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From Lazarus To Theophilus: How Manuscript Digitization Led To The
Historical, Chemical, and Technological Understanding of Iron Gall Ink and its
Counterparts

by Meredith Oliver

A thesis submitted to the faculty of The University of Mississippi in partial
fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2015

Approved by

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“The ink of a pen is simply the blood of the heart.” ~ Michael Biondi

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ABSTRACT

From Lazarus To Theophilus: How Manuscript Digitization Led To The Historical, Chemical, and Technological Understanding of Iron Gall Ink and its Counterparts

This paper examines the physical and chemical composition of iron gall ink, how such composition has changed throughout its use in history, and the current chemical, digital, and multi-spectral methods by which the digital humanities use to preserve ancient texts inscribed with such ink. By using spectral technology, I hypothesized it possible to date and locate the geographic origin of ink based on its chemical composition. Uv-vis, fluorescence, and micro-XRF spectrometry were used to analyze elemental composition. Ink samples were made to simulate the ink on ancient manuscripts for UV-vis and fluorescence spectral analysis. Micro-XRF was performed on the Vercelli Book and Codex A, two ancient manuscripts located in the Museo del Tesoro del Duomo in Vercelli, Italy. A multi-spectral light system and camera was also used to take photographs of the ancient manuscripts upon various wavelength exposures. I also hypothesized that thermography could help historians detect lost and valuable inscriptions within the parchment binding without damage to the manuscript. Thermographic imaging was performed on the same ink on parchment samples used for UV-vis and fluorescence analysis. While the UV-vis spectroscope and fluorometer were not promising in distinguishing the difference between chemically different inks, the micro-XRF proved sensitive enough to provide information regarding the chemical makeup of ink on parchment. This information can be used to further date and locate a manuscript's origin. The multi-spectral camera proved its capacity to obtain data on ink absorption during ultraviolet, visible, and infrared exposure. After micro-XRF analysis, the chemical makeup of the ink within the Codex A and Vercelli book strongly suggest the ink is of the iron gall and Theophilus type, respectively. The thermographer also proved successful in relaying ink presence across a leather binding.

PREFACE

Much like Lazarus himself, manuscripts – ancient and modern – lie in forgotten and unknown crypts, libraries, archives, and museums around the world. But as for the manuscripts, many have remained lifeless, unread, and untouched for much longer than Lazarus' four-day mortality. As time continues to pass, many texts are brought closer to an irrecoverable fate as damage and decay continue to consume their very pages.

However, textual science is dedicated to the digital preservation and restoration of such historical treasures. The digital humanities serves to integrate the humanities and technology for the purpose of reviving such lost information. Recently, I have had the esteemed privilege of working with such a group of committed individuals to aid in manuscript preservation and restoration. They call themselves, Lazarus Project Imaging; and no, they do not hail from Bethany, but rather, from all across the country. Lazarus Project Imaging is a collaborative group of varied experts who travel the globe to preserve and digitally rekindle historical, literary, and artistic works with multi-spectral imaging systems.

In the winter of 2012, they were searching for assistance in the form of dedicated, ardent, and innovative honors students. During this time in my academic career, the inventive and creative light within was growing dim and in need of resurgence. Desperate for a change, curious about science and humanity integration, and simply spellbound by their project proposals, I became an enthusiastic member of Lazarus Project Imaging.

Not long after, two valuable manuscripts would find me in their presence. Fondazione Museo del Tesoro del Duomo in the sleepy town of Vercelli Italy is home to an exceptionally matchless manuscript collection. In the previous guest bedroom of Pope John Paul II, the Lazarus Project sought to render clear, digital images of the variably illegible Vercelli Book, Codex A, Mappamundi, various palimpsests and book of hours. During image captures, the imaging system's ultraviolet lights triggered a subsequent visible reaction on the very pages of the Vercelli Book. Such a phenomenon sparked a curiosity of my previously insipid chemical knowledge: did I just witness fluorescence on the pages of the Vercelli Book? What in the pages of this ancient book was inducing such a spectral light show? Can someone go microwave a bag of popcorn to share?

It was this singular event that inspired the following pages and thus began my quest for a comprehensive understanding of the plausible cause: iron gall ink. Such a journey led me to distant lands, time spent with world's leading ink experts, and to incomparable friendships. While I had the privilege of bringing history to life through my involvement with the Lazarus Project, I had no idea how much this involvement would help me re-discover my scientific passion while fostering an omnipresent internal creativity, consequently bringing me back to life.

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HISTORICAL TIMELINE OF IRON GALL INK

- Ancient Egypt:** Ancient Egyptians use iron-tannin complex to dye papyrus and linen (Smith, 2).
- 77 CE:** Gaius Plinius Secundus (Pliny the Elder) is the first to record the chemical reaction between vitriol and gallnut extracts: the reaction between tannic acid and iron sulfate (Farusi).
- 4th Century:** Believed to be the time of the invention of iron gall ink (Carvalho).
- 410 CE:** Fall of the Roman Empire.
- 476-800 CE:** Monks throughout European monasteries create countless religious texts while also experimenting with iron gall ink. Most documentation is burned in the Crusades and other religious warfare (Carvalho).
- 8th Century:** Blue vitriol, yeast, less of wine, and rind of the pomegranate apple were used as common ink ingredients, characterizing this ink type as plant based, rather than iron gall ink (Carvalho).
- 800-900 CE:** Inks retain a reddish and tawny appearance, rather than a black one (Carvalho).
- 1126 CE:** the first known documentation of iron gall ink (Carvalho).
- 12th Century:** Iron gall ink was of a muddy consistency that deteriorated quickly, and comprised of an insoluble tanno-gallate precipitate (Carvalho).
- 12th Century:** Theophilus Ink was thought to have spread throughout the Western world and used by monks of this generation to write cleric manuscripts (Rabin).
- 13th Century:** Gum arabic is first introduced to Europe to be used in the creation of iron gall ink (Stijnman 15).
- 13th Century:** Jehan Le Bégune observes the many benefits of using acidic solvents instead of water (Merrifield, 168).
- 16th Century:** The time of iron gall ink's manufacture. Ink retained a grey hue (Carvalho).
- Late 16th Century:** With the production of iron nails, sulfuric acid is added to the nails to produce ferrous sulfate used in ink manufacturing (Farusi, 37).
- 17th Century:** Manufactured inks became more black in appearance, homogeneous in nature, and of a more durable quality (Carvalho).
- 1609:** French chemist Guyot created an ink of superior quality that served as a model for ink manufacturers (Carvalho).
- 1626:** The French government mandated the manufacture of Guyot's iron gall ink for commercial use (Carvalho).
- 1660:** Canneparius first provides iron gall ink chemistry with an ideal iron to tannin ratio of 3.7 to 1 (Neevel, 144).
- 1730:** Logwood is introduced and is used as a common darkening agent in iron gall inks via trade with the West Indies (Grieve).
- 1750:** The first aniline produced for iron gall ink use by Helot (Carvalho).
- 1765:** William Lewis, an English chemist, begins scientific inquiry into the chemical properties and reaction mechanisms behind iron gall ink (Carvalho).

- 1786:** Carl Scheele, a Swedish chemist, proves the tannin complex present in iron gall ink is gallotanic acid (Carvalho).
- 1797:** William Lewis scientifically confirms the validity of Canneparius's 3.7:1 iron to tannin ratio (Neevel, 144).
- 1798:** Ribaucort, a French inkmaker, explores the effects of excess galls on ink permanence and proves an excess of galls is just as injurious to the permanence of ink as an excess of iron (Carvalho).
- 19th Century:** German government employed the "Official Ink of the First Class" made solely from gallic acid, iron sulfate, and gum, devoid of undesirable additives (Carvalho).
- 1825:** Benzole was integrated into iron gall ink as an aniline produced by Faraday (Carvalho).
- 1827:** Professor Turner of the University of Edinburgh defines iron gall ink as the blue-black substance that is created upon mixing gallic acid with an iron salt (Carvalho).
- 1832:** John Clare, the English Poet, produces his own iron gall ink containing indigo (Smith, 3).
- 1850:** Cheap additives arose and were subsequently added by manufacturers, resulting in poor quality ink (Carvalho).
- 1855:** Alizarin became a popular aniline used for its color enhancing and fluid properties (Carvalho).
- 1856:** Mauve became a popular aniline for iron gall ink and other commercial uses (Carvalho).
- 1864:** Induline was introduced as an aniline ingredient in iron gall ink (Carvalho).
- 1868:** Nigrosine was an aniline implemented as an ingredient in iron gall ink (Carvalho).
- 1874:** Eosine was an aniline invented by a German chemist for its bright red color (Carvalho).
- 1879:** Orchil was an aniline discovered and used for its purple color (Carvalho).
- 1879:** William Inglis Clark, a noteworthy chemist, publishes his thesis "An Attempt to Place the Manufacture of Ink on a Scientific Basis," which contains many vital conclusions that help propel ink manufacture toward the most fluid and ideal ink (Carvalho).
- Late 19th Century:** Iron-gall ink begins to lose importance due to the development of various useful synthetic aniline dyes (Hahn, 234).
- 1894:** Henry John Horstman Fenton observes that some metals possess a strong catalytic power to oxidize hydrogen peroxide, a reaction he coins as "The Fenton Reaction" (Lenntech).
- 1897:** Artificial indigo, also known as "pure indigo," was invented by scientists for commercial use (Carvalho).
- 1931:** Scientists Haber and Weiss develop a reaction mechanism for the Fenton reaction (Barbusiński, 348).
- 1974:** Professor Penny of Anderson University concludes tannin is much more soluble in a colder water. He suggests a cold extraction method as the best means to obtain tannin for iron gall ink production (Carvalho).

- 1990:** Scientist Krekel proposes a dinuclear ferric pyrogallate structure as an explanation to the ferrous-gallate structure present within iron gall ink (Banik).
- 1991:** Wunderlich proposes a three dimensional octahedral configuration to explain the ferrous-gallate structure (Zaccaron, 59).
- 1994:** Barrow, Van Gulik, and Kersten-Pampiglione discover a 5.5:1 ratio of iron to tannin is most prevalent within historical iron gall inks existing over a period of five centuries (Neevel, 145).
- 1995:** Neevel et al. study concludes the proper iron to tannin ratio is 3:1 (Neevel).
- 1999:** Krekel proposes a second ferrous- gallate structure: a decarboxylated octrahedral configuration, which takes into account the presence of ferric impurities (Ponce, Lecture).
- 2006:** Scientists Russell Feller and Anthony Cheetham confirm Wunderlich's proposed octahedral structure by using Raman and infrared spectroscopy (Ponce, Lecutre).
- 2012:** Ponce et al. study concludes the ratio of iron sulfates to tannin has little to no effect on the extent of iron gall ink's caustic properties (Ponce, Lecture).

CHAPTER I

WHAT IS IRON GALL INK?

I. Introduction

Gossamer are the philosophies, histories and literature of the antiquarian without the proper accoutrements to record them. Religious texts and clerical notes, political documents, and the literary canon would cease to exist without a medium to record them. The ability to write and record the present on parchment pages has made it possible to understand our past, share ideas, and be entertained. Of course, no book would be complete without the pages, the binding, and, possibly, the illustrations. However, no manuscript medium is more important to decipher our past than ink, for it serves as a visual, physical, and chemical fingerprint.

The following nouns have been used by different languages to describe a prevalently used ink type: *Encaustum* from Latin, *enkauston* from Greek, *inchiostro* from Italian, *encre* from French, *inkt* from Dutch, *inkoust* from Czech, *deyo* from Hebrew, and *alchiber* from Arabic (Michon).¹ These nouns describe the acidic properties of iron gall ink. According to Carvalho in his comprehensive study, *Forty Centuries of Ink*, the pre-requisites of a good black writing ink require it to “flow readily from the pen, to indicate in a short time a black color and to penetrate the paper to an appreciable degree, and more importantly than

¹ Enkauston = Ἐγκαυστον, from ancient Greek **enkaiein**, *to paint in encaustic, to burn in*.

all the rest, to be of great durability” (Carvalho 132).² Iron gall ink possesses all these attributes, which is why it became the standard ink among writers for over a millennium. To begin an exploration into the history, chemical makeup, and reactivity of iron gall ink, an understanding of the four fundamental ingredients (tannin source, iron source, solvent, and binder) is essential.

II. The Fundamental Components of Iron Gall Ink

The first vital chemical component in iron gall ink is tannic acid. This naturally occurring chemical compound is found in plants, fruits, and other life. It has been extracted and utilized by civilizations for thousands of years.

This polyphenol is derived from plant leaves, such as the Sicilian sumac, and a variety of woods,

including mahogany, oak, and redwood and serves as a defense mechanism against numerous parasites. Tannic acid has also contributed to the cultural

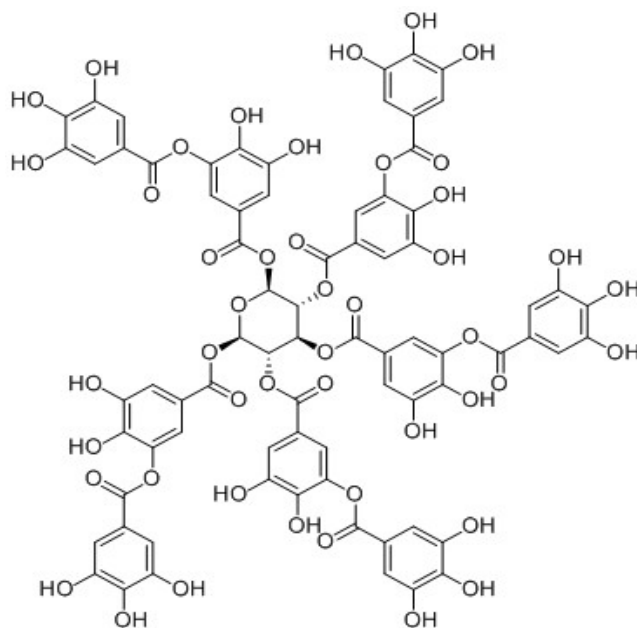


Figure 1.1: The chemical structure of tannic acid.

² While Carvalho extensively documents ink history and composition, it should be noted that his book is from the early twentieth century. Many of his claims are neither historically nor scientifically accurate. His research, however, is useful because few documents about iron gall ink have been published. One of the more up to date sources for iron gall ink information is Zerdoun’s *Les encres noires au Moyen Âge*.

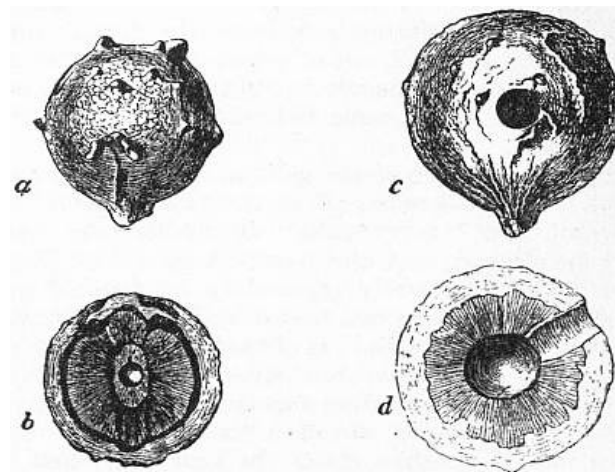
traditions of wine and tea enthusiasts, as it gives these beverages a bitter, firm, and dry quality (Stevenson, 51).³ Ink-makers need not look any further than upward and into the branches of the oak tree to find their tannin source of interest: the oak gall.

A gall is defined as an abnormal growth produced by a plant or other host under the influence of another organism (Redfern). These marble-sized growths are created by parasites, such as aphids, flies, and wasps, which entrust their eggs within the safety of a tree or plant (Banik). As the larvae feed upon the tree, an irritant is secreted by larval mastication (Banik). This irritant provokes the tree to form a circular growth around the site of parasitic development as the larvae mature to adulthood. This growth provides the eggs with nutrition and protection as they mature. Once the larvae develop into fully-grown parasites, the insect chews its way out, leaving behind the gall. Figure 1.2 depicts the external and internal structure of an Aleppo gall, a commonly used gall in the creation of iron gall ink due to its high tannin concentration.

Gall growths can take on a variety of shapes, sizes, and colors. Redfern and Shirley document the numerous forms of English oak galls in their field study, *Identification of Galls on Plants and Fungi*. The oak marble gall and oak apple gall species are among the most common oak galls. These terms are often confused and used interchangeably. However, both oak marble and oak apple

³ The medicinal properties of tea are attributed to the high tannin content and were first discovered five thousand years ago by Shennong, the esteemed Chinese emperor and father of Chinese medicine. One lazy afternoon, Shennong sat down under a camellia tree to rest and boil water to drink, the quiet wind guided a dried tree leaf into his boiling water. Legend has it that the Camellia leaf created the first cup of tea as it so delicately and sweetly flavored Shennong's boiling water (Asaido).

galls grow on twigs and leaves of oak trees, the marble gall possesses characteristics distinct from apple gall (*Medieval Manuscript Manual*). Marble galls are more round, small, and smooth with a distinct color depending on the season: green in the spring or brown in the fall (Redfern). Oak apples are much larger with an asymmetric shape and color pattern. Other oak galls include the rare red miniature doughnut-shaped silk button gall and the white button-sized caps of the smooth spangled galls (Redfern). While oak trees typically foster gall nut growth, galls can also be hidden underneath leaves and stems, nestled within flowers, or resting on a variety of plant roots (Farusi 37). Among the hundreds of galls documented by Redfern and Shirley, ink makers used the oak gall species of Aleppo, marble, and apple as the source of tannin. It's high tannin concentration, produced from the larval secretions and products left behind from the insect development, make the gall the perfect tannin source for an ink of interest.



T

Fig 1.2: The internal and external structure of an Aleppo gall. *a*, Aleppo “blue” gall; *b*, ditto in section, showing central cavity for grub; *c*, Aleppo “white” gall, perforated by insect; *d*, the same in section (natural size). Source: “Encyclopaedia Britannica: “G” to “Gaskell, Elizabeth”” *The Encyclopaedia Britannica*. 11th ed. Vol. 11. London: Encyclopaedia Britannica, 2011. Ser. 4. *Project Gutenberg*. Web.

The second essential ingredient within iron gall ink is iron sulfate. This metal salt has collected a variety of names throughout antiquity and into the

Middle Ages as its geographical sourcing changed and extraction techniques evolved. Throughout history, iron sulfate is commonly referred to as vitriol.⁴ The Greeks referred to it as *chacantum*, meaning *blood of copper*, and the Romans called it *atramentum*, meaning *black* or *making black* (Banik). Recipe books also refer to vitriol as ferrous sulfate, copperas, sal martis, sulfate of iron, copper red, English vitriol, Roman vitriol, vitriolum cyprinum, and vitriolum hungaricum (Banik). It should be noted that copper sulfate, also termed blue vitriol or blue copperas, was often used as an additive or substitute for iron sulfate (Lemay). No distinction was made between copper sulfate and iron sulfate for centuries. The lack of distinction and the use of common terms for both such as *sal martis*, *copper red*, and *vitriol*, it is difficult to know the exact source, elementals, and properties of the vitriol. However, the major chemical component of vitriol consists of iron sulfate, copper sulfate, or a combination of these two metal salts.

