compounds is used in the main text to refer to these complexes (Frešer et al., 2021)

All O atoms in tannic acid contributed to both lone pairs' complexation with iron ions for both structures. Besides this only similarity, there are lots of differences existing. First, in Krekel et al.'s diagram (Fig.5), a coordination centre is formed by two iron ions, linking to two gallic acid molecules and four water molecules. However, in Ponce et al.'s diagram (Fig.6.a), the centre is combined by three iron ions, linking to 6 gallic acid molecules, and undrawn 2.5-3.2 water molecules in one unit cell (Fig.6.b). Also, in the structures provided by Frešer et al. (2021) (Fig.7), only one iron ion presents in a coordination centre, linking to only one gallic acid molecule but four water molecules. Contrary to all these differences in the distribution of several monodentate ligands and bidentate ligands, what is unchangeable is a total dent number of six, which proved earlier deductions.

Additionally, according to Gimat et al. (2021), the stoichiometry of the coordination compounds of polyphenols with iron ions depends on the pH. In pH between 5.00 and

5

6.50, each iron ion would bind two or three polyphenolic ligands; in pH less than 4.00, every iron ion binds a single polyphenolic ligand (Frešer et al., 2021), which may give the reason for the existence of such a variety of structure raised by different researches.

Metal-Polyphenolic Complexes
The metal ions (Fe^{2+} and Fe^{3+}) in the metal-polyphenolic compound will be discussed later in the discussion part.

Effects of pH Value of Environment to Stability of Metal-Polyphenolic Complexes
Though as ligands, diethylenetriaminepenta-acetic acid (DFO), desferrioxamine (DTPA), and phytic acid (PHY) are all effective to stabilize iron, they perform the best in a basic environment, especially for PHY at pH=7 (Fig.8.a), for DFO at pH=8 (Fig.8.b), for DTPA at pH=9 (Fig.8.c).
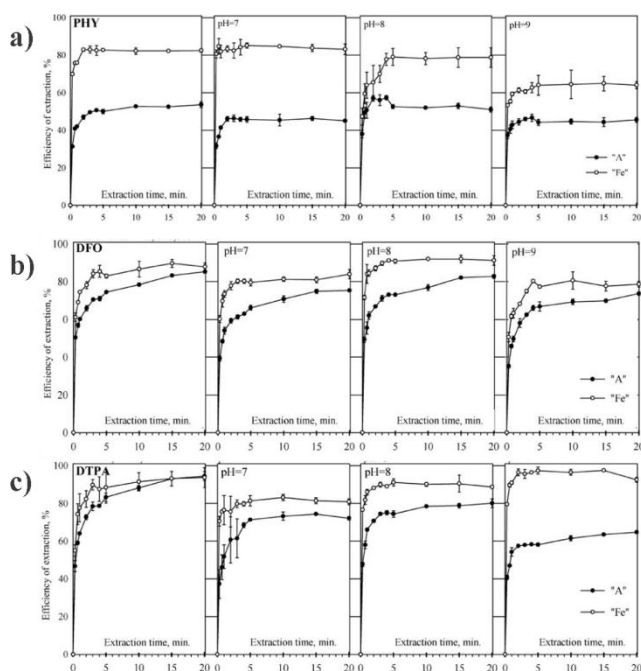
Figure 8. The rate and efficiency of extraction of iron from "Fe" and "A" model samples into solutions of a) magnesium-potassium phytate (PHY, c=0.005mol L^{-1}), b) deferoxamine mesylate (DFO, c=0.005molL^{-1}), and

c) diethylenetriaminepentaacetic acid (DTPA, c=0.005mol L^{-1}) (Wagner & Bulska, 2002)
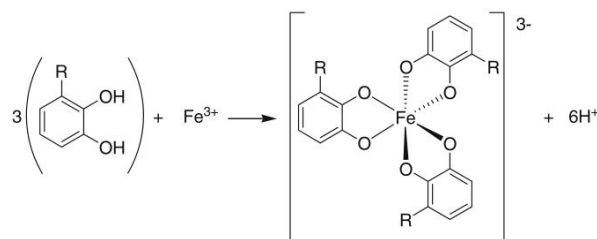
Figure 9. The expected octahedral coordination geometry of general iron-polyphenol complexes. Gallols, R=OH; catechols, R=H. Coordination requires deprotonation of the polyphenol ligands (Perron & Brumaghim, 2009)

It can be seen from Fig.8 that in weakly basic conditions (pH=7-9), the ligands extract iron better; thus, these ligands can be assumed to stabilize iron-polyphenolic complexes better when added in the modified recipes. Additionally, according to Perron & Brumaghim (2009), in the presence of iron pKa values between 7–9, which is suitable for the most acidic phenolic hydrogen, very stable complexes would form.