Ink makers obtained vitriol using a variety of techniques, depending on their geography and the available resources. The popular method of vitriol extraction involved mining salt formations within caves and later dissolving the iron in sulfuric acid (Lemay). Other ink makers positioned large iron pans at the base of a mineshaft in an effort to collect the mineral-rich run-off; this technique later produced vitriol crystals on a large rope as the fluid evaporated within a wooden barrel (Banik). Aluminum manufacturing produced iron sulfate as a byproduct, which ink makers collected to create iron gall ink (Banik). Upon the

⁴ The term *vitriol* encompasses not only iron sulfate, but also the many impurities and additives that inevitably made its way into iron sulfate through the mining process. Vitriol is therefore the most appropriate term when referring to the metal salt ingredient in iron gall ink.

invention of iron nails in the late sixteenth century, sulfuric acid was added to the nails to produce ferrous sulfate (Farusi 37). As industrialization occurred, trade routes throughout Europe increased and mining techniques improved. Germany became the primary supplier of iron sulfate to Western Europe, for the town of Goslar contained a large, pure concentration of this mineral (Banik).

While this large supply of German vitriol was considered a more pure source, it was not without metal impurities. The most predominant impurities were copper, copper sulfate, zinc, aluminum, and manganese, which do not contribute to color formation in the ink solution (Hahn 234). In addition, trace amounts of other mineral impurities were certainly present. These metal impurities affect the ink in undesirable ways. Ink made from the substitution or addition of copper sulfate produces soluble brown ink (Krekel). Micro-XRF analysis confirms that the tan or brown inks contain a higher amount of copper than their contemporaries (Hahn 236). To compensate for the undesired effects of copper and metal impurities, ink makers added iron strips to the iron solution in an effort to increase the iron content and mask the effects of metal impurities (Banik).⁵ The use of iron strips demonstrates the ink maker's understanding of metal impurities and the concept of chemical concentration. However, the presence of impurities was inevitable due to a lack in standardization techniques. The many methods used to both mine and manufacture vitriol as well as the geographic availability of vitriol contribute to the increasing variability of the metal sulfate ingredients in iron gall ink.

⁵ Metal impurities contributed to a lack of fluidity and color vibrancy in iron gall ink.

The third component of iron gall ink is the solvent of choice, which suspends the solid ingredients in solution. Ink makers used a variety of solvents in their recipes, including rainwater, wine, beer, or vinegar. Some recipes even include combinations of these various solvents. Very few recipes are precise in the amount of solvent added initially to the tannic source. It is understood by ink makers that the amount of required solvent is enough to completely soak the tannins.

The selected solvent in iron gall ink changed from recipe to recipe as ink makers disagreed on the best solvent to use for their prized iron gall ink. The majority of recipes call for rainwater, as it is more pure than the sooty, muddy water found in or below the earth. Other ink makers argue that acidic solvents, such as wine, beer, or vinegar, are more pure than water. Another advantage of alcohol as a solvent is its lower freezing point: ink made with alcohol based acidic solvents is less likely to freeze in winter (Banik). Acidic solvents also reduce the surface tension of the ink solution, allowing it to be absorbed more quickly by the paper fibers (Banik). This increases the desired permanence of iron gall ink. Vinegar retards the oxidation process. This chemical property of vinegar creates a visibly enchanting phenomenon: the seemingly translucent ink slowly becomes black as it penetrates into the paper fibers (Stijnman 15). Lastly, alcohol and vinegar exhibit preservative effects, inhibiting uninvited mold growth on the finished ink (Banik). The chemical properties of alcohol-based solvents make them most propitious to use in iron gall ink production.

Upon the addition of gall and metal sulfate to a solution, a fine black precipitate forms and settles to the bottom. In order to create viable ink, this

insoluble iron-tannin complex must be rendered soluble to be distributed homogeneously throughout the solution. To ensure this suspension occurs, a fourth component of iron gall ink is essential. The most prevalent binding agent used by ink makers is gum arabic. This water-soluble substance can be found in Africa, India and Australia. Gum arabic is a pale amber sap secreted from small round globules on tree bark (Lemay). Gum arabic has been used for centuries as a thickening agent in paints, varnishes, pharmaceuticals, and recently as an attractant within lithographic printmaking. Imported into Europe from North Africa, it was first introduced as an ink ingredient in the thirteenth century; however, it was not until the sixteenth century that gum arabic was a staple element of iron gall ink (Stijnman 15). After removing the hardened sappy exudate from the tree, ink makers ground the gum into a fine, off-white colored powder to be used in one of the last steps in the ink making process. Modern day society utilizes gum arabic as an emulsifier for tasty, sugary icings, fillings, and chewing gums. Its thickening properties make it a suitable binder in iron gall ink, as it not only thickens the ink, but also preserves and stabilizes the iron complex suspension and reduces the speed at which the ink is absorbed into the paper (Lemay). In addition to all of these essential ink qualities, gum arabic accelerates the rate of complex formation, subsequently enhancing the molecular stability and preventing acid hydrolysis degradation (Jancovicova, 394).⁶ This ingredient is essential to form desirable and stable iron gall ink.

⁶ Complex formation occurs between the tannin and metal salt, ultimately producing a ferric gallate complex that gives iron gall ink its characteristic pigment.

III. A Brief Look at Possible Additives in Iron Gall Ink

Historical recipes also include a variety of additives that have contributive effects to the chemistry of iron gall ink. Such additives include alcoholic solvents, natural dyes, plant derivatives, acids, metal salts, and for that matter, anything found in nature that ink makers believed would benefit their ink's permanent quality. The ink maker's choice of solvent is the ingredient that most governs to the permanence of ink.

Vinegar, beer, and wine have all been incorporated into iron gall ink recipes over the centuries, serving not only as the solvent, but also a preservative and acidifier (Lemay). The following thirteenth century observation by Jehan Le Bégune was rather advanced for his time and serves as the basis for chemical experiments revealing the acidity and tannicity of alcoholic solvents.

And note, that ink made with wine is good for writing books upon the sciences, because when books are written with it, the letters do not fade, and can hardly be scraped out or discharged from parchment or paper. But if they are written with ink made with water, it is not so, for they can easily be scraped out, and it may happen that the letters written with it will fade. (Merrifield 168).

As observed by Bégune, an acidic solvent exhibits great permanence, a fact that can be attributed to its heightened acidity.

Other minor ingredients include logwood, indigo, Brazil wood, madder, pomegranate rind, sugar, and honey (Banik). Dyes and pigments, such as logwood and indigo, are added to enhance the desired blue-black hue of the ink. William Lewis was among the first to advocate logwood as a tinctoral agent and supported his belief with chemical evidence (Carvalho 115). Indigo greatly improves the stability of the ink by forming a strong complex with ferrous and

ferric ions, subsequently removing these damaging ions from the paper or parchment (Larkworthy & Nyholm 1959). Because of its antioxidant properties, pomegranate rind decreases the corrosive behavior of iron gall ink (Stinjan 8). A variety of components including pomegranate rind, walnut husk, tree bark, and acidic solvents are added to increase the tannin concentration and indelibility of iron gall ink (Banik). Sugar and honey serve as plasticizing agents, added to improve the binding properties of gum arabic, creating a brilliant, vibrant and slow-drying ink (Lemay).

The color-enhancing additives that superseded logwood, Brazil wood, and indigo are collectively called anilines. The name aniline is derived from the Portuguese word *anil*, meaning indigo (Carvalho 184 XV). These anilines encompass a wide variety and number of additives, all used as a cheaper alternative to the formerly acclaimed indigo. The first discovered aniline was in 1750 by Helot (Carvalho 184). Alizarin, a product of the madder root, came into vogue in 1855 when Professor Leonhardi of Dresden spoke highly of its blue hue, color-enhancing properties, and increased fluidity (Carvalho, 125). Other color additives, orchil and eosine, were discovered in the 1880's and produced inks with purple and red shades, respectively (Carvalho, 185).⁷ Under the paradoxical name indigo pure, artificial indigo came into commercial use in 1897 (Carvalho, 186). While a plethora of additives have been used by ink makers, these

⁷ Orchil is also known as archil.

mentioned ingredients were the most commonly seen in recipes of the nineteenth and twentieth centuries for the manufacture of iron gall ink.⁸

⁸ Not all of the color-enhancing ingredients discussed here are necessarily positive contributions to the ink's quality. A more in-depth discussion will expose their demise in later sections.

CHAPTER II

A HISTORICAL PERSPECTIVE OF IRON GALL INK

I. Early Ink History

As historians trace the evolution of ink recipes, they notice this art form has impressively transcended a millennium of scientific discovery, cultural changes, and philosophical revolutions. Artisans simply used ingredients that were available and abundant in the area. Because of this geographic limitation, there exist many variations in the four principal ingredients and countless number of additives in iron gall ink, which have the ability to produce a multitude of recipes (Dorning 7). Artists, scribes, businessmen, nobility, and commoners alike concocted recipes they found fitting to their preferences (Banik). Individual and personal recipes were also practical for the widespread trade and exchange of iron gall ink ingredients (*Ancient Earth Pigments*).⁹

In the first century, Gaius Plinius Secundus, better known as Pliny the Elder, was the first to observe and record the corrosive principles of iron gall ink in his encyclopedia, *Naturalis Historia* (Farusi 36). At this time, leather was often processed and treated with verdigris (Farusi 36).¹⁰ However, many leather makers believed copperas to be a better, cheaper alternative.¹¹ Pliny the Elder devised a way to detect this fraudulent copper treatment by using nutgall infused

⁹ Trade was not common until the end of the Renaissance Age (*Ancient Earth Pigments*).

¹⁰ The chemical formula of verdigris is $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{Cu}(\text{OH})_2]$ (Farusi 36).

¹¹ The chemical formula of copperas is defined as $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$ (Farusi 36).

papyrus. He states in *Naturalis Historia*, "... The fraud may be detected using a leaf of papyrus, which has been steeped in an infusion of nut-galls: it immediately turns black when adulterated verdigris is applied..."(Secundus). This discovery marks the first record of iron gall chemistry: the reaction of gall-extracted tannic acid with iron sulfate.

Despite their lack of complex chemical understanding, ink makers regarded iron gall ink as superior in quality. This ink therefore became the primary ink in the Western Middle Ages (Eusman 1998). Scribes and writers used iron gall ink for over a millennium, despite chemical and scientific evolution, for its promise of permanence. The first use of iron gall ink is traced back to the fourth century. Micro-XRF spectroscopy strongly suggests the ink was on the Codex A manuscript, a fourth century Latin translation of the New Testament Gospels was iron gall ink (Illmo). In addition, the Codex Sinaiticus, a Greek Bible of this same time period, is created with iron gall ink (Heyworth 2014). To date, the first known iron gall ink recipe was written by Martianus Capella, a philosopher and teacher in North Africa, in his fifth-century *Encyclopedia of Seven Free Arts* (Eusman 1998). Technological investigation and historical record support the conclusion that iron gall ink was regularly used during the Middle Ages.

During the Middle Ages, members of the clergy frequently were also penmen or scribes: for they wrote, recorded, and translated extensive religious texts, documenting prayers, sermons, prophecies, and matters of the Church (Carvalho 43). Because of their prolific use of ink, these monks experimented with iron gall ink and documented recipe successes and failures. Therefore, any

information pertaining to the recipes and chemical understanding of iron gall ink during the Middle Ages were likely left by the clergy.

Unfortunately, scribal use of iron gall ink might have been too prolific. In order to have more paper to use, the venerable fathers unknowingly erased important inscriptions of the most eminent Greek and Latin authors of antiquity (Netz). Mistaking these erasures as a work of piety, the clergy continued to thoughtlessly write and record notes of ecclesiastical importance on top of the texts from antiquity.¹² A prime historical example of a famous palimpsest is the thirteenth-century monk's religious record on top of the tenth-century scholarly principles of Archimedes; this document is referred to as the Archimedes Palimpsest. The practice of palimpsest creation persisted for hundreds of years and into the Middle Ages.

While technological advancements have enabled today's historians to discern the cleric's over-text from the possibly more secular under-text, the treatments used by monks to erase the under text make it extremely difficult and time-intensive for experts to read the older record. Professor Roger Eason and Dr. Keith Knox, both members of the Lazarus project, have imaged the pages of the Archimedes Palimpsest to discern Archimedes' inscriptions from the clerical over-text, and also to further understand the work of Archimedes (Netz). But to revive all existing palimpsests through digitization would be a mission of unfathomable magnitude. The creation of palimpsests by the clergy has

¹² Such manuscripts that are effaced of the previous writing to create a recycled parchment for later writing are categorized as palimpsests.

essentially rendered manuscripts of the knowledge, history, philosophy, and progress of antiquity lost in time.

II. Iron Gall Ink in Vogue

With the increased use of iron gall ink throughout the Middle Ages, ink recipe documentation became more widespread throughout Europe, particularly between the thirteenth and fifteenth century (Lemay). Historians also note that medieval inks vary greatly in color and appearance according to their age and location (Eusman). Scribes seemingly used the resources accessible in their area and freely experimented with the various resources and endless possibilities of color additives to create an ink to their liking. Much of this variety can be attributed to the extensive additive ingredients available to ink makers.

The “Special Collections Unit of Preservation” Department at Yale University Library has compiled a booklet of various iron gall ink recipes during this three century period. It does not matter whether you examine two recipes produced at the same time period, or two crafted centuries apart: they all vary in method and composition. A recipe taken from fourteenth-century France instructs an ink maker to soak mashed galls in water for three days, boil the mixture after adding sweltering rainwater, and finally add the copperas and gum arabic to the mixture (*Le Ménagier de Paris* 265).¹³ Another fourteenth-century French recipe instructs one to soak macerated galls in rainwater overnight instead of for three days and then reduce the liquid by boiling and sieve through a

¹³ See A-1 in appendix for complete recipe.

fine cloth (Bat-Yehouda 178, 225).¹⁴ This second recipe also calls for the addition of gum arabic before the copperas, and gently pouring and mixing white wine over the vitriol before adding it to the final mixture. A sixteenth-century French and Italian recipe calls for one to soak the galls in rain water for six days, boil the mixture, add vitriol, and finally drizzle in vinegar soaked gum (Bat-Yehouda 297).¹⁵ While these recipes all differ in procedure and additives, they all contain the basic fundamental ingredients of iron gall ink: gall-extracted tannin, vitriol, gum arabic, and a solvent.

III. Industrialization and Iron Gall Ink

The Renaissance era, with the stabilization of European governments and a newfound interest in learning, demanded a change in the quality, ingredients, and methods whereby iron gall ink was produced (Eusman 1998). As trade routes encouraged exploration and interaction between countries, the ingredients used to make inks became less diversified. And as an industrialist, urban society began to replace the life of the simple farmer, manufacturers took over the ink making business and demanded a cheaper, reproducible, and more uniform ink.

Beginning in the Renaissance, governments insisted on creating a standard recipe to be manufactured for government, business, and book publication use (Eusman 1998). Many of these manufactured inks were formulated from the recipe employed by French chemist Guyot in 1609 (Carvalho 207). As the French government demanded and employed his uniform ink for

¹⁴ See A-2 in appendix for complete recipe.

¹⁵ See A-3 in appendix for complete recipe.

manufacture in 1626, recipes similar to his were quickly assimilated into manufacturing companies throughout Europe (Carvalho 207). Liked by governments, manufacturers, and contemporary writers alike, Guyot's ink was one that lacked added color (Carvalho 207). Governments and manufacturers demanded professional ink that was simple and uniform in nature, lacking in additives.

The seventeenth century became the height of iron gall ink manufacture with respect to widespread use, quality, and condition of the ink (Eusman 1998). More black inks began to appear on documents of every kind (Carvalho 126). The Dutch United East Indies Company produced a standardized ink formula they used for official trade documentation (Eusman 1998). In 1974, the German government employed what they called the "official ink of the first class" to be used in official documents, which consisted of tanno-gallate of iron ink with no added color (Eusman 1998). With this demand for homogeneity and simplicity, inks on every manuscript page exuded perfection.¹⁶

But this demand for mass-produced ink quickly led to a general lack of interest and understanding in regard to ink chemistry and composition. As the demand for ink increased in the eighteenth century, ink manufacturers naturally became primarily concerned with monetary gains. The quickest way for companies to make a profit was settling for ingredients of a lower grade. Therefore, synthetic dyes were developed and used into the twentieth century (Eusman 1998). The cheaper aniline alternatives proved to be unsatisfactory,

¹⁶ Simplistic in that these inks be devoid of added color, which only create variability.

binding to the tanno-gallate complex with low affinity. With the addition of cheap color enhancers, iron gall ink no longer possessed the caustic permanence and quality sought after by several centuries' worth of ink makers and writers. Throughout this time of inconsistent quality, iron gall ink begged for chemical understanding.

CHAPTER III

THE EVOLUTION OF CHEMICAL KNOWLEDGE CONCERNING IRON GALL INK

I. Introduction

Noticing the dire need to improve iron gall ink, English chemist William Lewis set out to uncover the properties and mechanisms behind ink in an effort to create an understanding of quality, fluidity and permanence (Carvalho 115). Lewis's scientific inquiry began in 1765 and initiated an era that sought to understand the chemical properties behind iron gall ink. A number of chemists in the late eighteenth and early nineteenth century joined Lewis in producing a variety of recipes and conducting scientific experiments on their creation to deepen their knowledge and understanding. As curious scientists and historians produced inks with a more scientific methodology, they sparked an urgency to write down their recipes and discoveries (Gambaro 202). As I discuss the basics of iron gall ink chemistry, I will explore the scientific discoveries of both European chemists during the enlightenment and ink chemists today and the impact their findings have on our current understanding of iron gall ink.

II. The Central Reactions of Iron Gall Ink

Ink makers, historians, and ink enthusiasts alike frequently term the gall-extracted tannin complex as 'tannic acid.' However, this term is not entirely chemically correct when referring to the ink component. In 1786, the Swedish

chemist Carl Scheele became the first to correctly identify the gall extracted tannin complex as gallotannic acid: a derivative of tannic acid (Carvalho 114). Tannic acid happens

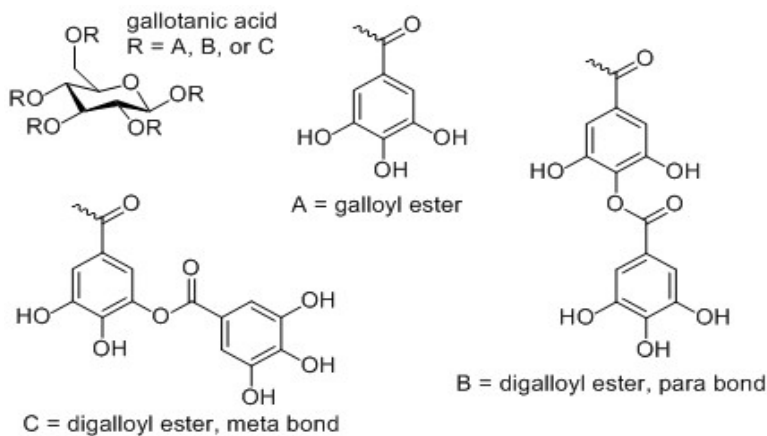


Figure 3.1: The chemical structure of gallotannic acid. Source: Farusi, Gianluca. "Monastic Ink: Linking Chemistry and History." *Science In Schools* Aug. 2007: 36-40. *Science In Schools*. Web. <<http://www.scienceinschool.org/2007/issue6/galls>>.

to be one type of many tannin polyphenol complexes, and gallotannic acid is one of two forms of tannic acid. The chemical structure of gallotannic acid consists of a glucose molecule and hydroxylic groups, all of which are esterified by a mixture of gallic, digallic, and polygallic acids.

Confusion often arises because the term ‘tannin’ accounts for a variety of tannin polyphenol complexes. The other form of tannic acid is quercitannic acid, found in the bark and leaves of oak trees and present in tea. From this point forward, I will appropriately refer to the tannin source present in iron gall ink as gallotannic acid.

The formation of iron gall ink occurs in two main sets of reactions. The first is the conversion of gallotannic acid to gallic acid via fermentation. The second is the addition of ferrous sulfate to this freshly created gallic acid to produce sulfuric acid and a ferrotannate complex, the primary component of ink pigment.

The first step in the ink making process is extracting the gallotannic acid by crushing and fermenting gall nuts. With the formula $C_{76}H_{52}O_{46}$ and molecular weight of 1701.18 grams per mole, gallotannic acid is a complex polyphenol with a variety of structures. This complex polyphenol has an extremely high melting point of $200^{\circ}C$, suggesting strong molecular forces exist between the molecules of gallotannic acid. Due to its many electronegative oxygen atoms, this molecule is polar and water-soluble. This water-soluble complex can undergo a hydrolysis reaction in the presence of water, resulting in the production of smaller tannin polymers. Gallotannic acid also readily reacts with metal ions to produce colored complexes, the principle chemical reaction responsible for creating iron gall ink.

While ink makers lacked the chemical understanding to reason the fermentation process, they ceased to question its importance as a necessity for creating good quality ink; for nearly every historical recipe requests the galls to be soaked in some type of water-based solvent for a period of time. Fermentation begins as gallotannic acid hydrolyzes into both gallic acid and glucose by the hydrolysis of gallotannic's ester linkages (Sjostrom 101). During fermentation, the aqueous solution used to soak the galls turns a muddy brown color. The reaction producing gallic acid is depicted in Figure 3.2.

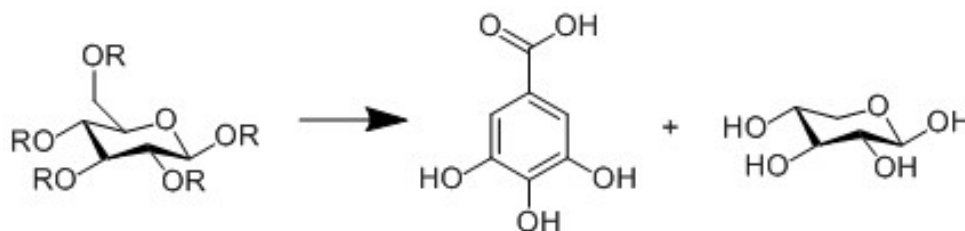


Figure 3.2: The hydrolysis of gallotannic acid to gallic acid and glucose. Source: Farusi, Gianluca. "Monastic Ink: Linking Chemistry and History." *Science In Schools* Aug. 2007: 36-40. *Science In Schools*. Web. <<http://www.scienceinschool.org/2007/issue6/galls>>.

Gallic acid, chemically named 3,4,5-trihydroxybenzoic acid, is a phenolic acid monomer with a pH ranging from 2.8-3.0 (Ponce). The production of gallic acid via fermentation is essential in the following steps to create stable and desirable ink. During fermentation, a generous amount of mold brings forth bacteria on the liquid-air interface.¹⁷ One vital biological member is the enzyme tannin acylhydrolase, simply known as tannase. This active tannase enzyme serves to catalyze the hydrolysis of gallotannic acid to gallic acid (Farusi 39). Due to the importance of the natural world in the creation of iron gall ink, it should be noted that biologically active organisms are present and active in each step of the reaction.

Before exploring the subsequent reaction step, it is necessary to comment on the variability of gallotannic acid concentration from recipe to recipe. The gallotannic acid concentration is attributed to both the gall nut source and extraction procedure. The Aleppo gall contains the highest concentration of tannic acid, roughly 65% per gall.¹⁸ Other galls of significance, such as the Acorn gall and Bassorah gall (mad apple of Sodom) contain 45-50% and 26% tannic acid, respectively (Farusi 37). These gall nuts all vary in locale. Therefore, inks made in a particular region are likely to be made from a local gall nut source. It is imperative to harvest the galls before the larvae chew their way out, for the gall contains the highest concentration of gallotannic acid at this point in larval development (Lemay 2). The concentration of tannins will also vary according to

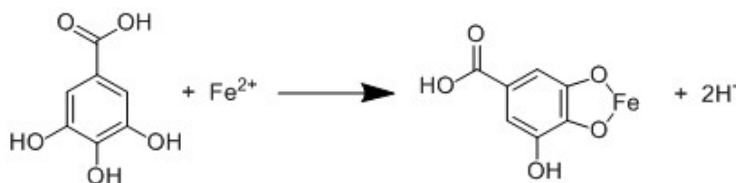
¹⁷ Leading German bacteriologists in the early twentieth century were even able to find bacilla of dangerous character within even the most ordinary inks. Such bacteria were potent enough to kill inoculated mice and rabbits in merely three days (Carvalho 202)!

¹⁸ See A-4 in the appendix for the complete chemical content of the Aleppo gall.

the method of extraction. The gall fermentation process has been tested and confirmed to produce the highest concentration of tannin (Lemay 2). Other extraction processes, listed in order of decreasing tannin concentration, involve cooking, macerating or simply mixing with water without fermentation (Lemay 2).

While extracting and fermenting galls to produce gallic acid is of vital importance, iron gall ink would be nothing without iron sulfate, the ingredient that grants the ink its lasting quality. The next phase of the reaction begins as iron sulfate is added to the gallic acid solution. The corrosive and acidic description of iron gall ink can be solely attributed to the properties of iron sulfate. Iron (II) sulfate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is the primary and desirable compound in vitriol. As iron sulfate heptahydrate comes in contact with aqueous solvent, the complex dissociates into Fe^{2+} and Fe^{3+} cations and SO_4^{2-} anions (Farusi 39).¹⁹ The iron cations chelate with tannin constituents to form ferrous gallate, as depicted in

Figure 3.3 (Jancovicová 392).



It should be noted that while vitriol is chemically referred to as

Figure 3.3: The production of ferrous gallate from gallic acid and ferrous cations. Source: Farusi, Gianluca. "Monastic Ink: Linking Chemistry and History." *Science In Schools* Aug. 2007: 36-40. *Science In Schools*. Web. <<http://www.scienceinschool.org/2007/issue6/galls>>.

iron (II) sulfate heptahydrate, traditional ink recipes mined vitriol from nature. Inevitably, this vitriol contains some or all of the following impurities: copper,

¹⁹ These Fe^{3+} cations are created during an oxidation-reduction reaction step, discussed later.

copper sulfate, zinc, aluminum, and other minerals in trace amounts. In many historic recipes, copper (II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is used instead of iron (II) sulfate heptahydrate. Therefore, it is important to recognize that while the reaction between iron (II) sulfate heptahydrate and gallic acid is the main and preferred reaction during the ink making process, it certainly is not the only one.

Ferrous gallate is a highly reactive, colorless, and water-soluble compound. Freshly prepared ink is very pale because the ferrous gallate complex has weak absorption bands in the visible spectrum of light (Smith 2). How, then, is this colorless solution transformed into the desired ink black? What mechanism continues to drive this reaction forward to produce the substance that has given humanity a written history? These chemical questions puzzled many chemists for nearly two centuries. Propelled by the desire to create a uniform recipe, chemists devised a plethora of experiments that have shaped our understanding and inspired the production of a seemingly ever-changing and evolving ink of perfect proportion.

III. Defining the Structure of Iron Gall Ink

It was not until 1827, as Professor Turner of the University of Edinburgh explored the reactive essence of ink ingredients, that scientists began to have a basic grasp of iron gall ink stability, indelibility, and reactivity. Turner built his foundation upon Scheele's 1786 discovery, that gallic acid was the principle tannin component of iron gall ink (Carvalho 114). He then furthered Scheele's argument. Turner's scientific observations and experiments concluded that gallic acid is always associated with tannin, yet distinguished from tannin by causing

no precipitate in a solution of gelatin (Carvalho 115). Turner also defined the basis of iron gall ink as the dark blue compound produced from the combination of gallic acid and iron salt (Carvalho 115). These properties postulated and concluded by Turner both distinguish gallic acid from every other tannin constituent and suggest the profound effects iron cations have on the overall ferrous-gallate structure.

A famous chemist, Dr. James Stark, undertook a twenty-three year investigation into the durability and permanence of popular manufactured inks. He studied the durability of two hundred twenty-nine of these inks produced in the mid-nineteenth century (Carvalho 122-3). Cited in Carvalho's *Forty Centuries of Ink*, Dr. Stark reported the following conclusions in 1855:

- 1) When freshly made, inks yield a durable quality. However, as the ink ages in the vial, the tanno-gallate iron complex separates, rendering a heavy precipitate in solution and subsequently an ink of poor quality.
- 2) The most permanent inks were shown to be made from six parts blue gall nuts of high quality, four parts copperas, and gum, by mass.²⁰
- 3) The immersion of iron wire or filings in the ink solution during ink production reduces ink durability.

The extensive investigations of Dr. Stark defined the most durable ink of his time and allowed him the opportunity to share with ink makers and manufacturers alike his conclusions in order to produce an ink of superior quality.

In 1894, Henry John Horstman Fenton coined a particular chemical observation, "The Fenton Reaction." This reaction expounds upon the very chemistry behind Turner's observation (Lenntech). Fenton observed the oxidation of tartaric acid by hydrogen peroxide in the presence of ferrous iron

²⁰ Permanence was tested by exposing paper containing the ink to sunlight and air. This was the only ink type that did not show a change in color appearance after twelve months of exposure to the conditions (Carvalho, 123).

ions.²¹ He argues that some metals, one being iron, possess a strong catalytic power to oxidize hydrogen peroxide to a highly reactive hydroxyl radical species (Lenntech). The Fenton reaction mechanisms below depict the products produced from the oxidation between iron (II) ion and hydrogen peroxide (Barbusiński 349). These mechanisms were not proposed by Fenton himself, but by two scientists, Haber and Weiss, in 1931 (Barbusiński 348).



Knowing free iron (II) and iron (III) ions are produced following the reaction of iron sulfate heptahydrate with aqueous solution in iron gall ink production, it can be understood that these ions would indeed interact with hydrogen peroxide in this proposed manner. The scientific development surrounding this principle first observed by Professor Turner in 1827 has been slow, yet progressive, relying on observation, experimentation, and theorization. This search continues even today as the implications of this mechanism further expose the final possible structure of iron gall ink.

²¹ Ferrous refers iron ions with a +2 oxidation state, opposed to ferric, which implies iron ions possessing the +3 oxidation state.

The Fenton reaction is categorized as an oxidation-reduction reaction, which involves changing the oxidation state of the involved atoms.²² As one atom is oxidized, losing electrons and therefore increasing its oxidation state, the other atom is reduced, gaining

electrons and thereby decreasing its oxidation state.

During the formation of iron

gall ink, after ferrous gallate is

produced, a redox reaction

immediately occurs as the

Fe²⁺ ions from ferrous sulfate

react with oxygen in the

atmosphere (Neevel, 143).

This reaction oxidizes a

fraction of Fe²⁺ ions to Fe³⁺

ions, which form water-insoluble complexes with gallotannins, glucose esters of

monogallic acid, or glucose esters of digallic acid (Neevel 143).²³ It is this very

reaction, as depicted in Figure 3.4, that slowly produces the highly light-

absorbing ferric pyrogallate complex, a compound that renders a black colored

ink (Smith, 2).

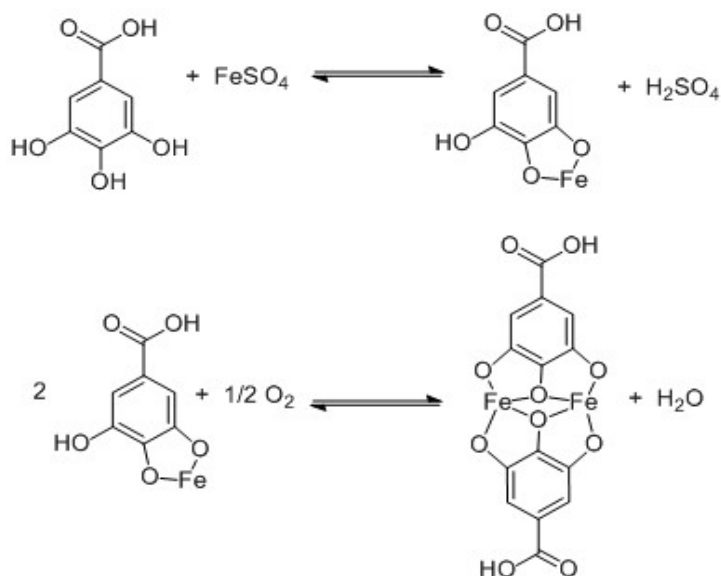


Figure 3.4: The production of ferric pyrogallate and water from ferrous gallate and oxygen. Source: Farusi, Gianluca. "Monastic Ink: Linking Chemistry and History." *Science In Schools* Aug. 2007: 36-40. *Science In Schools*. Web. <<http://www.scienceinschool.org/2007/issue6/galls>>.

²² Chemists often shorten *oxidation-reduction reaction* to simply *redox reaction*

²³ See figure 4.1 for the complete oxidation reaction. It is important to note that iron oxidation predominantly occurs after the ink is applied to paper, where the iron (II) ions are directly exposed to oxygen. However, due to the presence of reducing substances in the paper, iron gall inks on ancient manuscripts still contain a generous amount of iron (II) ions that have yet to oxidize.

Chemists arrived at their conclusion regarding the final iron gall ink structure from observation, experimentation, and technological advancement. The creation of iron gall ink occurs in the presence of oxygen. This observation reveals that an oxygen molecule could potentially serve as a required stoichiometric reactant for the final reaction: a redox reaction. Through experimentation, chemists theorize a redox reaction participates in the oxidation of the ferrous gallate complex into ferric gallate (Farusi 39). It is in this oxidation step that the ink maker observes a change in color from a light muddy brown soluble product to smooth, black insoluble one.²⁴ This blue-black pigment only becomes darker and more distinguished after it is applied to parchment, allowing it to be exposed to oxygen for several days (Banik).

Through observation and experimentation, chemists define the final, blue-black insoluble precipitate as ferric gallate. However, this conclusion conveys nothing regarding the product's structure, bond angles, or spatial arrangement. It wasn't until the 1990's when chemists C.

Krekel and C. Wunderlich utilized elemental analysis techniques to explore the possible spatial structure of the insoluble ferric gallate product (Banik). Both scientists created their own form of historic iron gall ink recipes of honorable, stable origin with a 1:1 ratio of gallic acid to iron. With the aid of scientific

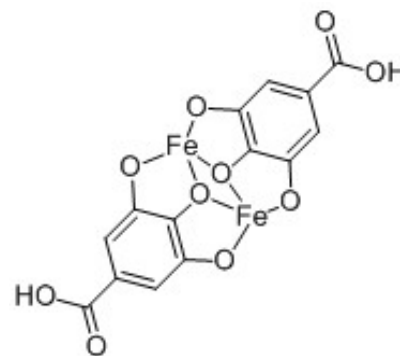


Figure 3.5: The chemical structure of ferric pyrogallate proposed by Krekel in 1990. Source: Ponce, Aldo A. "New Insights into the Chemistry and Structure of Iron Gal Ink." New Research on Iron Gall Ink. Library of Congress, District of Columbia. Oct 11 2012. Lecture.

²⁴ The addition of gum arabic acts as a binding agent to suspend the insoluble ink black product in the solution.

instruments, the scientist's products were analyzed to arrive at a possible ferric gallate structure. Krekel and Wunderlich use their knowledge of chemical stability to reason the potential acceptability of the technologically derived structure.

Krekel was the first to postulate a structure for ferric gallate in 1990. After examining the black pigment using mass spectrometry, infrared spectrometry and Mössbauer spectrometry techniques, he arrived at the dinuclear ferric pyrogallate structure depicted in Figure 3.5 (Banik).

This complex retains a tetrahedral arrangement from the formation of bonds through phenate oxygen atoms (Ponce). Noticing this structure exhibited awkward and unstable bond angles, Krekel was not convinced and sought to further explore the possible structure of the ink pigment. In 1999, he proposed a decarboxylated octahedral configuration, which takes into account the presence of ferric impurities in solution. While this greatly anticipated structure displays scientific progress from his originally proposed ferric pyrogallate configuration of 1990, the octahedral structure gives rise to abnormally long bond lengths that suggest a level of instability (Ponce). As a scientist, Wunderlich was not satisfied with either of these structures, for chemical knowledge of structural stability indicated a fault in Krekel's postulations.

One short year following Krekel's theorized ferric pyrogallate structure, Wunderlich created black crystals for analysis by reacting ferric chloride, FeCl_3 and gallic acid in a gel of sodium silicate in 1991 (Banik). These black crystals were analyzed using Mössbauer and X-ray absorption near edge structure

(XANES) spectroscopy. Instead of Krekel's unstable structure, Wunderlich utilized these imaging techniques to propose a three-dimensional one.

He theorized this three-dimensional complex is formed from the reaction between iron ions with both the phenol groups and the carboxyl group present within gallic acid (Banik). The major chemical feature that distinguishes ink's blue-black tone is

attributed to the coordination between iron ions and oxygen atoms within the conjugate bases of gallic acid (Ponce). This conformational bonding of iron to oxygen follows electron pair shifting in the benzene ring (Banik). Due to the iron-oxygen bonding, this 3D polymer structure, depicted in Figure 3.6, takes on a slightly distorted octahedral high spin complex (Zaccaron 59).

Wunderlich's monomeric ligands that create this octahedral structure depict the coordination of iron with the phenate oxygen atoms and carboxylate moiety separately. Each ligand, regardless of the structural conformation, possesses the chemical formula $\text{Fe}(\text{H}_3\text{O})(\text{H}_2\text{O})(\text{L})_n$, with n denoting the number of ligands considered and H_3O^+ cations neutralizing the excess negative charge (Zaccaron 58). Four of these ligands, two of each type, compose each octahedral conformation. First discussed is the phenate oxygen ligand, depicted in Figure 3.7, followed by the carboxylate ligand, depicted in Figure 3.8.

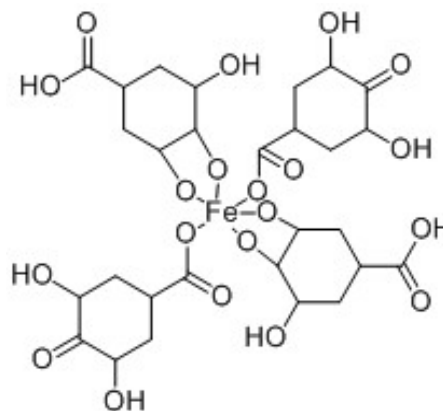


Figure 3.6: The three dimensional structure of ferric pyrogallate proposed by Wunderlich in 1991. Source: Ponce, Aldo A. "New Insights into the Chemistry and Structure of Iron Gall Ink." New Research on Iron Gall Ink. Library of Congress, District of Columbia. Oct 11 2012. Lecture.