Table 1. The maximum efficiency of Fe extraction into solutions of the chosen ligands

Concentration (mol L^{-1})	The efficiency of extraction from the "Fe" sample (%)		
	PHY	DFO	DTPA
0.001, pH≤3	74.1±1.0	83.2±1.7	84.3±1.1
0.001, pH=7	61.2±3.0	87.4±1.8	83.1±3.8
0.001, pH=8	67.5±0.5	83.5±2.0	80.3±1.6
0.001, pH=9	79.7±2.0	85.1±1.6	87.0±1.6
0.005, pH≤3	82.4±1.0	87.8±2.0	93.1±3.0
0.005, pH=7	83.1±3.0	84.0±2.0	80.9±1.5
0.005, pH=8	78.8±5.1	91.2±2.3	90.4±2.0
0.005, pH=9	64.0±3.0	87.8±1.5	97.1±1.0
0.01, pH≤3	89.2±2.0	98.8±2.0	96.0±1.0
0.01, pH=7	80.0±2.6	67.8±1.3	98.7±0.4
0.01, pH=8	not anal.	71.8±3.0	89.8±1.6
0.01, pH=9	not anal.	67.1±1.3	80.8±0.4

However, the stability of metal-polyphenolic complexes does not increase with pH value. Actually, in solutions with a pH value < 3, the ligands will perform even better than in a neutral environment. This may occur due to a more balanced ratio in a low pH solution of ligands and iron ions. As stated before, according to Gimat et al. (2021), the stoichiometry of the coordination compounds of polyphenols with iron ions depends on the pH; in pH between 5.00 and 6.50, each iron ion binds two or three polyphenolic ligands (Fig.9); in pH less than 4.00, every iron ion binds a single polyphenolic ligand (Frešer et al., 2021).

Effects of Coordinating Atom to Stability of Metal-Polyphenolic Complexes

Effects of Coordinating Atom Itself to Stability of Metal-Polyphenolic Complexes: it can be observed in Fig.8 the efficiency generally increases with pH value. Notably, the efficiency of extraction from "Fe" samples of PHY is usually lower than the other two, especially DTPA. This may be due to only oxygen being contained in PHY as a coordinating atom contributing lone pair of high electronegativity. In contrast, the coordinating atom nitrogen in DTPA and DFO is less electronegative than oxygen, thus more stable. Although nitrogen has a relatively lower electronegativity than oxygen, its electronegativity is enough to compress electrons in a 3d subshell of iron to form a hybridization of d_2sp_3. Also, d_2sp_3 hybridization is a structure of a more stable inner orbital complex.

Table 2. Reported stability constants for catechol and gallol polyphenol ligands with both Fe^{2+} and Fe^{3+} ions

Compound	Fe^{n+}, n=	Log K1	Log K2	Log K3	Log β
Catechol	2	7.95	5.55	N/A	13.50
	2	8.40	N/A	N/A	N/A
	3	20.01	14.69	9.06	43.76
3,4-dihydroxynaphthalene-1-sulfonate	2	8.99	7.50	N/A	16.49
Quercetin	2	9.44	3.86	N/A	13.30
2,3-Dihydroxy-N, N'-diethylerephthalamide	3	16.22	14.32	11.48	42.02
2,3-Dihydroxy-N,N-dimethylbenzamide	3	17.80	13.90	8.50	40.20
	3	N/A	N/A	N/A	39.80
2,3-Dihydroxy-N, N'-dimethylerephthalamide	3	16.37	14.40	10.91	41.68
2,3-Dihydroxy-N, N'-dimpropylerephthalamide	3	16.00	15.17	11.97	43.14
4-Nitrocatechol	3	18.29"	14.17"	9.20"	41.66"
Aminochelin	3	19.06	11.71	10.54	41.31
Enterobactin (LYSCAM)	3	N/A	N/A	N/A	49
	3	N/A	N/A	N/A	46
Gallic acid	2	7.00	N/A	N/A	N/A
	3	14	8.5	5	27.5
	3	11.15	8.53	4.42	24.09
Methyl Gallate	3	12.4	11.7	9.93	34.03
n-Propyl Gallate	2	9.1	N/A	N/A	N/A
MECAM	3	N/A	N/A	N/A	46
Protochelin	3	N/A	N/A	N/A	44.6
Quercetin	2	9.44	3.86	N/A	13.3

Throughout Table 2, there is an apparent phenomenon opposite to what has been shown by B. Wagner and E. Bulska (2002) in Fig.8. For each complex form from the ligands contained nitrogen atom (including 2,3-Dihydroxy-N, N'-diethylerephthalamide (figure cannot found), 2,3-Dihydroxy-N, N-dimethylbenzamide (Fig.10.e, f), 2,3-Dihydroxy-N, N'-dimethylerephthalamide, 2,3-Dihydroxy-N, N'-dimpropylerephthalamide (figure cannot found), 4-Nitrocatechol (Fig.10.g, h), Aminochelin (Fig.11.a, b), Enterobactin (LYSCAM) (Fig.11.c, d), MECAM (Fig.11.h, i), Protochelin (Fig.12.e)), their Logβ raise to at least above 40, which compared to other complexes showed a high instability. This contradicts the former discussion of beneficial ligands containing amine. However, these data all come from complexes coordinated with Fe^{3+} ion, which naturally is less stable than Fe^{2+} complexes. As discussed before through Catechol data, this instability may not be caused

by nitrogen atom but by Fe^{2+} ion. Additionally, comparing stability constants for Catechol (Fig.10 a, b) and 4-Nitrocatechol (Fig.10.g, h) ligands with Fe^{3+} ion, logβ of 4-Nitrocatechol is slightly lower than logβ of Catechol, which further supported this suggestion.
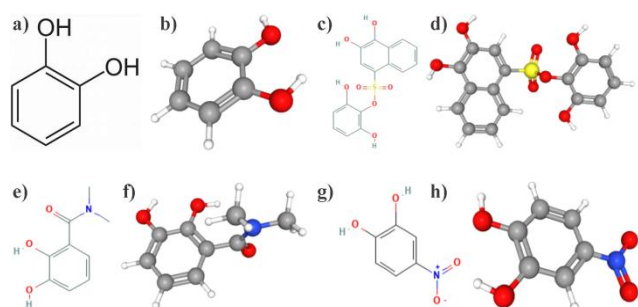

Figure 10. 2D & 3D structures of compounds listed in Table 2: a) the 2D structure of Catechol; b) the 3D structure of Catechol; c) the 2D structure of 3,4-dihydroxy naphthalene-1-sulfonate; d) the 3D structure of 3,4-dihydroxy naphthalene-1-sulfonate; e) the 2D structure of 2,3-Dihydroxy-N, N-dimethylbenzamide; f) the 3D structure of 2,3-Dihydroxy-N, N-dimethylbenzamide; g) the 2D structure of 4-Nitrocatechol; h) 3D structure of 4-Nitrocatechol
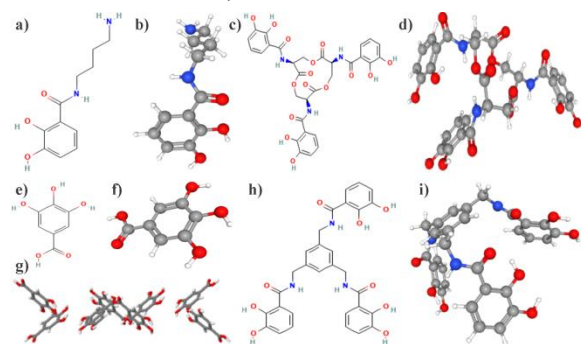

Figure 11. 2D & 3D & crystal (some) structures of compounds listed in Table 2: a) 2D structure of Aminochelin; b) 3D structure of Aminochelin; c) 2D structure of Enterobactin (LYSCAM); d) 3D structure of Enterobactin (LYSCAM); e) the 2D structure of Gallic acid; f) 3D structure of Gallic acid; g) Crystal Structure of Gallic acid; h) the 2D structure of MECAM; i) 3D structure of MECAM
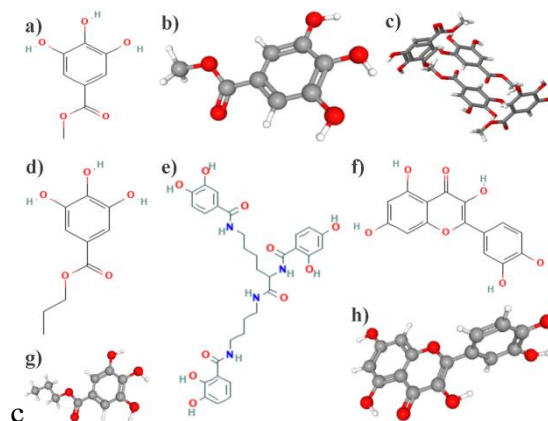
Figure 12. 2D & 3D & crystal (some) structures of compounds listed in Table 2: a) the 2D structure of Methyl Gallate; b) 3D structure of Methyl Gallate; c) Crystal Structure of Methyl Gallate; d) the 2D structure of n-Propyl Gallate; e) 3D structure of n-Propyl Gallate; f) the 2D structure of Protochelin; g) 3D structure of Protochelin; h) the 2D structure of Quercetin; i) 3D structure of Quercetin.

Effects of a Highly Electronegative Atom Linking with Coordinating Atom to Stability of Metal-Polyphenolic Complexes: in the former case of Catechol and 4-Nitrocatechol, a clear difference that may relate to the slightly more stable result complex is that two Oxygen atoms in 4-Nitrocatechol can be used as coordinating atoms are linking with a Nitrogen atom of high electronegativity of 3.0 (though lower than Oxygen atom of 3.5). These three atoms formed a NO2 group in resonance. This may reduce the electronegativity of Oxygen atoms as coordinating atoms, thus making the complex more stable.