The phenate oxygen atoms chelate two iron ions. Per octahedral, two of these phenate oxygen ligands coordinate with one iron ion in the *cis*-conformation (Zaccaron 59). This *cis* ligand binding grants a more stable conformation. The oxygen atom in positions three and five bond to iron with a bond length of 2.000 Å, while the oxygen atom in position four has a length of 2.028 Å (Zaccaron 59). This variation in bond length contributes to the overall stability of the phenate oxygen atom ligand. In addition, the oxygen atom in this fourth *para*-position acts as the bridging atom between this phenate oxygen ligand and the carboxylate moiety (Zaccaron 59).

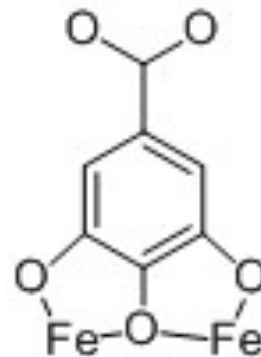


Figure 3.7: The phenate oxygen ligand proposed by Wunderlich. Source: Ponce, Aldo A. "New Insights into the Chemistry and Structure of Iron Gal Ink." New Research on Iron Gall Ink. Library of Congress, District of Columbia. Oct 11 2012. Lecture.

The carboxylate moiety is depicted to contrast the difference between this ligand and the phenate-oxygen one. Each carboxylate group acts as a bridging ligand between the two iron centers (Zaccaron 59). These two oxygen atoms exhibit *cis*-conformation to one another, further granting stability to the overall molecule (Zaccaron 59).

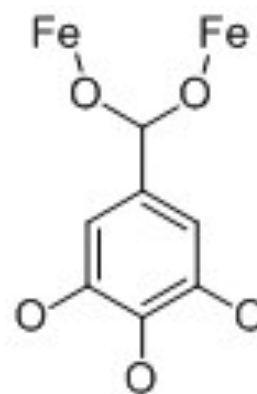


Figure 3.8: The carboxylate moiety proposed by Wunderlich. Source: Ponce, Aldo A. "New Insights into the Chemistry and Structure of Iron Gal Ink." New Research on Iron Gall Ink. Library of Congress, District of Columbia. Oct 11 2012. Lecture.

The iron-oxygen bond length within each carboxylate moiety is 2.006 Å (Zaccaron 59). Much like the phenate oxygen ligand, two carboxylate ligands make up the three-dimensional octahedral structure

(Zaccaron 59). Wunderlich proposed a three-dimensional octahedral structure produced from the binding of two types of ligands to create the most stable conformation attainable via observation, experimentation, and instrumental analysis.

In 2006, scientists Russell Feller and Anthony Cheetham synthesized ink precipitate from ferrous chloride, Fe(II)Cl_2 , to test the validity of Wunderlich's three-dimensional octahedron (Ponce). While their reactant expressed a different oxidation state from Wunderlich's, the formed product expressed the same crystalline structure. Raman and infrared spectroscopy analysis confirmed the legitimacy of Wunderlich's proposed structure by revealing the formation of a bridge complex between the carboxylate group in gallic acid to iron (Ponce). Despite the conclusions proposed by these scientists regarding the final structure of iron gall ink, the products are many, due to the complex chemistry between the various highly reactive species, and are not all completely known (Zaccaron 58). These scientists only sought to define the structure of the insoluble precipitate that gives ink its brilliant color. To add to the uncertainty, scientists are still perplexed by the existent oxidation and spin states of Wunderlich's iron centers (Zaccaron 59). Progress has been made, and conclusions drawn from scientific experimentation and analysis, but there is still much to be known about the complexity of iron gall ink.

Notwithstanding all the unknowns, researchers have progressed in formulating the most stable and accurate iron gall ink pigment structure. While fun to craft, iron gall ink serves us little to no purpose today. So why did Krekel and Wunderlich develop such experiments and perform extensive chemical

analysis for a seemingly lost art? To attract so much time, effort, and sentiment, this knowledge of iron gall ink chemistry must have a deeper consequence and implication. The reason for their scientific quest lies in the preservation efforts of the digital humanities. Nearly two millenniums of existing manuscripts offer the most direct means of teleportation into understanding past society, culture, philosophy, and development. By understanding iron gall ink chemistry scientists, historians, and curators are that much better able to preserve the valued material kept within the spines of the delicate manuscripts of history.

CHAPTER IV
THE DEGRADATION AND PRESERVATION OF MANUSCRIPTS
CONTAINING IRON GALL INK

I. Introduction

Conservators, scientists, historians, and literary experts have recently explored iron gall ink's detrimental effects on manuscript preservation. Modern day neutral inks sit on the surface. In contrast, iron-gall ink eats its way into the paper, corroding and altering both the cellulose chains present in the parchment, as well as the ink complex itself (Clemens 19). Before conservation and preservation efforts gained a comprehensive understanding of iron gall ink chemistry, nineteenth century ink makers believed a disproportionate presence of iron contributed to a lack of color vibrancy and an increase in ink precipitate, making the ink difficult to write with. Additional chemical investigations over the past two centuries have been propelled by a stability theory rooted in the stoichiometric ratios of iron to tannin.

II. The Iron to Tannin Ratio's Effect on Iron Gall Ink Stability

The first recipe to document the proper ratio of iron (II) sulfate to tannin was given by Canneparius in 1660 (Neevel 144). He stated that a stable, nonbleaching iron gall ink must possess an iron to tannin molecular ratio of 3.7 to 1. The first scientist to test Canneparius's ratio was eighteenth-century English chemist William Lewis. He theorized that an excess iron presence in iron gall ink

is detrimental to color permanence. After conducting several experiments, he published his results in 1797 confirming his theory; Lewis noticed that upon exposure to air, the ink with the excess iron salt turned brown, instead of a desired black (Carvalho 115). Lewis concluded that the proper iron (II) sulfate to tannin ratio corresponds exactly with Canneparius's recipe: 3.7 to 1 (Neevel 144). One year later, the French ink maker Ribaucourt explored the effects excess gall had on ink stability and concluded an excess of gall is just as injurious to the permanence of ink as an excess of iron (Carvalho 115).

While conducting experiments similar to Lewis and Ribaucourt, William Inglis Clark proved successful in creating a recipe with suitable amounts of iron and tannin that best stabilizes the precipitate. He submitted a thesis in 1879 titled "An Attempt to Place the Manufacture of Ink on a Scientific Basis" in which he presented a collection of conclusions (Carvalho 127). The finding that dictated the majority of his conclusions was the observation that the increase of iron in the solution had little to no effect on the composition of precipitate at first, but with the addition of iron beyond eight percent in solution, a precipitate is found in a greater, but disproportionate amount (Carvalho 128). He therefore concluded that the most stable ink should contain no more than eight percent iron. He also noted the proportion of iron in the precipitate decreases as the length of time the ink is exposed to oxygen is extended (Carvalho 128). Immediately after the production of iron gall ink, the precipitate contains 10% iron; however, after exposure to oxygen for forty to seventy days, Clark notes iron's presence in the precipitate is only 5.7% (Carvalho 128). Therefore, iron concentration in the precipitate possesses an indirect relationship with the time the ink is exposed to

oxygen. After all his experiments, Clark concluded the best ink for manufacture is composed of 16 parts iron (80 parts ferrous sulfate) and 100 parts tannin (Carvalho 129). Ink manufacture based on Clark's findings produced the most stable, flowing, and black ink of its time.

III. The Truth on the Stoichiometric Ratio of Ingredients

These studies performed in the eighteenth and nineteenth century examining iron's effects on stability proved successful in creating desirable mass produced ink. However, when twenty-first century scientists examined these conclusions for conservation purposes, they came to a different conclusion regarding the stoichiometric coefficients of iron and gallic acid. In an effort to devise chemically stable ink causing little to no manuscript degradation, Neevel et al. sought to determine the ideal ratio of tannic acid to ferrous sulfate. They concluded in 1995 that that ratio is 3:1, ferrous sulfate to tannin. However, seventeen years later, Ponce et al. re-opened the equation. In 2012, this team of scientists prepared iron gall ink precipitates from the following gallic acid to iron sulfate molar ratios: 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, and 1:9 (Ponce). After performing Raman, IR, and XPS analysis on the product, this team of scientists observed the same percent yield of insoluble product in each reaction mixture, with a shockingly sizeable 95% of the product proving soluble (Ponce). Data analysis concluded the iron gall ink product contains only a 5-8% yield of precipitate, completely independent of the gallic acid to iron sulfate ratio (Ponce). Due to the work of Ponce and his team, scientists currently acknowledge that the ratio of gallic acid to iron sulfate has little to no effect on the extent of iron gall

ink's corrosive properties; its destructive effects are inevitable.²⁵ Therefore, all historical ink recipes exhibit the same potential to degrade antique manuscripts.

While historical documents created with iron gall ink are subject to degradation regardless of the iron to tannin ratio, it is interesting to note that a predominating ratio exists among historical ink. A study conducted by Barrow, Van Gulik, and Kersten-Pampiglione impressively investigated the iron to tannin ratios present in over one hundred iron gall ink recipes from the fifteenth to nineteenth centuries. Figure 4.1 displays the distribution of molecular ratios of iron to tannin throughout five centuries of iron gall ink recipes.

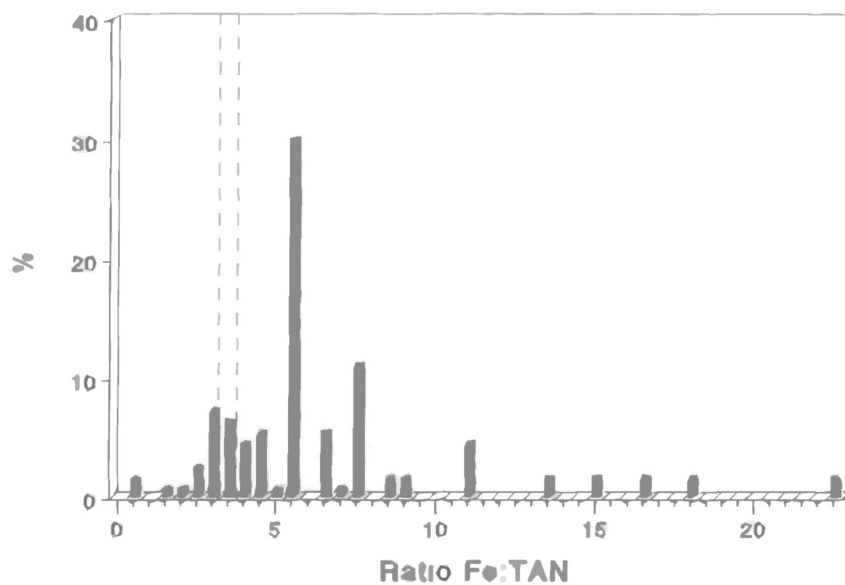


Figure 4.1: Distribution of iron (Fe) to tannin (TAN) molecular ratios in 104 ink recipes. Maitland, Crystal. "Where Archival and Fine Art Conservation Meet: Applying Iron Gall Ink Antioxidant and Deacidification Treatments to Corrosive Copper Watercolors." *The Book and Paper Group Annual* 28 (2009): 37-45. Web.

²⁵ Even though the ratio has little to no effect on the *causticity* of the ink, it should be noted, however, that a 3.6 to 1 ratio of iron to tannin produces the most balanced, fluid, and writeable ink (Banik 1997).

The results of the study showed that the majority of all iron gall inks contained a 5.5:1 ratio of iron to tannin (Neevel 145). Because this ratio most accurately represents the ratio found on late Medieval and early Renaissance manuscripts, a variety of experiments examining iron gall ink properties reproduce iron gall ink with a 5.5:1 ratio. Such experiments include the Neevel et al. study on the use of phytate as a conservative agent, Stefanis and Panayiotou's study on the deacidification of documents containing calcium hydroxide and magnesium hydroxide nanoparticles, and the Csefalvayová et al. study on iron gall ink's influence on paper aging.

IV. Oxidative Degradation, Acid Hydrolysis, & Surplus Transition Metals

Three chemical phenomena associated with iron gall ink are responsible for creating a damaged manuscript: (1) oxidative degradation, (2) acid hydrolysis, and (3) the presence of additional transition metals.

Iron-catalyzed oxidation contributes to the breakdown of cellulose chains within organic material, parchment, or paper. Organic radicals are directly produced from the oxidation of Fe^{3+} , as depicted in Figure 4.2 (Neevel 146).²⁶ An oxidation reaction occurs as the Fe^{2+} ions are oxidized to produce Fe^{3+} ions and superoxide, an organic radical (Jancovicová 391).

²⁶ Namely, vellum.

These peroxides react

further with Fe²⁺ ions

to produce highly

reactive hydroxyl

radicals. Free radicals,

especially those of

the hydroxyl species,

are highly unstable

due to the single unpaired electron. Radical species typically undergo a series of hundreds, sometimes thousands, of propagation steps, each producing harmful radicals of a new and different nature. These radical species are so reactive that they can extract a hydrogen atom off of almost any molecule (Maitland 40). As hydroxyl radicals integrate within the parchment, they readily remove the hydrogen atoms contained in the cellulose. The process of hydrogen abstraction from cellulose leads to, first, the

formation of organic radicals and,

secondly, the breaking of the 3-

glycosidic bond between glucose

units in the cellulose chain (Neevel

146). The breaking of these 3-

glycosidic bonds contributes to

both the mechanical weakening

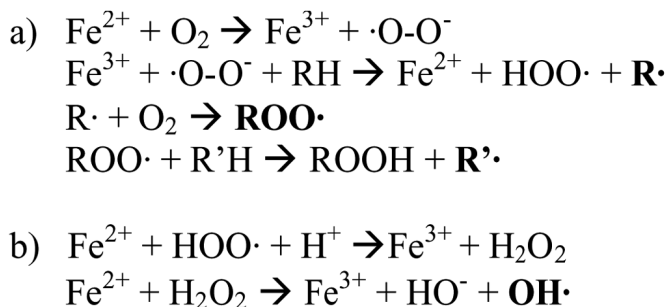


Figure 4.2: The iron-catalyzed oxidation reaction on cellulose. Source: Neevel, Johan G. "Phytate: A Potential Conservation Agent for the Treatment of Ink Corrosion Caused by Iron Gall Inks." *Restaurator* 16.3 (1995): 145. Web.

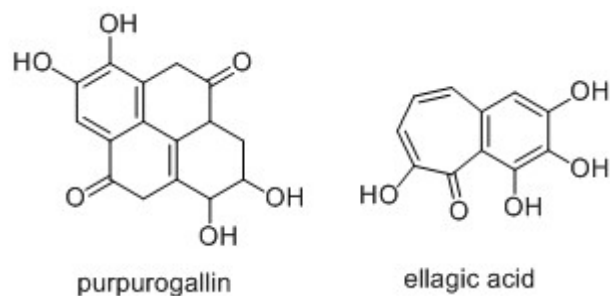


Figure 4.3: The two oxidative degradation products, purpurogallin and ellagic acid. Source: Maitland, Crystal. "Where Archival and Fine Art Conservation Meet: Applying Iron Gall Ink Antioxidant and Deacidification Treatments to Corrosive Copper Watercolors." *The Book and Paper Group Annual* 28 (2009): 37-45. Web.

and discoloration of the parchment (Csefalvayová 129). Two chemical structures of oxidative iron-gall ink degradation products, purpurogallin and ellagic acid, are illustrated in Figure 4.3 (Maitland 39).

The only known mechanism to prevent further oxidative degradation is to treat the document with phytic acid. Phytic acid is one of the few chelation agents known to inhibit the ferrous-ion catalyzed formation of hydroxyl radicals from hydrogen peroxide.²⁷ This agent acts by blocking the ferrous ion coordination site (Neevel 147).

Phytic acid is also known to prevent the corrosive consequences of acid hydrolysis. Treatment techniques with phytic acid for archival conservation are still under exploration. Figure 4.4 depicts the chemical structure of phytic acid.

Corrosive and permanent, iron gall ink possesses acidic properties that also contribute to the degradation of historical documents through acid hydrolysis. With a very low pH, ranging from 1.8-2.1, iron gall ink induces acid hydrolysis of glycosidic bonds within the cellulose of the parchment (Jancovicová 391). This shortening of the cellulose polymeric chains causes a reduction of parchment's mechanical properties (Csefalvayová 129). Deacidification techniques have been

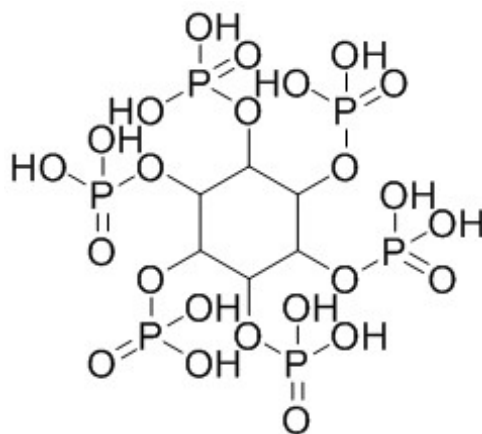


Figure 4.4: The chemical structure of phytic acid. Source: Farusi, Gianluca. "Monastic Ink: Linking Chemistry and History." *Science In Schools* Aug. 2007: 36-40. *Science In Schools*. Web. <<http://www.scienceinschool.org/2007/issue6/galls>>.

²⁷ The more appropriate chemical name for phytic acid is myo-inositol hexakisphosphate.

shown to slow ink corrosion via acid hydrolysis, however this is not as effective a technique as phytic acid treatment (Neevel 146).

Other transition metals often present in vitriol, like copper and manganese, are also capable of catalyzing chemical reactions in parchment, leading to cellulose deterioration over time (Charleton 2533). All transition metals with multiple oxidation states have the ability to catalyze cellulose degradation (Maitland 40). In particular, copper has the most impressive catalytic rate. At a pH of 8.0, copper is twenty times more effective at catalysis than iron, and at a pH of 9.0, nearly two hundred times more effective than iron (Kolar 2004). Gum arabic is a known ingredient to reduce and delay the degrading effects induced by the Fenton reaction and presence of transition metals (Remazeilles 220).

Scientists and curators alike examine vellum and parchment, the paper product of animal flesh, for degradation. These experts have questioned whether the flesh or hair side of the parchment undergoes more damage from the corrosive properties of iron gall ink, and have found the flesh side exhibits more ink corrosion than does the hair side. Manuscript decomposition has also been observed to occur much more quickly on the parchment's flesh side than the hair side. Experts within the Lazarus Project, including Michael Phelps, attribute this phenomenon to both the presence of gelatin on the flesh side, as well as the worn-down quality of the parchment's flesh side. Therefore, inscriptions written on the flesh side of a document's parchment can be expected to exhibit more damaged, corroded and difficult to read.