The same theory may also explain the extremely high stability of 3,4-dihydroxy naphthalene-1-sulfonate (Fig.10.c, d). Though in this case, the Sulphur atom replaced the Nitrogen atom to form an SO3 group, Sulphur is also an element of high electronegativity (2.5, lower than both Nitrogen and Oxygen). With

the existence of resonance throughout these three atoms, it can be deduced that the Sulphur atom of high electronegativity stabilizes metal-polyphenolic complexes through linking with coordinating atoms of higher electronegativity. Effects of Electron Donating Group (R Group) Linking with Coordinating Atom to Stability of Metal-Polyphenolic Complexes: comparing stability constants for complexes formed through Gallic acid (Fig.11.e, f), Methyl Gallate (Fig.12.a, b), n-Propyl Gallate (Fig.12.c, d) ligands combining with Fe^{2+} or Fe^{3+} ions, it showed that a coordinating atom linking with an R group might reduce the stability of the resulting complex. Comparing Gallic acid with its coordinating atoms linking to no R group, and n-Propyl gallate with one Oxygen atom in gallate's ester structure linking to a propyl group, though log K2, log K3, and logβ are not given, through log K1 it showed clearly that the metal-polyphenolic complex formed by n-Propyl Gallate is less stable than the one formed by Gallic acid. Also, both data lines of the metal-polyphenolic compound formed by Fe^{3+} and Gallic acid give lower log K1, log K2, log K3, and logβ than Methyl Gallate, which showed its more substantial stability. Thus, it can be deduced that an electron-donating group (R Group) linking with coordinating atoms may reduce the stability of metal-polyphenolic complexes.
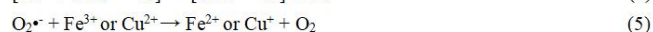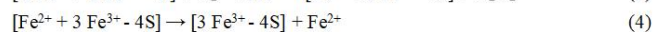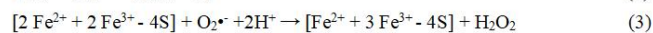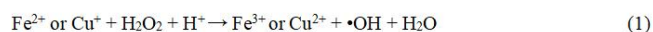
Destruction of Iron Gall Inks

Metal-polyphenolic complexes, meanwhile, are relatively unstable in iron gall ink. Thus, the introduction of strong acids and additives is necessary to avoid flocculation and achieve stable ink. But even in more stable modern recipes with the addition of basic stabilizing agents, sediments will form in 3-4 days (Zimmerman, 1935), which performs the risks
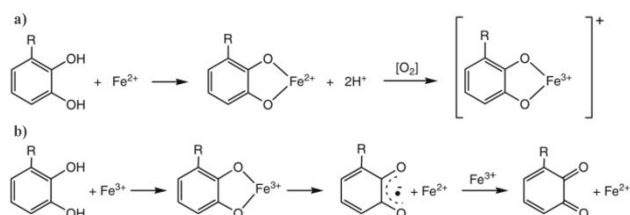
of causing pens to jam (Dai et al., 2019).

According to their research, iron gall inks mainly do damage to paper base in two ways: overused Fe^{2+} ions and other transition metal ions such as Cu^{2+} and Mn^{2+} mixed into inks as impurities deeply penetrated the cellulose, catalysing the hydrolysis through β-alkoxy elimination mechanism in an acidic environment, and Fenton like reaction producing O• free radical (Wagner & Bulska, 2002).

Fenton-Like Reaction

$$Fe^{2+} \text{ or } Cu^+ + H_2O_2 + H^+ \rightarrow Fe^{3+} \text{ or } Cu^{2+} + •OH + H_2O \quad (1)$$
$$2\ O_2•^- + 2H^+ \rightarrow H_2O_2 + O_2 \quad (2)$$
$$[2\ Fe^{2+} + 2\ Fe^{3+} - 4S] + O_2•^- + 2H^+ \rightarrow [Fe^{2+} + 3\ Fe^{3+} - 4S] + H_2O_2 \quad (3)$$
$$[Fe^{2+} + 3\ Fe^{3+} - 4S] \rightarrow [3\ Fe^{3+} - 4S] + Fe^{2+} \quad (4)$$
$$O_2•^- + Fe^{3+} \text{ or } Cu^{2+} \rightarrow Fe^{2+} \text{ or } Cu^+ + O_2 \quad (5)$$
$$H_2O_2 + H^+ + O_2•^- \rightarrow O_2 + •OH + H_2O \quad (6)$$

Above equations according to Perron & Brumaghim (2009) showed how Fe^{2+} or Cu^+ ions catalyse the formation of ROS (Reactive Oxygen Species), which is the main contributor of iron gall inks' destruction to paper bases. Noticeably, such reactions can only be catalysed by ions of transition metals with an intermediate oxidation state.

Figure 13. a) Coordination of Fe^{2+} by polyphenols and subsequent electron transfer reaction in the presence of oxygen-generating the Fe^{3+}-polyphenol complex; b) Coordination of Fe^{3+} by polyphenols, subsequent iron reduction and semiquinone formation, and reduction of Fe^{3+} to form a quinone species and Fe^{2+}. R=H, OH (Malešič et al., 2016)

In Fig.13.a, the process of forming Fe^{2+}-

Polyphenol complex is presented, with the process of its oxidation to Fe^{3+}-Polyphenol complex. It is clearly shown that the ligands have to be deprotonated to form complexes that provide reactants for Fenton-like reactions.