CHAPTER V
**INVESTIGATING THE QUALITY OF BOTH PLANT-BASED AND LAB-
GRADE IRON GALL INK**

I. Introduction to Experimentation

While researching the many and diverse iron gall ink recipes recorded throughout history, it was notable that both the ingredients and method of production were different from their scientific counterparts. Many scientists interested in uncovering iron gall ink chemistry used pure lab-grade tannic acid to create a standard in attempts to reproduce those created throughout history.²⁸ However, creating lab-grade ink with minimal variables may not grant scientists an accurate understanding of historical inks. Based on the researched knowledge of iron gall ink chemistry, historical ingredients and recipes possessed the necessary properties and biological enzymes that produce quality iron gall ink.

As early as 1786, Carl Scheele proved that gallotannic acid was the tannin derivative present within gall nuts (Carvalho 114). Gallotannic acid is simply one variety of tannic acid. However, many other varieties of tannic acid exist. For example, quercitannic acid is a very similar molecule derived from the bark and leaves of oak trees, but is often used to refer to tannic acid. However, this tannin

²⁸ Such experiments include the Neevel et al. study on the use of phytate as a conservative agent, Stefanis and Panayiotou's study on the deacidification of documents containing calcium hydroxide and magnesium hydroxide nanoparticles, and the Csefalvayová et al. study on iron gall ink's influence on paper aging.

source does not possess the ability to be converted to gallic acid. Gallotannic acid, however, can be converted to gallic acid.

This conversion of gallotannic acid to gallic acid is critical in creating iron gall ink similar to those seen throughout history. This process occurs via an enzyme-catalyzed reaction that occurs during gall fermentation in an alcohol- or water-based solvent. The presence of tannin acylhydrolase, an enzyme produced by the mold during fermentation, helps to catalyze this reaction (Farusi 39). Without the fermentation process, the desired gallic acid is not formed in the amount necessary to further interact with vitriol and produce quality ink. Historical recipes show evidence of a very scientific understanding of ink chemistry.

Before beginning in-depth research with the aim and for the benefit of manuscript preservation, I simply wanted to create iron gall ink and visualize the conflicting opinions between historian and scientist. This desire for a visual understanding spawned an experiment that compared the quality of ink produced from historical recipes and scientifically “ideal” ink produced according to modern standards. From researching the principles, history, and chemistry behind many centuries of iron gall ink, I hypothesized that recipes made from Aleppo galls produce inks of a higher quality than those made from lab-grade tannic acid.

In order to select the ink possessing the best writing capabilities, ink quality was chosen to be the qualitative measure of success. Carvalho states in *Forty Centuries of Ink* that an ink of superior quality must “flow readily from the pen, to indicate in a short time a black color and to penetrate the paper to an

appreciable degree, and more importantly than all the rest, to be of great durability.” Quality was thereby measured using the following qualitative criteria: ink appearance, fluidity while writing, and color intensity on paper. The ink color and homogeneity were observed as it appeared in the ink vial after production. Fluidity was assessed as standardized lines, letters, words, and phrases were drawn for each ink sample. Color permanence was observed twice: while the ink was applied to paper and ten seconds after application, allowing the ink time to oxidize on paper. All three criteria are assessed to judge the quality of the ink.

An appropriate scientific ink recipe was adopted from Emmanuel Stefanis and Costas Panaylotou and properly modified for this experiment (Stefanis 20). Twelve inks were created, all following this recipe. The first four were made from pure lab-grade tannic acid following a mixing procedure of subsequent ingredients. Four others were made from tannic acid extracted from the Aleppo gall via fermentation in direct sunlight. The remaining four inks were made from tannic acid extracted from the Aleppo gall via fermentation devoid of sunlight.

II. Materials and Methods

The iron gall ink made from pure lab-grade tannic acid began with dissolving 0.787 grams of gum arabic in 9.2 mL of distilled water.²⁹ The pure lab-grade tannic acid, 1.23 grams, was dissolved in 25 mL of distilled water.³⁰ Ferrous sulfate, 1.05 grams, was added to the 25 mL tannic acid solution and stirred

²⁹ Gum Arabic from CK Products, #76-3503.

³⁰ Tannic acid from Flinn Scientific, CAS#: 1401-55-4.

continuously for thirty minutes.³¹ The gum arabic solution was then added and stirred continuously for thirty minutes. This process was repeated four times to produce the four inks made from pure lab-grade tannic acid.

To keep consistent the stoichiometric ratios of tannic acid to iron sulfate with the first four inks, the mass of tannic acid was altered for those inks made from Aleppo galls.³² Five Aleppo galls were crushed to fine granules with a mortar and pestle. These finely crushed Aleppo gall granules, 1.89 grams, were added to 25 mL of distilled water. This solution was allowed to ferment in direct sunlight for nine days. After fermentation, gravity filtration was run for three hours to extract tannic acid from the fermented solution. This solution was diluted with 7.9 mL of water to a total volume of 25 mL. Gum arabic, 0.787 grams, was then dissolved in 9.2mL of distilled water. To the 25 mL tannic acid solution, 1.05 grams of ferrous sulfate was added and stirred continuously for thirty minutes. The gum arabic solution was then added and stirred continuously for thirty minutes. This process was repeated four times to produce the four inks made from the tannic acid fermented in the sunlight and extracted from the Aleppo gall.

A similar methodology was followed to create the iron gall ink made from Aleppo galls fermented in the absence of sunlight. The previously crushed Aleppo gall granules, 1.89 grams, were added to 25 mL of distilled water. This solution was allowed to ferment in a dark shoebox placed on the shelf of a closet for nine days. After fermentation, gravity filtration was run for three hours to separate

³¹ Iron (II) sulfate heptahydrate from Flinn Scientific, CAS#: 7782-63-0.

³² The average Aleppo gall contains 65% tannic acid. Aleppo Galls from Griffin Dyeworks and Fiber Arts, Model #: DY-GALLWHL.

precipitated tannic acid from the fermented solution. Water, 8.45 mL, was added to dilute this solution to 25 mL. Gum arabic, 0.787 grams, was dissolved in 9.2mL of distilled water. To the 25 mL tannic acid solution, 1.05 grams of ferrous sulfate was added and stirred continuously for thirty minutes. The gum arabic solution was then added and stirred continuously for thirty minutes. This process was repeated four times to produce the four inks made from the tannic acid fermented in complete darkness and extracted from the Aleppo gall.

A gall nut's tannic acid concentration is dependent on both the origin and species. An Aleppo gall species, containing 65% tannic acid, was used in this experiment due to its abundant use throughout ink history.³³ Due to the impact the gall nut's location of harvest can have on concentration, it is difficult to determine the exact tannin concentration of the galls used in this experiment. The location of harvest of the Aleppo galls used remained unknown. Thereby the five Aleppo galls were assumed to have tannic acid concentration of 65%.

III. Results

The quality of the ink created from lab-grade tannic acid was first observed and then tested using a glass dip pen on paper parchment on the day the ink was created. Dark globular precipitates floated throughout the grey colored translucent ink solution. The pen wrote a discontinuous line that left deposits of the precipitates on the paper. Words, phrases, and names were attempted using this ink. Constant dipping of the pen in the ink was required

³³ According to the Food and Agriculture Organization of the United Nations Corporate Document Repository.

following each and every letter. The nib made multiple scratches in the paper due to the lack of ink flow. It took ten seconds for the translucent ink to dry on paper, leaving a faint remnant of the written shapes patterns, and letters.

The quality of the gall nut-based inks was also assessed on the day the ink

was created. This ink possessed a

homogeneous nature

with a dark purple-

black color. This gall

nut-based ink was darker than the lab grade ink and devoid of chunky

precipitate. The pen wrote a continuous line, devoid of any precipitate deposit.

Words, phrases, and

names were

attempted using this

ink. Five to ten

words could be

easily written before having to reapply ink to the pen. It took ten seconds for the

ink to dry on paper, leaving a rich black pigment. Both the gall-based inks created

in sun fermentation and in dark room fermentation wrote in this way.

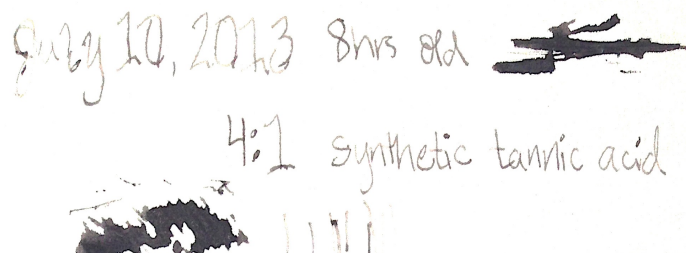


Figure 5.1: Lab-grade ink on parchment 8 hours after ink creation.

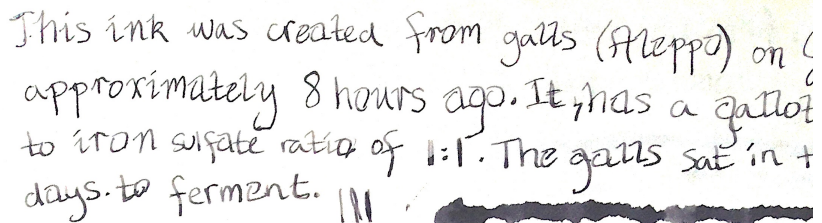


Figure 5.2: Gall nut-based ink on parchment 8 hours after ink creation.

After a week passed, the inks were qualitatively analyzed again in the same manner. The lab-



Figure 5.3: Lab-grade ink on parchment 7 days after ink creation.

grade ink continued to possess black precipitate at the bottom of the lightly colored and translucent ink solution. When applied to paper, the ink appeared tremendously faint and practically invisible to the naked eye. The pen required constant reapplication of ink to create words. The only distinguishable inscriptions were those made from the chunky precipitate after they were allowed to dry on paper

for ten seconds. All lines, words, phrases were



Figure 5.4: Gall nut-based ink on parchment 7 days after ink creation.

discontinuous. The gall nut-based inks appeared and wrote the same as they did upon the day they were created.

After forty-one days passed, the inks were qualitatively analyzed for the last time in the same manner as before. The precipitate in the lab-grade ink continued to be more pronounced. When applied to paper, the lab-grade ink exhibited all the same properties from the previous observation, with the only difference being it

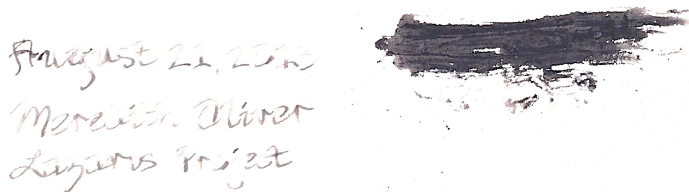


Figure 5.5: Lab-grade ink on parchment 41 days after ink creation.

wrote with an even
more faint quality.

The gall nut-based
inks possessed all the

same observational qualities but also had a more faint appearance when applied
to paper.

August 21, 2013
Meredith Oliver
Lazarus Project



Figure 5.6: Gall nut-based ink on parchment 41 days after ink creation.

IV. Discussion and Conclusion

The ink made from lab-grade tannic acid did not write well. The ink's appearance alone suggested a lack of fluidity: small black chunky precipitates existed within the grey-black translucent ink solution. As the pen attempted to draw a simple line, the precipitate deposited on the parchment and left no continuous trace of ink, an obvious lack of fluidity. The ink was rather translucent on paper as well, exhibiting no color permanence even after given time to oxidize. The pen needed to be dipped in the ink solution after each letter was written. The quality and visual appearance of the lab-grade ink is neither efficient for the writer nor effective in conveying meaning to the reader.

All inks created from the Aleppo galls wrote with great quality. Dark in color, the purple-black ink solution exhibited a desired uniformity devoid of precipitate particles. The pen not only wrote a continuous line, but also several words before reapplying ink; this is a noted characteristic of marvelously fluid ink. After the ink was allowed time to oxidize on parchment, it exemplified a rich black and visible quality that was unquestionably legible. The Aleppo gall based inks exhibited all the qualities demanded by ink makers and enthusiasts

throughout history: a dark purple-black appearance, exceptional fluidity, and legibility.

No distinguishable differences were noted between the Aleppo gall nut based ink fermented in the sun compared with the other fermented in the absence of light.

As the ink aged over the course of a month, the ink's legibility decreased. This observation supports Dr. Stark's principle conclusion regarding the durability and permanence of iron gall ink; ink exhibits its most durable quality when freshly made. As the ink ages in the vial, the tanno-gallate iron complex separates and precipitates out of solution, leaving an ink of poor quality. Therefore, freshly made iron gall ink is concluded to be of best quality.

This experiment confirmed that gall-based inks are higher in quality than their more scientific counterparts. This observation supports the chemical foundation explained in Chapter 3, where the enzyme catalyzed formation of gallic acid provides a substrate of great affinity for the metal salt, compared to large and sterically hindered tannic acid substrate.

After performing this experiment, I understand why scientists might use lab-grade tannic acid in replace of the Aleppo gall. Each Aleppo gall contains a slightly different concentration of tannic acid, averaging 65%. Scientists are also not as interested in producing an ink of good writing quality, but an ink with the necessary variables for experimental purposes. If creating a control is more important to the scientist than creating a more accurate portrayal of historical ink, using lab-grade tannic acid may be a wise decision. However, if the scientist's desire is an ink of good writing quality, look no further than historical documents

containing ink recipes, for ink makers had perfected the iron gall ink recipe over several centuries and knew the fermentation of gall nuts created an ink of outstanding quality. Ultimately, scientists should strongly consider the reaction mechanisms that serve as the chemical foundation to create an ink of historic interest and lasting quality.

CHAPTER VI

A TECHNOLOGICALLY INTEGRATIVE APPROACH TO DISCERNING TRACE ELEMENTS AMONG INK SAMPLES

I. Introduction to Experimentation

As previously explained, vitriol is not solely composed of iron sulfate. Vitriol may contain a variety of metal impurities, of which copper, zinc, aluminum, and manganese predominate. The elemental composition of vitriol is dependent on the excavated location, mining technique, various additives, and time period.³⁴ This simple principle raises an important historical, scientific, humanitarian, and conservation question: If ink's elemental composition can be easily detected on parchment, then is it possible to determine manuscript provenance?

To help answer this question, UV-vis and fluorescence spectroscopic methods were used to collect data on a variety of lab-made iron gall ink solutions.³⁵ These instruments excited the ink solutions within a 200-800 nm window and recorded both their excitation and emission spectra. The absorbance and emission information is useful because each transition metal absorbs and emits light at a characteristic wavelength. By distinguishing the presence of trace

³⁴ The time period is heavily dependent upon the mining technique, for the technique used to extract iron sulfate for iron gall ink use is indicative of the resources and technology available to the people at that particular period of history.

³⁵ Each ink solution contained a trace amount of a one transition metal that could be expected to be present in any historical iron gall ink.

elements within ink based on its excitation and emission spectra, it might be possible to classify and categorize ink according to its elemental composition.

More promising and revolutionary is the possibility of integrating UV-vis and multi-spectral imaging data using Photoshop. The data collected from UV-vis measurements produces a graph of absorbance versus wavelength, where UV and visible absorbance of the liquid-state ink samples are recorded. Photoshop, employed on the multi-spectral images, might serve as an effective method to detect the relative color intensities of the ink on parchment. Here, I plan to compare multi-spectral color data, using the Lazarus camera system and extracted with an image-editing program such as Photoshop, with solution phase UV-vis data to try and find a correlation. My hope is that we can use the Lazarus Multi-spectral imaging system to perform the same kind of analysis that would be performed using a UV-vis spectrometer, thus allowing us to perform laboratory type experiments on ancient documents in library conservatories. This offers the chance to add a new scientific dimension to the field of digital humanities.

II. Materials and Methods

Five laboratory iron gall inks were created, each made from of a different metal sulfate. Each of the five inks consisted of the following ingredients: lab-grade tannic acid, ferrous sulfate heptahydrate, water, and gum arabic. The inks varied in the metal salt present in combination with **iron** (II) sulfate heptahydrate. These metal salts include **copper** (II) sulfate pentahydrate, **zinc** (II) sulfate heptahydrate, **aluminum** sulfate hexadecahydrate, and **chromium** (III) potassium sulfate dodecahydrate. Copper, zinc, and aluminum were chosen

because these three metals are known to exist in historic iron gall ink due to both the geographic representation and the manufacture of vitriol as previously discussed. Chromium, another metal, was chosen due to the unknown color and fluorescent effects it may have within iron gall ink. The physical properties of each ingredient are listed in A-5. The mass of ingredients used in each of the five inks is listed in A-6.³⁶

To create ink that best reproduced those in history, a ratio of 5.5 moles of iron to 1 mole of tannin was chosen based on the conclusion of the Barrow, Van Gulik, Kersten-Pampiglione study and this ratio's use in a variety of other iron gall ink experiments. The appropriate mole fraction of 0.7 moles of metal salt to 1 mole of iron was chosen to ensure no overabundance of metal salt exists in solution, according to the Maitland et al. study.

Iron gall ink was prepared by mixing 0.787 g of gum arabic in 9.2 mL of distilled water. This solution was made five times, one solution per ink. The appropriate weight of each metal salt, specified in A-6, was weighed and added slowly its respective gum arabic solution. Lab-grade tannic acid was weighed and 1.23 g of it was dissolved in 25 mL of distilled water. This tannin solution was made five times, one solution per ink. Each of the five metal salts and gum arabic solutions were then slowly added to each tannic acid solution, producing five inks all containing tannic acid, gum arabic, iron sulfate, and the variable metal salt.

The water was stirred constantly while both the gum arabic and tannic acid were added to its respective beaker of water to avoid clumping and enhance

³⁶ Inks are named both by a designated number and according to the variable ingredient in combination with iron (II) sulfate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

solubility. If too much gum arabic or tannic acid was added at once, the gum arabic coagulated with the insoluble tannin complex and precipitated to the bottom of the beaker, unable to dissolve properly in water.

All inks turned black upon combining the final solution with the tannic acid solution in the presence of oxygen. This observation indicated a redox reaction. All inks remained black, with the exception of the ink containing aluminum sulfate, which appeared as a dark sooty gray color. These inks were stored in a screw-capped vial and a dark room.

As prepared ink solutions settled in these vials for six days, all solutions, including the aluminum sulfate containing ink, became black with a violet hue. This can be attributed to the oxidation process occurring within the vial.

Before taking UV-vis absorbance and fluorescence spectroscopies, ink solutions were placed in both sonicator and vortex mixer to aid in particle suspension.

The dark blue-black ink was diluted for spectroscopic analysis. 0.05 mL of ink is diluted in 100 mL of distilled water to render reliable absorbance and emission spectra. UV-vis absorbance spectroscopy was first performed on each ink sample to collect an excitation peak. The exact excitation peak information was necessary to operate the fluorescence spectrometer, as the fluorometer was first set to excite the ink sample at each and every excitation peak recorded by the UV-vis spectrometer. The fluorometer recorded the emission spectrum of the ink. Both of these spectroscopic methods were used to shed light on the ink's fluorescent properties.

UV-vis absorbance and fluorescence spectroscopies were both performed first on a dilute sample of tannic acid in a water solvent to compare the fluorescent properties of tannic acid to the tannin containing iron gall ink. Parchment samples with the recently made ink were prepared for multi-spectral and Photoshop analysis. Parchment samples were made from four-inch square parchment scraps.³⁷ Each sample was uniformly inscribed with the same characters, yet distinguishable from one another by their chemical formula and elemental mass denoted in the center of the page. Six parchment samples were made in all. A-7 denotes the ink samples used on each respective parchment sample. Sample A-7, containing the ink made from both iron (II) sulfate and copper (II) sulfate, is displayed in Figure 6.1.



Figure 6.1: Prepared parchment sample for multispectral and Photoshop analysis.

The parchment samples served to simulate historical manuscripts imaged by the multi-spectral camera system. A multi-spectral imaging system was used to collect digital images of the ink samples exposed to specific frequencies of the ultraviolet, visible, and infrared spectra. Two raking lights and two transmissive lights emitted particular electromagnetic wavelengths ranging from 360-940 nm. As each desired wavelength was emitted onto the document of interest, a digital

³⁷ Parchment scraps were provided by ©Pergamena and could be made from any of the following: calfskin, deerskin, goatskin, or sheepskin.

camera took a photograph of the document.³⁸ Twelve images were taken for each parchment sample, each one exposed to a different wavelength.

These processed images were further analyzed in Photoshop to obtain gray scale intensity values. For each sample, the darkest ink spot was chosen on the parchment sample for analysis. A low number, such as 70, corresponds to a very dark gray scale value, while a high number, such as 250, corresponds to a white gray scale value in Photoshop. Gray scale values were obtained from each of the twelve multispectral images and plotted against wavelength in Excel. The spot chosen for gray scale analysis on sample 0 and sample 3 are shown, respectively, in Figure 6.2 and Figure 6.3.

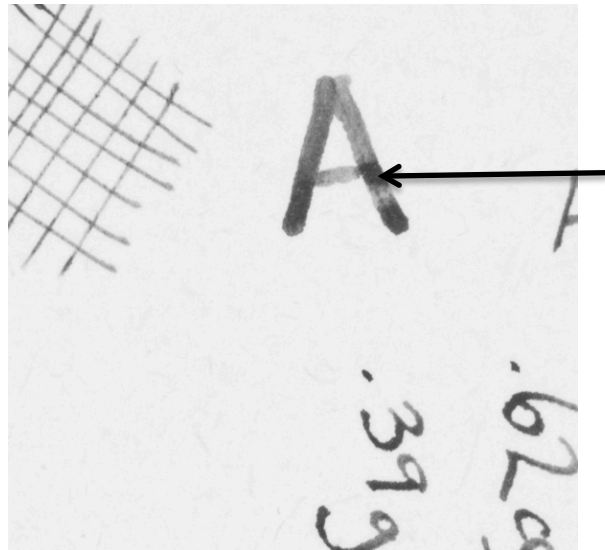


Figure 6.2: Ink spot chosen for gray scale analysis on sample 0.

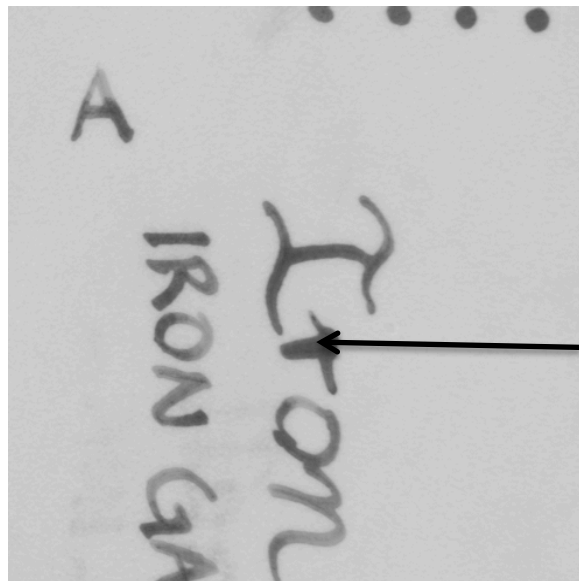


Figure 6.3: Ink spot chosen for gray scale analysis on sample 3.

³⁸ Monochrome E7 50-megapixel back and a 120mm f4.5 hyperspectral lens provided by MegaVision with 13.5cm travel capabilities via rail and bellows.

The UV-vis spectroscope plots absorbance against wavelength, where absorbance is defined, by the Beer-Lambert Law, as $\log(I_0/I)$.³⁹ This equation was therefore utilized to analyze the photoshop data as well, allowing for a theoretically sound comparison between the UV-vis data and the data obtained by the multispectral imaging system. Consequently, a gray scale value was also obtained from the white parchment to be used as a comparator and control value against the black one. Grayscale values for the ink spot and white parchment were compared on this logarithmic scale, using the equation $\log(I_0/I)$ where I_0 corresponds to the grayscale value of the white parchment and I corresponds to the grayscale value of the ink spot. Therefore, I_0 serves as a point of comparison, or reference, to the intensity obtained from the ink sample.

III. Results

The first set of data, depicted in Figure 6.4, relates to the relative differences in light absorption between the diluted liquid ink samples created with various metal salts. The UV-vis spectrum plots absorbance against wavelength. As the excitation peaks were obtained, from the wavelength at the highest absorbance, the fluorometer recorded the following emission spectra at the respective excitation wavelength. Two emission spectra are shown in Table 6.1.

³⁹ I_0 is the intensity of light passing through the reference cell obtained from the initial sample of distilled water. I is the light intensity passing through the dilute ink sample.

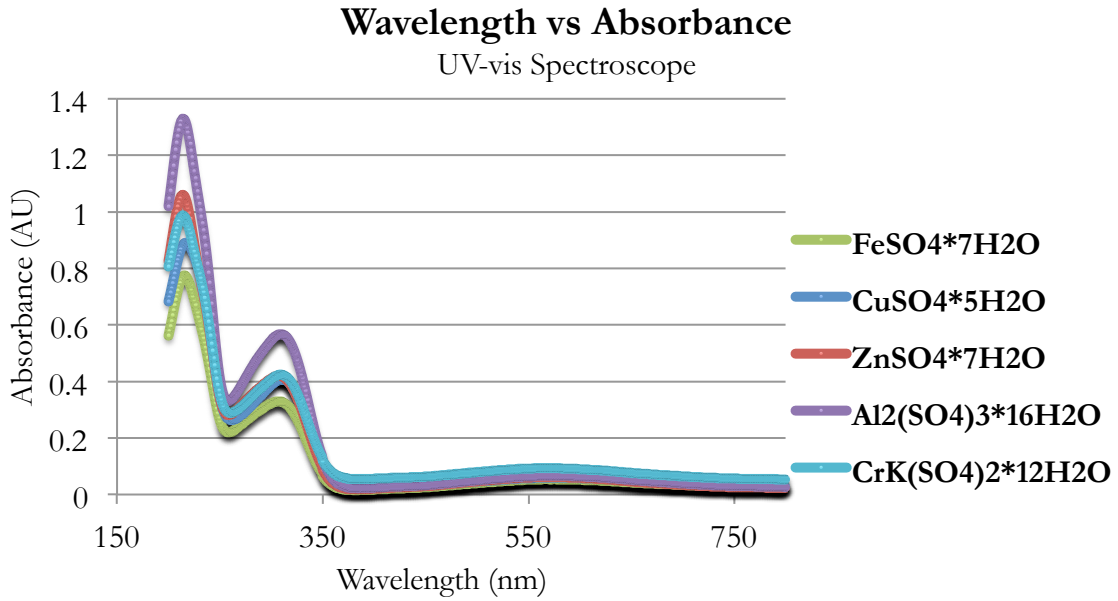


Figure 6.4: Comparison of the inks with various metal salts via UV-vis spectroscopy.

Once multi-spectral images of the ink samples on parchment were obtained and gray scale analysis was performed via Photoshop, samples containing iron (II) sulfate, copper (II) sulfate, and zinc (II) sulfate were compared plotting, first, the ink's gray

Table 6.1: Emission spectra obtained from fluorescence spectroscopy.			
Ink	Excitation Peaks (nm)	Emission Peaks (nm)	Intensity
FeSO ₄ •7H ₂ O	306	432	128
		486	196
		541	493
		587	154
		611	266
CuSO ₄ •5H ₂ O	310	438	144
		488	222
		544	521
		581	610
		610	276

scale intensity value against wavelength exposure, as depicted in Figure 6.5.

Wavelength vs Grayscale Intensity Values Multispectral Imaging System

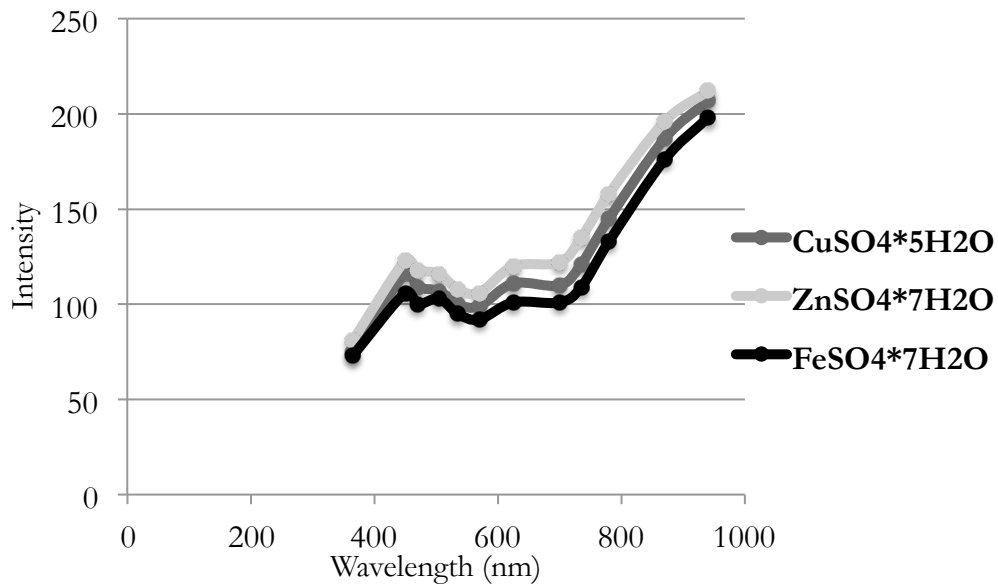


Figure 6.5: Comparison of three inks grayscale values at various wavelength exposures delivered by the multispectral imaging system.

These same three parchment samples were further compared, as total intensity was plotted against wavelength exposure. Total intensity, in Figure 6.6, is defined as the logarithm of the parchment's gray scale value divided by the ink's gray scale value on the same sample at the respective wavelength exposure.

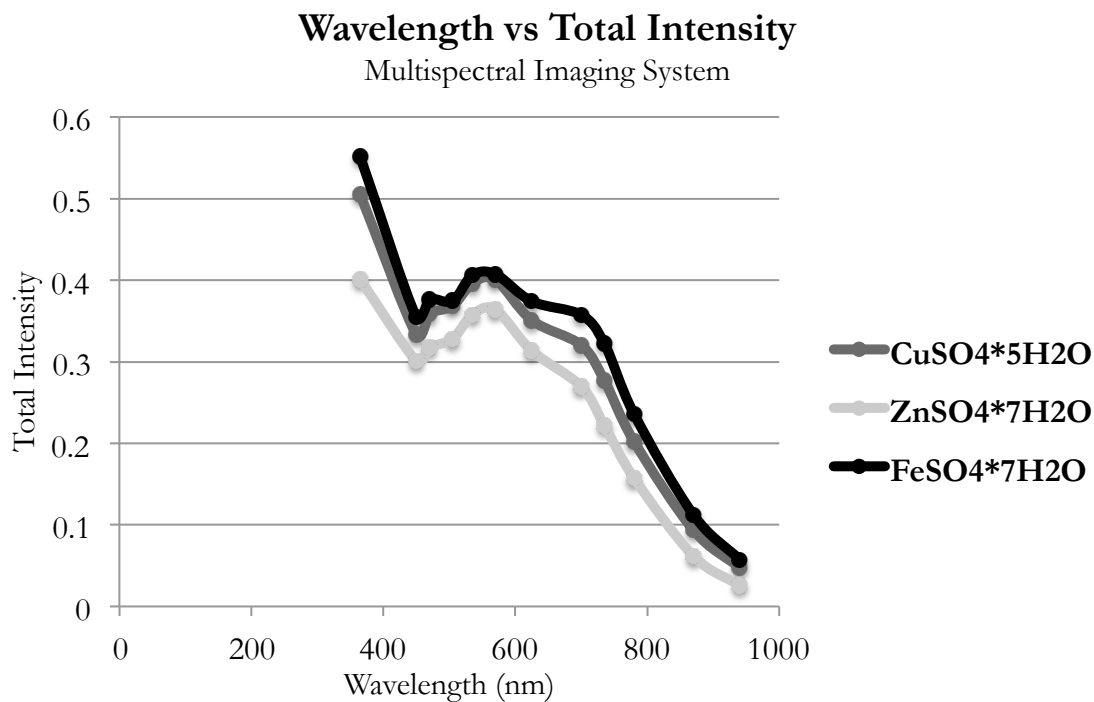


Figure 6.6: Comparison of three inks total intensity values at various wavelength exposures by the multispectral imaging system.

Because the same equation was used to obtain either absorbance or intensity for both UV-vis absorbencies and multi-spectral images, respectively, Figure 6.7 displays the comparison between the UV-vis data and multi-spectral imaging data for the three selected ink samples.

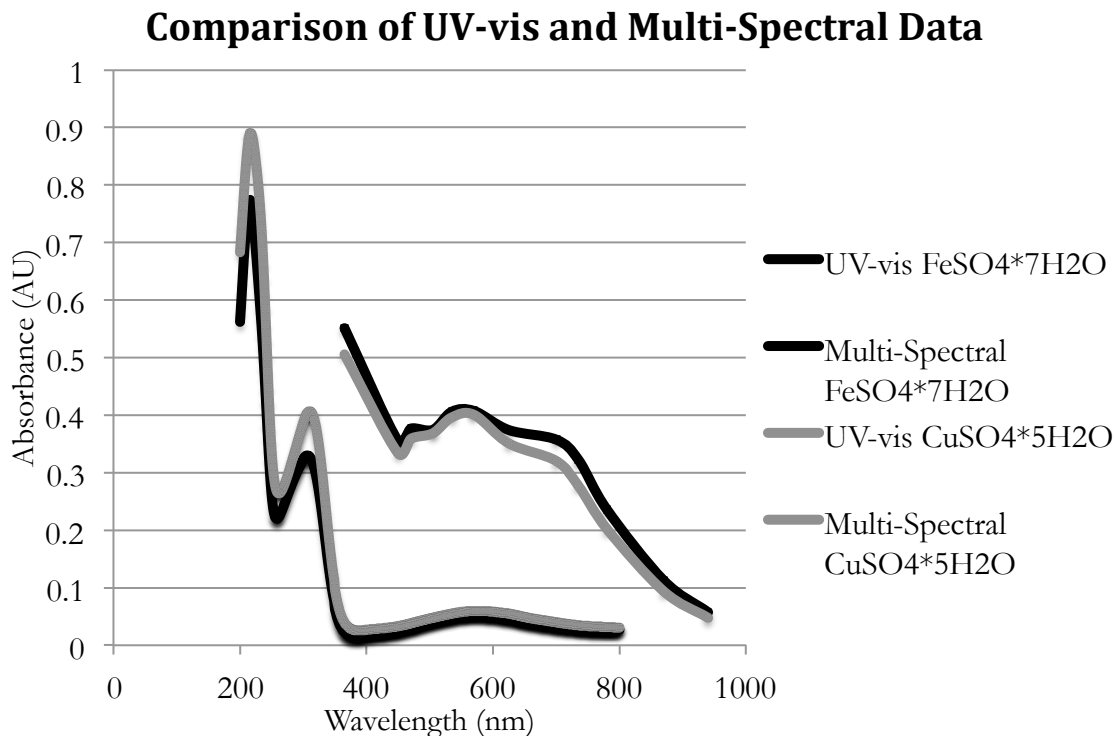


Figure 6.7: Comparison of UV-vis and multi-spectral imaging data using two ink samples.

IV. Discussion and Conclusion

The initial question under investigation examined the potential for UV-vis and fluorescent spectroscopy to detect the slight variations in inks containing trace amounts of metal salts. The possible implications of this question include the detection of slight variation among ink, allowing researchers and historians to place a time and location stamp on the inks under question.

Upon examining the UV-vis and fluorescence data collected, the absorbance of each of the inks varied slightly. However, to distinguish the ink samples based on the present trace element, the wavelength peaks would have to differ. All inks exhibited the same excitation and emission wavelength. For each ink sample, the UV-vis collected two sharp wavelength peaks at 218 nm and 319 nm and a subtle peak at 577 nm. For each excitation wavelength obtained by the

UV-vis spectroscope, the same emission wavelengths were obtained for all inks analyzed.⁴⁰ For the two inks made from iron and copper metal salts, respectively, the same five emission wavelengths were obtained from their one characteristic excitation wavelength. None of the ink samples exhibited an excitation or emission peak at a different wavelength. Therefore, two spectroscopes were unable to detect the differences between inks containing trace amounts of metal salts. Most likely, this was due to the lack of sensitivity of the machines to detect such a trace amount of the metal salt present in the ink. Machines of this type and sensitivity would not be able to provide information regarding the precise chemical composition and, subsequently, the location and time period of the ink.

Another question under investigation was the possible power of the multi-spectral imaging system in detecting the trace element variations among the ink samples. Unlike the UV-vis and fluorescence spectroscope, which can only analyze liquid ink samples, the multi-spectral imaging system has the capacity to detect these ink differences on the old manuscripts. However, upon examining the grayscale data collected from the multi-spectral imaging system, each ink sample displayed excitation peaks at the same wavelengths. For the three inks chosen for investigation, a small peak is observed around the 450 nm wavelength, a plateau peak occurring at both 625 and 700 nm wavelengths, and a high peak occurring at the 940 nm wavelength. Similar to the previous conclusion, the CCD sensor in the camera most likely lacks a spectral response sensitive enough to detect trace element variation. Therefore, the multi-spectral imaging system proved incapable of detecting the slight variation among the created ink samples.

⁴⁰ +/- 10 nanometers.

Historians, scientists, and curators should not use these methods to either date or locate the origin of ancient manuscripts.

Although both of these methods proved ineffective in identifying the slight variations among ink samples, there is still significance in the attempt to answer a greater question regarding the importance and promise of the digital humanities and the work of the Lazarus Team. A more pressing question examines the usefulness and power of the multi-spectral imaging system: does the system have the ability to detect both the absorbance of the various wavelengths produced by the lights and the corresponding intensity values of the ink on parchment? If the UV-vis absorption data can display a correlation with the intensity values obtained from the multi-spectral imaging system, researchers may be able to bypass using UV-vis spectrometer all together and simply use the multi-spectral system to obtain ink's absorption peaks within the pages of manuscripts.

The absorption peaks with the UV-vis spectroscope exist at 218, 319, and 577 nm. The intensity peaks with the multi-spectral system exist at 450, 625, and 940 nm. At first glance, no correlation seems to exist between the UV-vis and multi-spectral data. However, the principle governing absorption data in the UV-vis spectra contains a data point of comparison. A data point of comparison must be employed, along with the Beer-Lambert equation, to obtain a new intensity value for the multi-spectral data. The plain parchment background, devoid of ink, served as the comparator point to obtain a new, total intensity value. A new, total intensity was obtained and displayed peaks at the starting 365 nm and 570 nm

wavelength values. By creating this comparator value, the multi-spectral data became comparable to the UV-vis data for a more accurate analysis.