By binding a catecholate or gallate ligand to Fe^{3+}, the polyphenol can reduce the iron to Fe^{2+}. The polyphenol is oxidized to a semiquinone during this process (Fig.13.b). Meanwhile, the semiquinone ligand is protonated at low pH and, therefore, a neutral ligand. Once the semiquinone form of the polyphenol is generated, it can reduce another equivalent of Fe^{3+}, simultaneously oxidizing the semiquinone to the quinone (Fig.13.b). Previous studies showed that Fe^{3+} reduction behaviour is performed at a very low pH. At higher pH, more polyphenol compounds will link with the same iron ion in the complexes formed. This may be the reason that such reactions occur much more slowly around pH 7 (Malešič et al., 2016).

Thus, even though Fe^{3+} ion is not so stable as Fe^{2+} ion, it can reduce the effect of transition metal ion catalysed Fenton-like reaction to paper bases.

Acid-Catalysed Hydrolysis

The hydrolysis effect is a significant question concerning iron complexes and all transition metal complexes. The degradation of cellulose depends on the pH of the macromolecular environment. The mechanism leading primarily to depolymerization of cellulose with low initial pH values is acid-catalysed hydrolysis. However, as the pH of the paper is increased, the relative importance of acid hydrolysis decreases (Malešič et al., 2016).

It is significant that the effect is amplified with

oxidation state increasing, so that Fe^{2+} containing chemicals will promote the stability of the iron complex in some aspects and can assuage the impact of metal ion catalysed acidic hydrolysis. Also, the acid-catalysed hydrolysis effect can be reduced simply by reducing concentration or increasing the pH of the iron gall ink solution.

Comparing Iron Gall Ink to Other Ancient Inks

Moreover, the benefits of iron ions in metal gall inks and the privileges compared to other ancient inks should be discussed in this study. Though iron gall inks destroy handwritten materials drastically once the pH value becomes too low (Zaccaron et al., 2019), copper gall inks perform this kind of destruction much more seriously. In solution systems, at 25°C and pH 8, the rate of hydroxyl radical production is 20-times higher in copper than in iron-containing systems (Malešič et al., 2016). Moreover, so-called "mixed ink" on some ancient Herculaneum papyri discovered by Synchrotron Radiation (SR) X-Ray Fluorescence (XRF) should be discussed (Sibilia et al., 2021). This kind of ink was produced by intentionally mixing soot or charcoal with metallic compounds, such as lead-based minerals, possibly added to enhance the ink-black pigmentation and against the blur of writing caused by soaking into water (Sibilia et al., 2021). Though carbon particles do not fade over time even when bleached or exposed to sunlight, these inks are chemically stable and do not threaten the paper's strength and durability. Carbon inks (Fig.14.a, b) made from charcoal or lamp-black thickened with gum afraid of humidity and water. Another kind of mixed ink is a mixture of logwood ink and metal gall inks that vary its colour, hue, and durability

(Bicchieri et al., 2008).
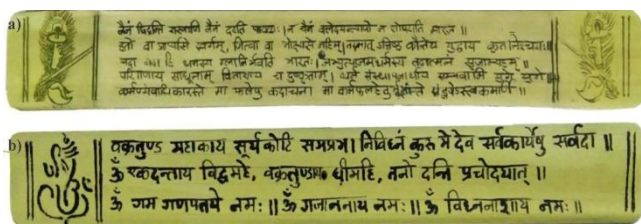
Figure 14. a) Incision with Lampblack ink on Palm leaf; b) surface writing with Lampblack ink on Palm leaf (Panda et al., 2021)

Figure 15. a) Illustration with Almond Shell Ink on birch bark. Notably, other inks prepared did not work well on the birch bark surface (Panda et al., 2021). b) Inks on ancient Egyptian linen textiles (Festa et al., 2019). c) A bottle of logwood ink with a demonstration of its colour. d) Iron-gall ink inscriptions on a Stradivari's violin containing iron, copper, and zinc. e) the six inner wooden forms, f) detail of an inscription on the form E.901.1, and g) four of the eight smaller items with inscriptions. Collection Musée de la musique, Paris, France. Photos. h) C. Giordan, i, j) Claude Germain Cité de la musique—Philharmonie de Paris(de la Codre et al., 2020)

The literature above discussed ancient and modern recipes with their components and production procedure and the structure of iron-gallic acid complexes, also effects of pH value of the environment and coordinating atom to metal-polyphenolic complexes, and destructions of iron gall inks as well comparison between iron gall inks and other ancient inks. Based on reviews of this literature, the later discussions about how to improve the recipes of iron gall inks can proceed in a much more scientific and practical way.

Comparison between Fe^{2+} ion and Fe^{3+} ion

This question was seldom meaningful in ancient recipes since only Fe^{2+} containing chemicals were used. However, in modern recipes, this question becomes essential and debatable since both ferrous containing chemicals (especially ferrous sulphate) and ferric containing chemicals (especially ferric sulphate and ferric chloride) are widely accepted as central components in modern recipes (Table S1). In this case, the corrosion effect and stability in ligands as a central atom of ferrous ions and ferric ions must be discussed from a variety of aspects.