A limitation exists in the multi-spectral system in that a wavelength of 365 nm is the lowest wavelength emitted by the light system. The UV-vis spectroscope is capable of emitting a wavelength of 200 nm. Therefore, data points in the 200-365 nm range cannot be compared between the two systems. However, by observing the comparable data points in range, a clear correlation between the UV-vis and multispectral data can be seen. The multi-spectral data follows the curvature of the UV-vis excitation peaks. The peaks exist near the 300 nm wavelength and 570 nm wavelength. Both graphs experience an excitation low around 385-450 nm and both display a negative slope in the 700-800 nm window, indicating a lack of excitation upon exposure to these wavelengths. It can be concluded that a correlation exists between the UV-vis and multi-spectral excitation and absorption, respectively. Therefore, the multi-spectral imaging system shows great promise in revealing information in regard to ink's absorption capabilities within the pages of manuscripts.

CHAPTER VII

INSIGHTS INTO THE VERCELI BOOK AND CODEX A

I. Introduction to Experimentation

Collaboration among scholars from a variety of fields has aided manuscript dating, digitization, and preservation efforts. Each and every specialist is essential to the project at large: the paleographer necessary to decipher the time period and hand of the script, the camera inventor crucial in creating the system used to generate digital images of the degrading document, the computer scientist vital to understand and create image processing techniques, and the students needed to create new ideas, perform a variety of basic imaging tasks, and carry on the knowledge of and passion for the digital humanities. Individuals involved in the Lazarus Project Imaging team collaborate to carry out the mission and vision of document restoration. This very vision and expertise was requested by the Fondazione Museo Del Tesoro Del Duomo E Archivio Capitolare in Vercelli, Italy for the investigation and preservation of two manuscripts: the Codex A and Vercelli Book.

The Codex A is reputed to be the oldest existent Latin translation of the New Testament's four Gospels (Illmo). Written by Saint Eusebius, the first Bishop of Vercelli, this manuscript is estimated to date back to the period between 345 and 371 A.D (Aceto 286). Due to its prodigious importance to both scholars and clerics, the Codex A requires digitization and chemical examination

to digitally preserve, read with greater clarity, and accurately date the document. This manuscript is under direct observation and study by the Lazarus team because of the XRF spectrometry Maurizio Aceto performed on the Codex A in 2008. Aceto's results suggest a significant presence of iron gallate, gum arabic, and sulfate anion in the ink, made possible by XRF analysis (Aceto 288). Such results suggest that Codex A is the earliest known document written with iron gall ink. However, skepticism exists among scholars over Aceto's methodology: the XRF spectrometer used in his study is of the spot tracer model, which exhibits quick measurements with low sensitivity (Rabin). This spot tracer is considered to produce results of questionable precision, and therefore should not be used to study palimpsest documents. With the help of ink experts Ira Rabin and Oliver Hahn and their ARTAX line scanning micro-XRF spectroscope, the Lazarus Project Imaging Team sought to prove the authenticity of Aceto's conclusion and determine the precise elemental composition of the ink embedded within the pages of the Codex A.

In addition to this unique undertaking, another manuscript beckoned for care and analysis. The Vercelli Book, a tenth-century Old English anthology, contains twenty-three religious homilies and six poems. It is one book in a series of four Old English anthologies; the other three are named the Junius Manuscript, Exeter Book, and Nowell Codex. Due to the anthological nature of this manuscript, not all homilies or poems were created in the 10th century; some of the Vercelli Book's contents may have been written much earlier. Scribes attempting to translate this document have permanently damaged twenty-one folios with a brown reagent, now concealing all of the original text and

consequently rendering these folios illegible to historians. These damaged folios of Vercelli Book beckon for digital restoration, which can be provided only by technological tools available to the Lazarus imaging team. This manuscript is also important because it was created during a time when little is known about the use of iron gall ink. Information regarding the ink within tenth century manuscripts has essentially gone unstudied, for iron gall ink was not widely documented until the beginning of the thirteenth century (Rabin). While the ink within the Vercelli Book is hypothesized to be of the iron gall ink type, elemental analysis on this unidentified ink is fundamental in understanding the possible inks used during this particularly uncharted period of ink history.

To answer these particularly innovative questions, the Lazarus Project Imaging crew and multispectral system collaborated with the expertise and line scanning XRF spectroscopy of Ira Rabin and Oliver Hahn.

The multi-spectral imaging system and micro-XRF are used in conjunction to reach a conclusion regarding the nature of the two manuscript's inks. The imaging system and camera generate a visual image while the micro-XRF grants scientists the ability to analyze the elemental composition of both the manuscript's ink and parchment. During a manuscript's digital capturing, the multi-spectral imaging system is able to locate characters on the document's pages with exceptional precision and resolution. This visual data is crucial for the micro-XRF operators, who are then better able to choose a specific sample spot of micrometer detail. This collaborative method between the multi-spectral system and micro-XRF helps to generate an elemental analysis with ideal accuracy.

The spectrum produced by the micro-XRF gives a complete and comprehensive view of the specific elements present within the spot being analyzed, whether ink or parchment. The spectrum produced by micro-XRF analogously serves as the ink's chemical fingerprint. Each fingerprint is unique to a specific historical ink; no two are alike. However, recognizable patterns exist between inks of the same type. These patterns are dependent on the fundamental ingredients used to create the ink as well as the concentration of the ingredients. Oliver Hahn claims that with these composition fingerprints, it is possible to characterize distinguishable inks of one artist to classify different chronological ink types and, further, to date unknown fragments that have not so far been integrated into the lifework of the artist (Hahn 234). This hopeful possibility is the driving force behind this collaborative scientific study on the Codex A and Vercelli Book inks.

Knowledge of the elemental composition of carbon-based, plant-based, and iron gall-based inks is crucial to decipher the spectrum and correctly determine the type of ink used to write the manuscript. The most basic carbon ink is a made by combining soot with a water-soluble binding agent (Rabin). These carbon inks were first created in the Orient and were popular from the sixth to twelfth centuries (Rabin). Plant-based ink, like iron gall ink, is made from a tannin source, most commonly tree bark. However, iron sulfate is not an ingredient in plant-based inks and therefore does not chelate with the tannin source. This chelation phenomenon is only present in iron gall ink (Rabin).

By using micro-XRF analysis, historians are able to decipher the chemical spectra to further characterize the manuscripts ink as carbon, plant, or iron gall

based. When iron is the most prevalent element and a presence of sulfur is detected, it can easily be confirmed that the ink under speculation is indeed that of iron gall. As previously discussed, vitriol possibly contains a variety of additional transition metals including copper, zinc, manganese, aluminum, iron sulfate, and potassium aluminum sulfate. If the presence of sulfur is detected by micro-XRF, iron gall ink presence can easily be confirmed by the spectral presence of the transition metals within vitriol. Calcium, manganese, and potassium are elements that always exist in the parchment and can be expected to be present in trace amounts. A sharp increase in these elements hints that the ink is of the iron gall type, for iron gall ink absorbs the calcium, manganese, and potassium present within the parchment (Rabin). Potassium is an element present in both parchment and in the organic material of galls, gum Arabic, and tannins. It would therefore be detectible in any manuscript's micro-XRF analysis. Recognizing and understanding the spectral pattern increases the likelihood that the ink type is confirmed and subsequently dated for provenance.

For final conclusive evidence concerning ink identity, the DinoLite digital microscope camera is most useful. This diminutive handheld microscope contains built in near-infrared LED lights that serve to shine spectra of low frequency and high wavelength in the visible and near-IR range on manuscripts. It has been determined that iron gall ink is only visible on parchment below a 1230 nm wavelength. Any photograph of iron gall ink taken with a longer wavelength of light will be invisible. Plant based inks disappear completely on parchment at a much lower wavelength at 750 nm. Carbon based inks are the only inks visible at all spectra, due to carbon black's impressive light absorption

properties. A quick elemental analysis can be found by selecting a 940 nm wavelength. At this wavelength, plant based inks are undetected, iron gall ink is less discernable than in the visible spectrum, and carbon based inks appear as rich and legible as they appeared under any of the multi-spectral wavelengths. Combining the knowledge of ink properties with the DinoLite NIR microscope, it is easy for scientists to distinguish the difference between plant-based, vitriol-based, and carbon-based inks.

II. Materials and Methods

An x-ray fluorescence spectroscope is used to assess the inorganic elemental composition of various locations on both the Codex A and Vercelli Book. The multi-spectral imaging system aids the selection of a point of interest on the manuscript. The XRF emits x-rays, which are absorbed by the atoms at the selected point. The absorption of these x-rays is enough to eject electrons from their atoms with significant kinetic energy. These ejected electrons are collected by the micro-XRF, as the machine measures the electron's kinetic energy. The specific pattern of electron energies is characteristic of different atoms. Once the data is collected, an elemental analysis spectrum is displayed on the computer.

When elemental composition from XRF analysis is under question, the DinoLite digital microscope camera is used to confirm ink identity.

III. Results

Regarding the ink of Codex A, the elements of iron, sulfur, potassium, and copper are distinctly present in the micro-XRF spectrum of the manuscript's ink. Iron is the predominant element. Near-IR frequency rendered the text illegible at extremely long wavelengths.

Regarding the ink of the Vercelli Book, the elements of calcium, iron, potassium, and lead correlated with the ink's written forms. Calcium was the most prevalent element present on the pages of the Vercelli Book. However, there was no noteworthy difference between calcium's presence in the ink and the calcium levels on parchment. There was no indication of sulfur, copper, zinc, manganese, or aluminum. The ink is homogeneously distributed on the page and exhibits no degradation to itself or the page. Near-IR frequency rendered the text illegible at extremely long wavelengths.

IV. Discussion

Conclusions are still being drawn from the Codex A's ink analysis. The micro-XRF spectra analysis suggests iron gall ink due to the clear presence iron, sulfur, and copper. The prevalence of each element correlates well the iron gall ink fingerprint. Near infrared LED exposure confirmed the ink present on the pages of the Codex A is not carbon ink. Before confirming Aceto's conclusion, further analyses are being conducted on additional pages of the Codex A. However, if it can be proven that this ink is indeed of the iron gall type, it will be the earliest known use of iron gall ink in history.

More interesting to note is the Lazarus team's first visit to Vercelli. In the spring of 2013, the Vercelli book was imaged for digital preservation without elemental micro-XRF ink analysis. Due to the team's lack of in depth knowledge and understanding of ink diversity, the ink was simply speculated to be that of the iron gall type. Among the team, little was known about plant-based inks. However, the Lazarus Project found themselves back in Vercelli in the summer of 2014 for a subsequent imaging session. This time, the technological capability and ink knowledge of several experts made ink typing on this document possible.

The data collected concerning the ink within the pages of the Vercelli book was unexpected. This ink showed very little correlation with the characteristic patterns of iron gall ink. While experts anticipated iron to dominate, the main element in the ink proved to be calcium. While iron was present within the Vercelli Book's ink, no other characteristic iron gall ink elements, such as sulfur, copper, zinc, manganese, or aluminum, were present in any noteworthy concentration. Another curious observation was that calcium's presence did not show significant decrease in the parchment. Iron gall ink is known to absorb the elements found within the parchment, calcium being one of those. This XRF-analysis suggests that the ink is not of the iron gall type.

Several more conclusions can be drawn from exploring other properties of the Vercelli Book's ink. The near infrared LED microscopic camera rendered the text illegible upon exposure to the mid-infrared spectrum. Because carbon based inks are legible at such high wavelengths, this ink cannot be of the carbon type. Upon close examination, this ink appeared very homogenized. Iron gall ink, by contrast, is insoluble and creates damage chiefly through to the Fenton reaction

and acid hydrolysis. Due to its absence of vitriol and metal sulfates, the ink within the pages of the Vercelli Book does not cause the degrading effects of acid hydrolysis. Therefore, the pages and contents are expected to exhibit less damage than a document prepared with iron gall ink of the tenth century. The homogenized ink of the Vercelli book supported this hypothesis and truly exhibited less damage than would be expected from iron gall ink. After performing these thorough analyses, this ink has been proven to be of neither the iron gall nor carbon-based types. The quantifiable data obtained from this study suggest an ink of a specific plant-based nature.

V. A Further Discussion: The Plant Based Ink of Theophilus

Plant-based inks, prevalent around the eleventh century, are tannin based.⁴¹ These inks are similar in composition to iron gall ink, except the plant-based ones lack the iron sulfate component. Like recipes for iron gall inks, plant-based recipes varied depending on location and resource availability. These inks were popular in the Middle Ages, but were used by scribes long before that time. Plant-based inks exhibit a homogeneous quality and a dark brown hue (Rabin). Unlike iron gall inks, which turn black after application to paper and fade to a brown, the inks of the plant type are brown upon application and retain the brown coloration throughout their lifetime. Because they lack the metal sulfate component of iron gall ink, plant-based inks do not undergo acid hydrolysis and thereby only degrade via the Fenton reaction if trace amounts of iron exist in

⁴¹ The tannin source is that of tree bark, rather than the nut gall (Rabin).

their elemental makeup.⁴² After elemental analysis, it was no question that the ink within the Vercelli Book was of the plant-based type. But upon further speculation, it was hypothesized that this particular ink is of a plant-based ink in vogue around the dawn of the twelfth century: Theophilus Ink.

Theophilus Presbyter was a German monk of the early twelfth century Benedict order (The Editors of Encyclopædia Britannica).⁴³ In his book, *De Diversis Artibus*, he records a recipe that was made popular due to its lasting qualities. Theophilus' recipe was thought to have spread throughout the Western world and used by monks of his generation to write cleric manuscripts (Rabin). Below is a record of the complete Theophilus recipe, as recorded and translated into English by Carvalho in *Forty Centuries of Ink*:

To make ink, cut for yourself wood of the thorn-trees in April or May, before they produce flowers or leaves, and collecting them in small bundles, allow them to lie in the shade for two, three, or four weeks, until they are somewhat dry. Then have wooden mallets, with which you beat these thorns upon another piece of hard wood, until you peel off the bark everywhere, put which immediately into a barrellful of water. When you have filled two, or three, or four, or five barrels with bark and water, allow them so to stand for eight days, until the waters imbibe all the sap of the bark. Afterwards put this water into a very clean pan, or into a cauldron, and fire being placed under it, boil it; from time to time, also, throw into the pan some of this bark, so that whatever sap may remain in it may be boiled out. When you have cooked it a little, throw it out, and again put in more; which done, boil down the remaining water unto a third part, and then pouring it out of this pan, put it into one smaller, and cook it until it grows black and begins to thicken; add one third part of pure wine, and putting it into two or three new pots, cook it until you see a sort of skin show itself on the surface; then taking these pots from the fire, place them in the sun until the black ink purifies itself from the red dregs. Afterwards take small

⁴² It was common to observe trace amounts of iron in plant-based inks, either from intentional input of iron or from natural trace amounts in the solvent.

⁴³ Also known under the pseudonym Roger of Helmarshausen (The Editors of Encyclopædia Britannica).

bags of parchment carefully sewn, and bladders, and pouring in the pure ink, suspend them in the sun until all is quite dry; And when dry, take from it as much as you wish, and temper it with wine over the fire, and, adding a little vitriol, write. But, if it should happen through negligence that your ink be not black enough, take a fragment of the thickness of a finger and putting it into the fire, allow it to glow, and throw it directly into the ink.⁴⁴

This recipe details the methodology for creating the most pure and lasting ink known during the dawn of the twelfth century.

The ingredients and methodology of Theophilus' ink demand an explanation to understand the chemical background and historical timetable in which this ink is placed. The first ingredient mentioned by Theophilus is the wood of the thorn-tree native to Europe and Northern Asia. Writers believe these thorn-trees are of the Norway spruce species.⁴⁵ In addition to being this ink's chief tannin supplier, the thorn-tree produces Burgundy pitch, extracted from the bark's sap (Carvalho 79). Water acts as the solvent, which suspends the bark during an eight-day fermentation. The repetitive boiling process creates a thorn-tree bark reduction, thereby concentrating the tannin. The addition of a pure wine favorably increases the acidity of the solution. All of these ingredients and steps favor the formation of a quality, readable, and lasting ink. This recipe

⁴⁴ In the original Theophilus recipe, recorded in Latin, the word *atramentum* is used. No one knows what *atramentum* meant during the time of Theophilus. Translators believe this word translated to "vitriol." However, during the time of Pliny, *atramentum* meant carbon. Ink experts believe *atramentum* suggested to add carbon to this ink recipe, rather than vitriol (Zerdoun 154). See Zerdoun's *Les encres noires au Moyen Âge* for a comprehensive explanation of the original Latin recipe.

⁴⁵ This tree is called a thorn-tree due to the thorny and needle like appearing leaves, which are short, thick, and green in appearance. While a collection of writers support this claim, the opinion of Carvalho believes the thorn-tree to be of a different species not mentioned. The claim should therefore be approached with skepticism due to differing opinions (Carvalho 79).

speaks with chemical understanding and permanence unbeknownst at the time of its creation.

The last line of this recipe proves most interesting. It states that one should “take a fragment of the thickness of a finger and putting it into the fire, allowing it to glow, and throw it directly into the ink” if the ink does not appear black enough in appearance. We have already seen that iron is often added to plant-based inks to increase their blackness. Instead of iron added in the form of vitriol, the iron source is heated and placed directly into the ink to create a legible iron oxide (Rabin). It is speculated that this fragment, likely a sword, could be made only of iron.

Upon observation of eleventh- and twelfth-century manuscripts, Carvalho noted that they appeared as bright as when they were first written. Because the eleventh and twelfth century were a time when plant based inks were used prolifically, it indicates that these plant-based inks possess a greater permanence than those of iron gall ink. This can be explained chemically due to the absence of metal sulfates in plant-based inks, which only contribute to acid hydrolysis and subsequent degradation. While a variety of plant-based ink recipes must have existed in the eleventh and twelfth centuries, Theophilus’s recipe left a remarkable imprint on the manuscript collections of this time. From iron gall ink to Theophilus, I believe we have reached a conclusion, Vercelli.

All of the historical facts and elemental analysis conducted on the Vercelli Book strongly suggest that its ink is of the Theophilus type. No indication of metal sulfates present in the pages of the Vercelli Book. The ink was homogeneously distributed on the page, characteristic of plant-based inks. The

ink has a deep, rich brown permanence that could only be characteristic of plant-based ink. But most importantly, this document was created during the time when Theophilus ink gained popularity and was widely used throughout Europe.

CHAPTER VIII

THERMOGRAPHIC DETECTION OF IRON GALL INK PRESENCE IN MANUSCRIPT BINDING

I. Introduction to Experimentation

During the Lazarus Project visits to the archives of the Fondazione Museo, it was observed that many damaged spines contained parchment within the binding that exhibited fascinating inscriptions. These inscriptions were of a different hand, from an earlier time, and sometimes of a different language, than the writings within the pages of the manuscript itself. While this binding serves to support the manuscript of interest, the parchment that makes up the spine is new potential for historical relevance that is worth inspecting in its own right.