Comparing through Coordination Chemistry

Based on the former analysis on the various structures of iron-gallic acid complexes proposed by different groups of scientists, researchers can debate on the stability of Fe^{2+} and Fe^{3+} ions in the iron gall inks from coordination chemistry. According to Perron & Brumaghim (2009), the binding of polyphenol ligands to Fe^{2+} lowers the reduction potential of iron, and enhances the rate of iron oxidation, with the rate of Fe^{2+} auto-oxidation dependent on the anions of the Fe^{2+} containing chemicals. However, upon binding a catecholate or gallate ligand to Fe^{3+}, the polyphenol can reduce the iron to Fe^{2+}. Polyphenol ligands firmly stabilize Fe^{3+} over Fe^{2+}, since Fe^{2+} is stabilized relative to Fe^{3+} by neutral unsaturated ligands due to the more excellent crystal field stabilization of a d6

electronic configuration (Fe^{2+} with all electrons are paired) than that of a d5 system (Fe^{3+} with an unpaired electron). Additionally, the reduction of Fe^{3+} generates Fe^{2+} that can participate in the Fenton reaction and cause reactive oxygen species generation.

According to Perron & Brumaghim (2009), iron ions' electronic configuration demonstrated that d6 electronic configuration (Fe^{2+} with all electrons are paired) is more stable than that of a d5 system (Fe^{2+} with an unpaired electron) is obeyed. For example, of catechol's two complexes with iron ions of different oxidation states in II and III, the stability constant value given in each research (according to Table 2) is similar for Fe^{2+} complexes but increased by two folds for Fe^{3+} complexes. Additionally, for gallic acid, though only logK1 is given for its complexes with ferrous ion to compare with its complexes with ferric ions, it could be observed that, both complexes with ferric ions increased largely in contrast to the value of logK1 of gallic acid's complexes with ferrous ion (doubled for first complexes with ferric ion and increased half of its original value for the second).

Comparing through Stability Constants (logβ)
When the iron ions are linked to ligands, the stability of Fe^{2+} and Fe^{3+} can be compared by measured stability constants. According to B. Wagner and E. Bulska (2002), for diethylene triamine penta-acetic acid (later referred as DFO): logβ $Fe^{2+}L=16.0$, logβ $Fe^{3+}L=27.5$; for desferrioxamine (later referred as DTPA): logβ $Fe^{2+}L=10.0$, logβ $Fe^{3+}L=30.7$, and for phytic acid (later referred as PHY): logβ $Fe^{2+}L=18.2$, logβ $Fe^{3+}L=29.3$ (Wagner & Bulska, 2002). Additionally, throughout Table 2, a clear trend could be observed that for both ligands

(catechol and gallic acid) provided with data of its complexes formed with both ferrous ions and ferric ions, all the stability constants available to compare between Fe^{2+}-polyphenol complexes and Fe^{3+}-polyphenol complexes showed the previous one is more stable for lower stabilizing constants. These all clearly showed complexes formed from Fe^{2+} ions are much more stable than those formed from Fe^{3+} ions.

Comparing through Fe(II)/Fe(III) Redox Equilibrium with the Effects of Acidic Containments
According to Frešer, F. et al. (2021), the presence of polyphenols impacts $Fe^{2+}/$ Fe^{3+} redox equilibrium. In several previous studies, it was claimed that the presence of polyphenols might prolong the oxidation of Fe (II) into Fe (III) for several days (Wunderlich et al., 1991), and it was proven by data in Table S2, especially in presence of both tannic acid and gallic acid, or high concentration of acidic stabilizing agents, for example oxalic acid and tartaric acid. However, it was showed by other researchers that Fe^{2+} ions can oxidize relatively rapidly after the formation of coordination compounds with polyphenols in the presence of oxygen from the solution (Malešič et al., 2016). Additionally, according to Perron & Brumaghim (2009), a process commonly referred to as auto-oxidation (Fig.13.a) would change acidified Fe^{2+}-polyphenol complexes to Fe^{3+}-polyphenol complex cations, for polyphenol ligands strongly stabilize Fe^{3+} over Fe^{2+}. These arguments added to the arguments about whether coordination compounds between polyphenolic ligands and Fe^{3+} ions are generally more stable than that of the identical ligands with Fe^{2+} ions (Yu et al., 2020). Nevertheless, in consideration of practical environment, the inks are mostly stored in a

well-sealed container with limited amount of oxygen, thus the reaction previously mentioned as auto-oxidation (Perron & Brumaghim, 2009) would unlikely to happen most of the time while the container is sealed without the presence of sufficient oxygen. This condition limited the opportunity of acidified Fe^{2+}-polyphenol complexes being changed to Fe^{3+}-polyphenol complex cations and form sediments inside the ink bottle, thus, from the measurement of preservation, the Fe(II)/Fe(III) Redox Equilibrium would be an negligible factor. However, when the ink was transferred to a pen, the ink and Fe^{2+}-polyphenol complexes contained became totally exposed in oxygen. Being acidified by gall extracts (gallic acid and tannic acid) and acidic stabilizing agents and with sufficient oxygen, the auto-oxidation was allowed to happen, and form Fe^{3+}-polyphenol complex cations which resulted in sediments would jam the pen. Still, auto-oxidation could benefit the speed of oxidation of ferrous ion to ferric ion in air to give visible ink tracks without presence of other dyes and pigments, or the speed of endarkening and stabilizing the ink tracks against water and some cleaning agents.

Methods of Modification through Providing Effective Ligands and Suitable Environments for the Ligands

Though the recipes were much improved in the 20th century, the effect of earlier deficient recipes cannot be reduced. Instead, it needs the effort of heritage scientists to enact repairments and preservation. In a few latest works, scholars raised a few effective treatments for the ancient archives endangered by the iron gall inks (or mixture with copper gall inks), which can inspire this study in the aspect of using stabilizing agents beneficial to the paper.

Diethylenetriaminepentaacetic acid, which functioned the best in pH=9, allowed the extraction of active iron ions and deactivation of the residual amount of iron by forming a stable complex with them (Wagner & Bulska, 2002). Also, according to Malešič et al. (2011), the oxidative degradation of paper may be retarded by the addition of various antioxidants, such as phytate, some quaternary ammonium salts, or imidazolium salts, which all contained high potential to form complexes with ferrous ions and ferric ions of high stability due to previous data provided (Fig.8) for phytate, and nitrogen coordinating atoms for the other two kind of salts. Additionally, in a mildly alkaline environment interleaving with papers impregnated with antioxidant tetrabutylammonium bromide can stabilize iron and copper ions under given conditions. The extent of stabilization is directly proportional to the concentration of quaternary ammonium salt in the interleaving papers. Tetrabutylammonium bromide, chloride, and dodecyl trimethylammonium bromide can do some effect when their solutions are introduced into documents that need repair. Also, calcium hydrogen-carbonate can be added to reduce acidity (Malešič et al., 2016). This method of reducing acidity was also introduced by Circular 426 of inks (C.E. Waters, 1940) for reducing the acidity of ink produced. However, this method may cause sediment formed by calcium ion with anions dissociated from acids in aqueous solution, for example poorly soluble calcium sulphate in presence of sulfuric acid, which is a common situation. Although most of sediments could be removed by filtration, for sediments partially soluble in water, the sediments may form again in variation of temperature and time.

Nevertheless, the so-called "Calcium phytate/Calcium hydrogen carbonate" method (Neevel, 1995) is one of the most known to treat documents affected by iron-gall ink corrosion (Zaccaron et al., 2019). Additionally, Calcium phytate can chelate several different metal ions, such as Mn^{2+}, Zn^{2+}, Co^{2+} and Cu^{2+} (Schmitt, Bortmann, Spiess, & Schlewer, 2010; Tsao, Zheng, Lu, & Gong, 1997).

All the ligands mentioned above process the extraction of iron gall ink by using two pieces of paper soaked with the solution of a ligand to press the manuscript under treatment (Wagner & Bulska, 2002), which is a time-costing procedure would waste lots of solutions. Thus, probably these ligands can be added into iron gall ink directly as a stabilizing agent, instead of undergoing the time-wasting and uneconomic treatment mentioned above. Also, this could reduce the chance from the first place of the iron gall inks to damage the paper base and pen jam.

In addition, gelatine can slow down iron gall ink corrosion, reducing ion mobility or complexes metal ions (Gimat et al., 2021) Nevertheless, the role of gelatine in hampering cellulose degradation due to iron gall inks is still debated since other authors have shown that, on strongly unbalanced inks, its action is incidental (Poggia et al., 2021). Also, gelatine has its disadvantage of its insolubility in water, while a vast majority of modern iron gall inks and ancient iron gall inks are water-based.

In this case, gelatine is directly spread on the manuscripts under treatment, but cannot be used as a stabilizing agent in iron gall inks.

Methods Proposed for Modification of Iron Gall Inks

From the earlier discussion in this study, many methods can be concluded. First, an inorganic stabilizing agent with the same anion as the Fe^{2+} containing compounds should be used (except for chloride). Second, Fe^{2+} containing compounds should be chosen instead of those containing Fe^{3+}. With oxygen's presence in acidic environments, the ferrous ions would catalyse the acid-catalysed hydrolysis and Fenton-like reaction to damage the paper base and cause ink burn phenomena, especially with the presence of excess iron ions. Additionally, the Fe(II)/Fe(III) Redox Equilibrium would favour ferric ions and form Fe^{3+}-polyphenol complex cations which resulted in sediments would jam the pen, also, some researchers supported ferric ions' stability over ferrous ions' stability. Still, the data provided shows the stability of Fe^{2+}-polyphenol complexes are much higher than Fe^{3+}-polyphenol complexes. With most of the authors of modern recipes of iron gall inks in favour of iron salts containing ferrous ion rather than those containing ferric ions, Fe^{2+} containing compounds should be utilised instead of those containing Fe^{3+}. Besides, organic stabilizing agents with Nitrogen atoms can be used as coordinating atoms. Also, organic stabilizing agents with Oxygen atoms in resonance with another atom of high electronegativity should be utilized. Furthermore, do not use organic stabilizing agents with coordinating atoms in an ester structure. Additionally, the pH value of iron gall ink solutions should be kept around 3, for this is the minimum acidity required to achieve the most efficient binding of organic ligands to iron ions instead of water. Thus, in spite of the effects of acid-catalysed hydrolysis and acid-caused corrosion to pen, a weakly acidic

environment of pH value equals to 3 should be created for iron gall inks.