While damaged spines revealed this phenomenon, the majority of manuscript spines remain intact and in good condition. Due to the widespread use of older manuscript parchment for binding purposes, it is highly likely that the majority of antiquarian manuscripts contain even older inscriptions under their leather spine. How, then, might it be possible to discover inscriptions of historical importance without damaging the spines of perfectly well-preserved manuscripts?

The Lazarus Project Imaging team has recently been interested in technological methods to help detect the presence of ink underneath the manuscript's leather binding without damaging the spine. A recent partnership with Thermal Wave Imaging may provide a solution to this challenging

investigation. Infrared thermography might provide the necessary capability of detecting the presence of inks. This technology utilizes a camera's capability to detect infrared energy emitted from objects and subsequently transforming that energy into temperature data. This data is collected and displayed using a visible infrared image (Avio Web). A common misconception of this technology is that it can see concealed or veiled objects. Infrared thermography simply detects the energy emitted from the surface of the sample of interest. However, it is possible to estimate the rear side of the sample if a temperature distribution exists on the sample surface. This is attributed to the difference of heat conductivity between the sample's surface and the concealed object of interest (Avio Web). This principle is utilized in the following experiment to reveal the presence of ink beneath the leather pseudo-binding.

II. Materials and Methods

The parchment samples prepared with the ink made for multi-spectral analysis in Chapter VI were recycled and used again in this experiment. Parchment samples were made from four-inch square parchment scraps.⁴⁶ Each sample was uniformly inscribed with the same characters, yet distinguishable from one another by their chemical formula and elemental mass denoted in the center of the page. The parchment samples served to simulate the binding present within ancient manuscripts that contain the inscriptions from potentially earlier periods.

⁴⁶ Parchment scraps were provided by ©Pergamena and could be made from any of the following: calfskin, deerskin, goatskin, or sheepskin.

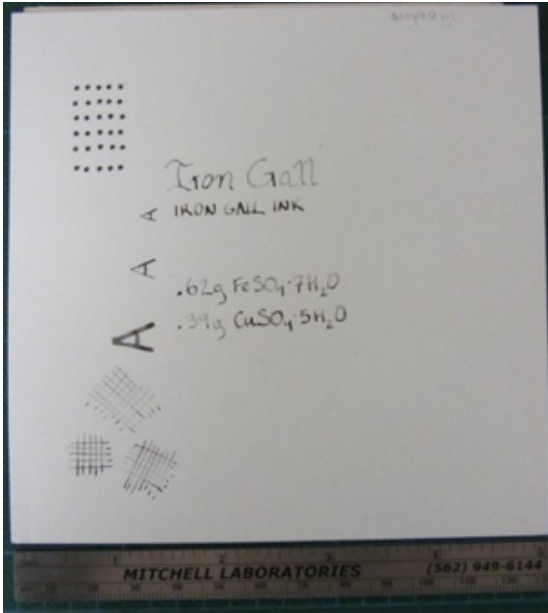


Figure 8.1: Prepared parchment sample for thermographic testing.

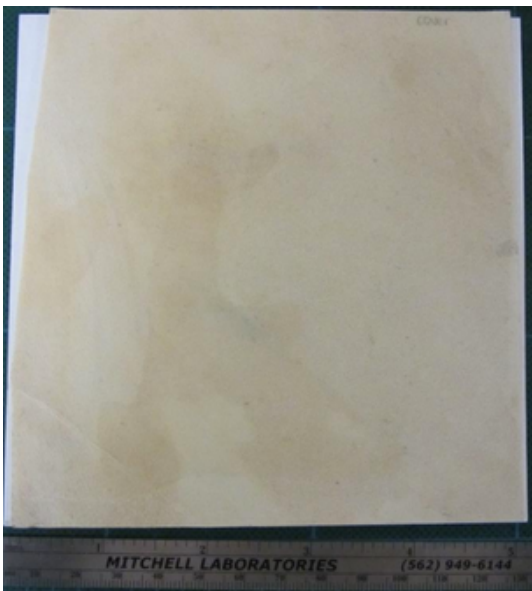


Figure 8.2: Thick vellum cover slip to simulate leather binding; placed on top of parchment sample during thermographic testing.

Thermal Wave Imaging conducted the experiment in their lab using their own flash infrared thermographer. A single layer of leather was placed over the parchment sample to be tested to simulate the depth of the book's leather binding. The infrared thermographer gathered multiple data points over a period of seconds on each parchment sample overlaid with leather. This experiment was

repeated with the addition of a single blank parchment layer between the leather pseudo-spine and parchment sample of interest. A second blank parchment layer was further added to assess the potential penetrative effects of the infrared thermographer.

III. Results

Thermal Wave Imaging sent the Lazarus team the results of the flash thermography experiment. Two thermographic images are displayed in Figure 8.1 and Figure 8.2, one taken after 1.83 seconds of energy emission and the other after 2.37 seconds of energy emission, respectively.

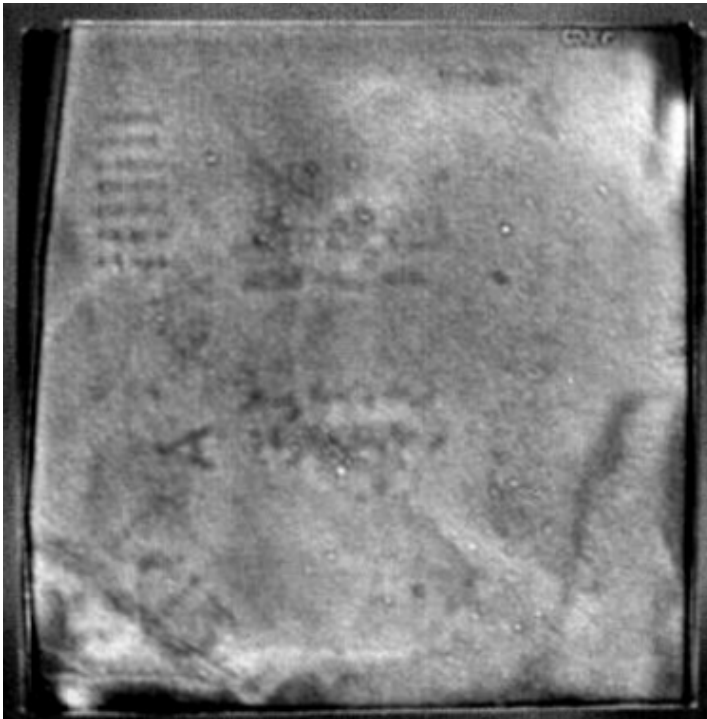


Figure 8.3: Thermographic image of ink on parchment at 1.83 seconds.



Figure 8.4: Thermographic image of ink on parchment at 2.37 seconds.

IV. Discussion and Conclusion

Flash thermography was able to detect a contrast between the emitted energy of the ink and parchment. A visible contrast exists between the ink and parchment when observing the obtained infrared energy data during both time points. The thermographic image taken after 1.83 seconds appears to be of a sharper and clearer quality than the image taken after 2.37 seconds of emission. Most impressively, this contrast is present when an accompanying leather cover slip is placed between thermographer and parchment sample.

These results prove most promising in the Lazarus Team's effort to soon detect the presence of lost records and literary contributions in the spines of ancient manuscripts. No longer will spines of manuscripts need to be blindly damaged to search for lost text. By investing in thermography, digital

humanitarians, conservators, and the like will be able to mindfully take apart manuscript binding, when necessary, to recover lost texts in the spine. Because this technology has proven its ability to detect ink on the binding's parchment, the scientist's next step would be to further examine the penetrative capacity of ink detection.

CONCLUSION

As the Lazarus Project imaging team worked diligently to capture spectral images of the Vercelli Book in the Museo del Tesoro in Vercelli Italy, a phenomena occurred within its pages: ink fluorescence. The multi-spectral imaging system, emitting wavelengths of ultraviolet, visible, and infrared light, induced this fluorescence as the ink absorbed and subsequently emitted the light's wavelengths at a different frequency. Questions began to circulate throughout the room: what ink properties contribute to this phenomenon? What are the chemical constituents within this ink? What type of ink was used to create the Vercelli Book? If the team knew the answers to these questions, then the document's date and location of origin might be possible to determine. The implications this chemical knowledge potentially has on the historical and preservation effort of the digital humanities could be profound.

The original hypothesis of this work follows that if the chemical composition of the ink used on ancient manuscripts were known, then it would be possible to create a characteristic chemical stamp that would correspond to the date and location of origin of the document. Because the ink on the pages of the Vercelli Book was believed to be of the iron gall ink type during the first visit to Vercelli, my search began with an extensive study on the physical and chemical composition of iron gall ink, in addition to the evolution of the ink's components and quality over the centuries. Before beginning any scientific research to test

this hypothesis, the literature and historic testimony of iron gall ink revealed that the answer to this question is much more complex than the Lazarus Project initially envisioned.

It can be said that no ink maker created the same ink. While the ingredients used to make the ink were gathered from the local region, the amounts and proportions used for production varied between individuals. Because each gall species possesses a characteristic tannin concentration, it might seem promising to analyze the tannin concentration in the ink to determine the gall nut of origin. However, the tannin concentration within the ink is also impacted by the tannin extraction method. Extracting tannin from the gall via cooking grants the ink a higher tannin concentration than simply mixing the gall with water. As trade routes improved and gall nuts were transported far distances for ink production, locating documents based on the tannin concentration and corresponding gall nut characteristic of a particular region also complicates this question. In addition to these obstacles, ink makers had a solvent preference; the ink made from an alcohol solvent contains higher tannin concentration than does one made from water. The variety of additives also contributes to the tannin concentration present within the ink. To date and locate a document based on the tannin concentration would be infeasible due to the fact that a variety of ingredients contribute to the tannin concentration, rather than simply the gall nuts used.

To complicate matters, no explicit distinction exists between the various terms used to refer to iron sulfate: vitriol, copperas, sal martis, copper red, among others. Vitriol often contained metal impurities, including copper, zinc,

aluminum, and manganese. Ink makers would also use copper sulfate as a substitute for iron sulfate and term the ingredient 'vitriol' in the recipe book. The mining techniques used to extract the metal sulfate varied among regions and time periods, and directly contributed to the presence of particular metal impurities in the ink. It seems most daunting to answer this question when simply considering the variability that exists simply in the vitriol component of ink.

A variety of factors have been shown to contribute to iron gall ink's chemical composition. Therefore, the prospect of creating a date and time stamp for characteristic chemical constituents within the ink seems highly unlikely. However, with the help of spectroscopic methods, the prospect of estimating a document's relative location of origin and time period proved possible, still.

Before applying multi-spectral and micro-XRF analysis on the Vercelli Book and Codex A, UV-vis and fluorescent spectroscopy were employed to see if trace metal variation could be detected among ink samples created in the lab. Of the five ink samples that were created, all five exhibited the same two excitation peaks around 220 nm and 320nm. Therefore, these two spectroscopes proved unable to detect the difference between inks containing trace amounts of metal salts. This method possesses a limitation in that ink samples on parchment cannot be tested for trace metal analysis. In addition, these spectroscopes were not sensitive enough to detect the slight variation in elemental composition among the created inks.

However, the use of UV-vis and fluorescence spectroscopy did not go discarded. The multi-spectral camera of the Lazarus project team obtains a

plethora of data while taking photographs of the text upon ultraviolet, visible and infrared light exposure. This camera possesses the ability to acquire data regarding the light absorption of the ink. To confirm this plausibility, multi-spectral data was normalized with that of the UV-vis absorption data to compare the excitation peaks for a correlation. Because the two absorption peaks existed in the same narrow wavelength window and the excitation curvature of both spectral machines visibly mirrored each other throughout the 365-800 nm wavelength window, it was concluded that the multi-spectral imaging system possessed the ability to collect absorption data on the manuscript's ink and parchment.

Although historical evidence suggests creating a time and location stamp for ink recipes is an unlikely task, the micro-XRF data and analysis performed on both the Vercelli Book and Codex A were able to give insight into the chemical composition and, subsequently, both create new and confirm old beliefs regarding their date and location of origin. First, knowledge of the elemental composition of carbon, plant, and iron gall based inks proved crucial in deciphering the spectrum and accurately typing the ink. Iron, sulfur, potassium, and copper were detected in the ink of the Codex A. These elements existed in a precise proportion indicative of iron gall ink. Near infrared LED exposure confirmed this ink is not of the carbon-based type. Scientists claim more tests must be done to conclude this ink is of iron gall origin. However, if this ink is confirmed to be of the iron gall type, this fourth century document will serve as the earliest extant example of iron gall ink use for literary purposes. This conclusion, while spectacular, is not outrageous, considering Pliny the Elder first

described the basic chemistry behind the staining properties of tannin and vitriol in first century AD. In addition, it is known that a significant amount of the documents created before the fall of the Roman Empire were damaged during the Middle Ages and Crusades. Any information historians would have had regarding the use and recorded recipes of iron gall ink would have very likely been destroyed during these periods.

Micro-XRF was also performed on the Vercelli Book for ink typing purposes. A year previous to this micro-XRF analysis, it was speculated the ink on this twelfth century document was of the iron gall type. However, the conclusion offered by the expertise of the micro-XRF suggested this ink is of a different one. Even though iron was detected, the main element present was calcium. Sulfur, copper, zinc, manganese, aluminum, while expected to be present in iron gall ink, was not detected by the micro-XRF. Near infrared LED confirmed this ink is not of the carbon type. This analysis suggests the ink within the Vercelli Book is of the plant type.

However, the elemental composition of this ink was indicative of a well-regarded plant-based recipe during the twelfth century. Not only would the specific type of plant ink be known, but also it would further support the claim that this document was created in the twelfth century. Thanks to the collaborative efforts and knowledge of ink experts, the Lazarus Project team was able to reach a conclusion regarding the specific type of plant based ink used by the scribe of the Vercelli Book: Theophilus ink.

This discovery is a testament to the importance of collaborative efforts of both humanitarian and scientist. Without the knowledge of the historian, one

would never know to look to Theophilus as a significant contributor and revolutionary player in the development of his plant based recipe. And if it were not for the operational understanding and elemental analysis of the scientist, no conclusions could be reached regarding the chemical ingredients within the ink of the Vercelli Book. The digital humanities rely on a variety of experts and scholars to uncover, preserve, and redefine history. Without collaboration, innovative efforts of any kind are severely limited.

Collaborative efforts also aided the Lazarus Project team in understanding the effects thermographic imaging can have on their archival effort. The manuscripts in the city of Vercelli were found to have inscriptions within the binding, buried beneath the thick spine. With so many spines in tact, the risk of breaking them to discover inscriptions of importance was too great. With the help of thermographic imaging, the Lazarus Team speculated that it would be possible to detect the presence of ink beneath the book's spine without even touching the manuscript. Thermographic imaging was performed on ink samples created to simulate the spine of a book. After analysis, a visible contrast could be digitally seen, indicating that this technology has the power to detect the presence of ink beneath layers of leather. This technology is recommended to be used by the digital humanities for historical, scientific, and preservation purposes.

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APPENDIX

A-1: Fourteenth Century French Recipe.

To make 3 quarts of ink, take 2 ounces each of galls and gum arabic, and 3 ounces of copperas. Break the galls and soak them for 3 days, then boil in three half gallons of rainwater or water from a still pond. And when they have boiled long enough so that nearly half the water has boiled off – that is, there is only about 3 quarts left – take off the fire, and add the copperas and gum, and stir until cool. Store in a cold, clamp place. Note that after 3 weeks, it will spoil.

Le Ménagier de Paris. Traité de morale et d'économie domestique compose vers 1393 par un bourgeois parisien, Tome Second, Paris, 1846, p. 265.

A-2: Fourteenth Century French Recipe.

If you wish to make a good ink or a good “dye”, take twelve pounds of rain water and two pounds of gall nuts and, put the galls in the rain water to macerate until morning. Boil this liquor until it is reduced by half; then carefully filter it through a fine cloth and put it back over the fire; take four ounces of gum arabic and boil it with the liquor until it is dissolved. Filter again; then take one pound of very clear white wine, and three ounces of vitriol and mix them well; add this mixture to the liquid and let it boil a little bit; carefully filter again. This will make a good ink.

Bat-Yehouda, Monique Zerdoun. *Les encres noires au Moyen Âge (jusqu'à 1600)*, Éditions du CNRS, Paris, 1983.

A-3: Sixteenth Century French/Italian Recipe.

Take one ounce of gall nuts crushed to pieces, then place them in a piece of cloth that you will tie not too tight; put the galls to soak in twelve ounces of rain water and let macerate at least six days; once this is done, boil until the mixture is reduced to eight beautiful and unctuous ounces; then you will put in it one quart of German vitriol well ground and a half ounce of gum that will have soaked in vinegar; only use as much vinegar as is necessary and you will make a marvelous ink.

Bat-Yehouda, Monique Zerdoun. *Les encres noires au Moyen Âge (jusqu'à 1600)*, Éditions du CNRS, Paris, 1983.

A-4: Chemical content of the Aleppo gall.

Component	Percent
Tannic acid	65.0
Gallic acid	2.0
Ellagic acid and luteo-gallic acid	2.0
Chlorophyll and volatile oil	0.7
Brown extractive matter	2.5
Gum	2.5
Starch	2.0
Woody Fibre	10.5
Minor Components sugar, albumen potassium sulphate/gallate potassium, phosphate gallate and oxalate of lime	1.3
Moisture	11.5
Total	100.0

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A-5: The physical properties of ingredients used.

Chemical	Molecular Weight
Tannic Acid	1701.19 g/mol
Gum Arabic	0.25 x 10 ⁶ g/mol 2.5 x 10 ⁶ g/mol
Iron (II) Sulfate Heptahydrate [FeSO ₄ •7H ₂ O]	278.01 g/mol
Copper (II) Sulfate Pentahydrate [CuSO ₄ •5H ₂ O]	249.68 g/mol
Zinc Sulfate Heptahydrate [ZnSO ₄ •7H ₂ O]	287.54 g/mol
Aluminum Sulfate Hexadecahydrate [Al ₂ (SO ₄) ₃ •16H ₂ O]	630.40 g/mol
Chromium (III) Potassium Sulfate Dodecahydrate [CrK(SO ₄) ₂ •12H ₂ O]	499.40 g/mol

A-6: Weighted mass of ingredients used.

Ink	Tannic Acid	Gum Arabic	FeSO₄•7H₂O	Metal Sulfate
#1: Control	1.23 g	0.787 g	1.05 g	-
#2: CuSO ₄ •5H ₂ O	1.23 g	0.787 g	0.62 g	0.39 g
#3: ZnSO ₄ •7H ₂ O	1.23 g	0.787 g	0.62 g	0.45 g
#4: Al ₂ (SO ₄) ₃ •16H ₂ O	1.23 g	0.787 g	0.62 g	0.33 g
#5: CrK(SO ₄) ₂ •12H ₂ O	1.23 g	0.787 g	0.62 g	0.39 g

A-7: Parchment samples.

Ink	Parchment Sample
#1: Control	1
#2: CuSO ₄ •5H ₂ O	0, 2
#3: ZnSO ₄ •7H ₂ O	3
#4: Al ₂ (SO ₄) ₃ •16H ₂ O	4
#5: CrK(SO ₄) ₂ •12H ₂ O	5