Suggestions for Future Studies

About Choosing Suitable Metal Ions

Though many studies related to this question were done before, no clear conclusion was given by anyone. Most research showed that Fe^{2+} ions are more stable than Fe^{3+} ions. Still, considering the catalysing effect of Fe^{2+} ion to Fenton-like reaction, while much weaker for Fe^{3+} ion, it becomes hard to decide whether Fe^{2+} ion or Fe^{3+} ion should be chosen as a better component in iron gall ink. Thus, more studies should be done to find the answer to this vital question.

Also, though copper is another widely used metal in metal gallate inks, it was not so compatible as iron for its powerful catalysing effect to Fenton-like reaction (20 times of iron), which perform great destruction to paper base, made it hard to preserve. Still, researchers can investigate another better metal for producing metal gall inks, considering its stability, protection toward paper, and cost, which is a direction hardly covered.

About Choosing Effective Ligands

From previous studies, three suggestions are made: First, Nitrogen is a better coordinating atom than Oxygen. Second, an atom of high electronegativity can stabilize metal-polyphenolic complexes through linking with coordinating atoms of higher electronegativity. Last, an electron-donating group (R Group) linking with coordinating atoms may reduce the stability of metal-polyphenolic complexes. However, the first suggestion is opposed by some studies, and the latter two are concluded

from insufficient data. Thus, more experiments toward different compounds are needed to prove the correctness of these three suggestions.

About the Most Suitable pH Value

From an earlier literature review, a complex compromise must be made to choose the most suitable pH value. First, ligands with Nitrogen as coordinating atoms that perform better than Oxygen prefer weak basic conditions, which can make the formation of metal-polyphenolic complexes relatively ineffective since more ligands will link to one iron ion (no matter Fe^{2+} ion or Fe^{3+} ion) (Frešer et al., 2021). The number of water molecules linking with iron ions will decrease, which may cause unstable metal-polyphenolic compounds easier to become precipitates (Ponce et al., 2016). So that although in strongly acidic conditions acid-catalysed hydrolysis will hurt paper, and causing pen jam due to acid catalysed auto-oxidation, still the iron gall ink should be made in a weak acidic condition of pH value around 3. However, this is a suggestion made by deduction from the previous study, which has not undergone experiments to prove it, thus need further studies to prove and find the exact best pH value for iron gall inks considering both its stability, cost, and protection toward paper base and pen.

Conclusion

This study thoroughly reviewed a brief history of iron gall inks (including their main components, other additives, and production processes) in terms of both their ancient and modern recipes. Furthermore, the structures and stability of particles, especially metal-polyphenolic complexes, and the destruction of iron gall inks were reviewed. Based on the earlier research, the comparison of Fe^{2+} ion and

Fe^{3+} ion was conducted. The effectiveness of ligands and the best external conditions for the ligands were discussed. Besides, methods for modification of iron gall inks are proposed. Significantly, a compound containing Fe^{2+} pairing with the same anion as its inorganic stabilizing agent should be used (except for chloride). Furthermore, the essential suggestions on organic stabilizing agents would be focusing on coordinating atoms of the ligands. First, the coordinating atom can be nitrogen. Second, suppose the coordinating atom is oxygen. In that case, it should be in resonance with other highly electronegative atoms, for example, nitrogen and sulphur. Additionally, the oxygen coordinating atom should not be in an ester structure. The most important condition is that the pH value of iron gall ink solution should be kept around 3.

Based on this analysis, some outlooks were proposed into the future study of the modification of iron gall inks: First, even though Fe^{2+} is preferred in this study according to cross-references of earlier research, this conclusion is not proven by actual practices and data. Second, the suggestions of choosing effective ligands are concluded from inadequate data to be questionable. Last, ligands such as magnesium-potassium phytate, deferoxamine mesylate, diethylenetriaminepentaacetic acid, Tetrabutyl-ammonium bromide/chloride, dodecyl trimethylammonium bromide, calcium hydrogen-carbonate, and calcium phytate, that combined with iron ions can be added in iron gal link directly as a stabilizing agent instead of covering the manuscript as a more effective treatment method. Also, the prediction of the suitable pH value of iron gall ink is approximate and made out by compromising between a few contradictory factors. Thus, all suggestions mentioned above should be researched carefully in the future to prove their validity.

Nevertheless, this study analyzed both ancient and modern recipes and concluded clear advice for future investigations in modifying iron gall ink recipes. Though many suggestions need to be proven in further research, much insight and inspiration can be obtained for researchers from this study.

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